

**Complex Environmental Fate of Organic Pollutants in a
Highly Anthropogenic Affected Meso-Scaled Catchment System
– the Case Study Rur**

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Abstract

River systems and humans have always been closely connected. Anthropogenic impacts are not just limited to engineering measures for navigation or flood protection, but also include the withdrawal of water for industry and agriculture, as well as the discharge of (treated) wastewater. In general, due to their highly dynamic nature, rivers have long been used as a means of dissolving and transporting anthropogenic waste. Particularly in the last century, this has resulted in complex water contaminations. However, it was just at the end of the 1970s that public awareness began to grow. Since then, there has been not only an increase in research activities, but also greater political interest and the founding of various nature conservation organizations. Nevertheless, further research is still necessary, as new pollutants are constantly emitted into the environment and detected by improved analytical methods. This applies, in particular, to organic pollutants. Due to their high structural variety and diversity, they often have environmentally relevant properties such as a high persistence, toxicity, or a strong tendency to bioaccumulate. Previous studies on aquatic pollution have mostly been limited to large river systems or specific compartments and/or pollutant groups. Therefore, the main focus of this doctoral thesis is a comprehensive analysis of the complex environmental fate of organic pollutants in a highly anthropogenic affected meso-scaled catchment system. For this purpose, the river system of the Rur was chosen, as it shows a diverse emission situation with multiple, but clearly definable anthropogenic impacts despite its rather short course length.

In order to determine the overall fate and behavior of organic pollutants, four regular, bi-annual sampling campaigns were carried out. Samples of the aqueous (river water) and the sedimentary phase (riverbed) were taken along the entire river course. Furthermore, event-related sampling of floodplain sediments was performed after two floods as well as a geochronological investigation of sediment deposits in a reservoir in the Rur catchment.

Using organic-geochemical treatment methods and gas chromatographic/mass spectrometric analysis, a broad spectrum of organic contaminants with different physicochemical properties was identified and subsequently quantified. More than 60 low-molecular weight organic compounds were detected in both the river water and the riverbed. Most of the substances were so-called xenobiotics. These are not of natural origin and have been introduced into the river systems through anthropogenic activities. They include, for instance, pharmaceuticals, constituents of personal care products, or various industrially used substances (such as plasticizers or flame retardants). For all detected compounds, emission profiles over the course of the river were created and possible emission sources were assigned.

Throughout the entire catchment, effluents from wastewater treatment plants were identified as the most important source. The treatment plants in the catchment often treat both municipal and industrial wastewaters. In particular, the influence of the paper industry was evident in the pollutant spectrum identified. Generally, there was a clear bipartition in the contamination of the river itself, with a rather low level of contamination in the upper reaches and a highly contaminated lower course. The latter reflects the much stronger urban and industrial land use in this part of the catchment. From there on, the pollution remains at an almost constant level up to the mouth of the Rur, and thus presumably contributes to the pollution of the superior Meuse river system. In general, the transport of organic substances in the aqueous and particulate phases is closely connected and is only interrupted by major anthropogenic impacts such as the dam system in the Eifel. The dams also had a significant effect on the transport of sediment-associated pollutants during flood events. Interestingly, the floodplain sediments deposited by the floods were less polluted than the riverbed itself. Thus, instead of a washout effect, there was a direct enrichment of pollutants. Contrary, particularly seasonal influences were detected for the aqueous compartment. In a long-term perspective, the pollution of a drilling core from the Urft reservoir could be easily correlated with catchment-specific and general political and technical improvements, e.g., in wastewater treatment.

Overall, this dissertation project enabled a comprehensive assessment of the organic, mainly anthropogenic pollution of the Rur river system. Important emission sources, the diversity of organic substances, as well as accumulation areas and their remobilization potential were defined and consequently provide an essential basis for risk assessments and the evaluation of further research needs on the Rur and other river systems.

Zusammenfassung

Flusssysteme und Menschen sind schon immer eng miteinander verknüpft. Die menschlichen Eingriffe beschränken sich dabei nicht nur auf wasserbauliche Maßnahmen für die Schifffahrt oder den Hochwasserschutz, sondern umfassen auch die Entnahme von Wasser für Industrie und Landwirtschaft sowie die Einleitung von (gereinigten) Abwässern. Generell wurden Flüsse aufgrund ihrer hohen Dynamik lange als eine Art Lösungs- und Transportmittel für anthropogene Abfälle genutzt. Dadurch entstanden insbesondere im letzten Jahrhundert komplexe Gewässerbelastungen. Diese rückten jedoch erst seit Ende der 1970er Jahre vermehrt ins öffentliche Bewusstsein. Seitdem kam es nicht nur zu vermehrten Forschungsaktivitäten, sondern auch stärkerem politischen Interesse und der Gründung diverser Naturschutzorganisationen. Nichtsdestotrotz besteht auch weiterhin ein akuter Forschungsbedarf, da immer neue Schadstoffe in die Umwelt emittiert und mithilfe verbesserter Analysemethoden detektiert werden. Dies gilt insbesondere für organische Schadstoffe. Aufgrund ihrer hohen strukturellen Vielfalt und Diversität weisen sie oft umweltrelevante Eigenschaften wie eine hohe Persistenz, Toxizität oder eine starke Tendenz zur Bioakkumulation auf. Bisherige Studien zur aquatischen Verschmutzung beschränken sich zumeist auf große Gewässersysteme oder bestimmte Kompartimente und/oder Schadstoffgruppen. Daher liegt der Hauptfokus dieser Doktorarbeit auf einer umfassenden Analyse des komplexen Umweltverhaltens organischer Schadstoffe in einem anthropogen stark überprägten Flusseinzugsgebiet mittlerer Größe. Hierfür wurde das Flusssystem der Rur gewählt, da der Fluss trotz seiner eher kurzen Lauflänge eine vielfältige Emissionslage mit multiplen, aber klar abgrenzbaren anthropogenen Einwirkungen aufweist.

Zur Bestimmung des allgemeinen Verbleibs und Verhaltens von organischen Schadstoffen erfolgten vier reguläre, halbjährliche Probenahmekampagnen. Dabei wurden entlang des gesamten Flussprofils Proben der wässrigen (Flusswasser) sowie der sedimentären Phase (Flussbett) entnommen. Weiterhin erfolgten eventbezogene Probenahmen von Auensedimenten nach zwei Hochwasserereignissen und die geochronologische Untersuchung der Sedimentablagerungen innerhalb eines Stausees im Einzugsgebiet der Rur.

Mithilfe organisch-geochemischer Aufbereitungsverfahren und gaschromatographisch/massenspektrometrischer Analysemethoden wurde ein umfangreiches Spektrum an organischen Kontaminanten mit unterschiedlichen physikochemischen Eigenschaften identifiziert und anschließend quantifiziert. Sowohl im Flusswasser als auch im Flussbett wurden je mehr als 60 niedermolekulare organische Verbindungen nachgewiesen. Bei den meisten Substanzen handelte es sich um sogenannte Xenobiotika. Diese sind nicht natürlichen Ursprungs und werden über anthropogene Aktivitäten in die Flusssysteme eingetragen. Dazu gehören beispielsweise Arzneimittel, Bestandteile von Körper-

pflegemitteln oder verschiedene, industriell eingesetzte Substanzen (etwa als Weichmacher oder Flammschutzmittel). Für alle detektierten Verbindungen wurden Emissionsprofile über den Flussverlauf erstellt und mögliche Emissionsquellen zugeordnet.

Im gesamten Einzugsgebiet konnten Einleitungen der Kläranlagen als wichtigste Eintragsquelle identifiziert werden. Diese behandeln im Einzugsgebiet zumeist kommunale sowie industrielle Abwässer. Vor allem der Einfluss der Papierindustrie konnte anhand des identifizierten Schadstoffspektrums herausgestellt werden. Generell zeigte sich für die Belastung des Flusses eine deutliche Zweiteilung mit einem eher gering kontaminierten Oberlauf sowie einem stark belasteten Unterlauf. Letzteres spiegelt die deutlich stärkere urbane und industrielle Nutzung in diesem Bereich des Einzugsgebiets wider. Die ermittelte Belastung bleibt von da an bis zur Mündung der Rur auf einem etwa gleichbleibenden Niveau und trägt somit vermutlich ebenfalls zur Kontamination des übergeordneten Flusssystems der Maas bei. Grundsätzlich ist der Transport der eingetragenen organischen Substanzen in der wässrigen und partikulären Phase eng verknüpft und wird nur durch bedeutende anthropogene Eingriffe wie das Talsperrensystem in der Eifel unterbrochen. Die Talsperren hatten auch einen deutlichen Effekt auf den partikulären Schadstofftransport während der Hochwasserereignisse. Interessanterweise waren die infolge des Hochwassers abgelagerten Auensedimente jedoch geringer belastet als das Flussbett selbst. Statt einem Auswascheffekt kam es dort also zu einer direkten Schadstoffanreicherung. Für die wässrige Phase wurden dagegen vor allem saisonale Einflüsse ermittelt. In der Langzeitperspektive konnte die Verschmutzung eines Bohrkerns aus der Urfttalsperre gut mit einzugsgebietsspezifischen und allgemeinen politischen und technischen Verbesserungen, beispielsweise in der Abwasserbehandlung, korreliert werden.

Insgesamt ermöglichte dieses Dissertationsprojekt eine umfassende Bewertung der organischen, hauptsächlich anthropogenen Belastung des Flusssystems der Rur. Wichtige Emissionsquellen, die Vielfalt an organischen Substanzen sowie Akkumulationsflächen und deren Remobilisierungspotential wurden definiert und bieten infolgedessen eine wesentliche Grundlage für Risikoabschätzungen und die Bewertung des weiteren Forschungsbedarfs an der Rur und anderen Flusssystemen.

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List of Abbreviations

An	anthracene	LOQ	limit of quantification
AIBN	azobisisobutyronitrile	m a.s.l.	meters above sea level
ASE	accelerated solvent extraction	MQ	median river runoff
ASEs	alkylsulfonic acid phenyl esters	MTBT	2-methylthiobenzothiazole
ATBC	acetyl tributylcitrate	NBBS	N-butylbenzenesulfonamide
BaA	benzo[a]anthracene	NETSA	N-ethyl-toluenesulfonamide
BCF	bioconcentration factor	NIST	National Institute of Standards (USA)
Bghi	benzo[g,h,i]perylene	OECD	Organisation for Economic Cooperation and Development
BHT	butylated hydroxytoluene	PAHs	polycyclic aromatic hydrocarbons
BHT quinone	2,6-di- <i>tert</i> -butyl-1,4-benzoquinone	PCBs	polychlorinated biphenyls
BUND	Bund für Umwelt und Naturschutz Deutschland (German Federation for the Environment and Nature Conservation)	PCPs	personal care products
BT	benzothiazole	Ph	phenanthrene
Ch	chrysene	POPs	persistent organic pollutants
DBP	4,4'-dichlorobenzophenone	Py	pyrene
DCM	dichloromethane	REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
DDD	dichlorodiphenyl-dichloroethane	TAED	N,N,N',N'-tetraacetylenediamine
DDE	dichlorodiphenyl-dichloroethylene	TBP	tributyl phosphate
DDT	dichlorodiphenyl-trichloroethane	TC	total carbon
DEET	N,N-diethyltoluamide	TCEP	tris(2-chloroethyl)phosphate
DEHP	bis(2-ethylhexyl) phthalate	TCPP	tris(chloropropyl)phosphate
DIPNs	di- <i>iso</i> -propylnaphthalenes	TEP	triethyl phosphate
DMPA	2,2-dimethoxy-1,2-diphenylethanone	TIC	total inorganic carbon
DPE	1,2-diphenoxyethane	Tm	17 α -22,29,30-trisnorhopane
ECHA	European Chemicals Agency	TMDD	2,4,7,9-tetramethyl-5-decyne-4,7-diol
EDC	endocrine disruptor compound	TMSN	tetramethylsuccinonitrile
EU	European Union	TOC	total organic carbon
Fl	fluoranthene	TPP	triphenyl phosphate
GC/MS	gas chromatography/mass spectrometry	TPPO	triphenylphosphine oxide
HCB	hexachlorobenzene	Ts	18 α -22,29,30-trisnorneohopane
IP	indeno[1,2,3-cd]pyrene	TXIB	2,4,4-trimethylpentane-1,3-dioldi- <i>iso</i> -butyrate
K _H	Henry Laws constant	UBA	Umweltbundesamt (German Environment Agency)
K _{ow}	octanol-water coefficient	UNCED	United Nations Conference on Environment and Development
LABs	linear alkylbenzenes	USA	United States of America
LASs	linear alkylbenzene sulfonates	WFD	water framework directive
LOD	limit of detection	WWTP	wastewater treatment plant
LOI	loss on ignition		

Thesis Outline

The first chapter provides an introduction to the human impact on fluvial systems, particularly with regard to the organic contamination and the corresponding theoretical approaches to the behavior and fate of different organic pollutants. Additionally, the main objectives and specific research questions of this thesis are outlined. In chapter 2, the study area of the Rur catchment is presented to indicate relevant emission sources as well as topographic and (hydro)geological differences along the course of the river. Furthermore, chapter 3 deals with the state of the art of organic pollution research on river systems in general and the Rur catchment in particular. Chapters 4 to 7 present the individual studies of this doctoral thesis, which are already peer-reviewed published or submitted to be published:

Chapter 4: ***Structural Diversity of Organic Contaminants in a Meso-Scaled River System***

This study focuses on the highly dynamic aqueous phase and the corresponding pollutant transport. It analyses the variety and structural diversity of pollutants in the Rur river and compares the pollution situation in 2020 to earlier sampling campaigns of 2004 and 2015.

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DOI: 10.1007/s11270-022-05503-1

Chapter 5: ***Distribution, Remobilization and Accumulation of Organic Contaminants by Flood events in a Meso-Scaled Catchment System***

This study deals with the distribution, remobilization, and accumulation of organic contaminants in floodplain sediments as a result of two different flood events in 2021. A particular focus is placed on the different dimensions and effects of the two events and the associated relevance of pollutant input, (re)distribution, and deposition.

Published in Environmental Sciences Europe (2023), Volume 35, article number 15.

DOI: 10.1186/s12302-023-00717-4

Chapter 6: ***Dynamic Transport and Distribution of Organic Pollutants in Water and Sediments of the Rur River***

The aim and focus of this study are a comprehensive data evaluation and a holistic view of the environmental behavior of organic contaminants in a river system (particularly between the

dissolved and particulate phase). Therefore, it includes both the river water and the riverbed as well as several sampling campaigns between 2020 and 2022.

Published in Water, Air, & Soil Pollution (2024), Volume 235, article number 9.

DOI: 10.1007/s11270-023-06786-8

Chapter 7: ***Reconstruction of the Pollution History of the Urft Reservoir – An Organic-Geochemical Investigation***

This study deals with the reconstruction of the pollution history of the Urft reservoir (as part of the Rur catchment) regarding various organic contaminants. Emission profiles are correlated with catchment-specific and general developments such as land use changes or political regulations.

Published in Environmental Sciences Europe (2024), Volume 36, article number 103.

DOI: 10.1186/s12302-024-00929-2

The individual studies and results are summarized and discussed in chapter 8. Finally, the doctoral thesis is concluded in chapter 9 with an outlook and the relevance of this study for a holistic understanding of the fate and behavior of organic pollutants in riverine systems.

1 Introduction

1.1 Contamination of Fluvial Systems

Rivers are often referred to as lifelines, not only for humans but also for other living beings and, due to their function as ecological systems, for landscapes in general (e.g., Koenzen, 2005; Mauch & Zeller, 2008; Patt, 2016). Besides their natural functions, e.g., as important habitat for numerous plant and animal species or for sediment and nutrient transport and retention, they have also been a preferred settlement area for thousands of years. This is based on various reasons, ranging from the supply of industrial and drinking water, the discharge of treated wastewater, river regulation, energy production and transportation, to the usage of river systems as recreational areas (Gregory, 2006; Patt, 2016). Accordingly, the human impact and urbanization processes have nowadays drastically modified and altered the appearance of rivers so that their current shapes and structures are rarely a natural phenomenon (Chin, 2006; Koenzen, 2005). Especially in the last centuries, river manipulation and adjustments have mostly aimed on enhanced navigation and shipment, as well as flood protection, and consequently the reduction of property and life loss (Patt, 2016; Wohl et al., 2015). In addition to these structural changes (e.g., channelization, the construction of dams and weirs, or land cover changes), human evolution and development have also led to an increased pollution of river systems. Due to the highly dynamic nature of rivers, they have long been regarded as a means of dissolving and transporting anthropogenic waste and are now ubiquitously used, e.g., for wastewater discharge (Patt, 2016; Schwarzbauer & Jovančičević, 2018). Accordingly, a mixture of inorganic (e.g., heavy metals) and organic pollutants has entered and still enters the river systems.

Particularly, the introduction of organic pollutants needs to be considered for risk and hazard assessments, as they often have toxic and bioaccumulative properties and can persist in different environmental compartments for long periods of time (Walker et al., 2019). Due to their usage in various fields of application (e.g., agriculture, industry, and households), there is a high variety of compounds showing a great diversity of physicochemical properties and accordingly fates and behaviors. In 2006, there were already more than 100,000 substances registered in the European Union (EU) that pose a potential risk to humans and animals once they are released into the environment (Schwarzenbach et al., 2006). Additionally, from 2008 to 2023, more than 22,000 further substances were registered according to the REACH (registration, evaluation, authorization and restriction of chemicals) regulation of 2006 (ECHA, 2023; European Parliament and Council, 2006). Moreover, there are many unknown compounds with unknown fates and behaviors in our river systems, such as by-products, and transformation products (e.g., Morin-Crini et al., 2021; Richardson & Kimura, 2020). Combined with increasingly advanced instrumental analytics, the amount of organic pollutants

identified in the environment will continue to rise in the future (e.g., Lorenzo et al., 2018; Tang et al., 2019). All of these substances create a “pollution cocktail” and may interact with each other in the aquatic environment, leading to unknown and complex environmental consequences (Catalan, 2015).

Table 1.1 Overview on the German environmental legislation showing selected political decisions or acts and corresponding large reforms/major revisions. A more detailed compilation can be found in the Appendix to Chapter 1.

Year of coming into force	Political decision or act	Year of large reforms / major revisions
1957	Federal Water Act	2010
1972	National Waste Disposal Act	1996, 2012
1972	Foundation of the Council of Environmental Experts	
1974	Federal Immission Control Act	2002
1974	Foundation of the German Environment Agency	
1977	Federal Nature Conservation Act	2010
1977	Fertilizer Act	2009
1990	Environmental Impact Assessment Act	
1992	Start of the development of a uniform environmental legislation	
1995	Environmental Audit Act	
1999	Ecological Tax Reform Act	
2000	Renewable Energy Sources Act	2004, 2009, 2012, 2014, 2017, 2021, 2023
2004	Greenhouse Gas Emissions Trading Act	2011
2005	Electrical and Electronic Equipment Act	2015
2007	Environmental Damage Act	

Despite the massive structural and ecological interventions, it has taken a long time before public interest was aroused in the increasing environmental and specifically water pollution, and before the corresponding chemical status as well as the adverse effects were examined in more detail. For example, one of the first important publications was “Silent Spring”, published in the USA in 1962 (Carson, 1962). It dealt with the use and (negative) effects of pesticides, thus attracting the interest of the general public. Subsequently, mainly since the beginning of the 1970s, environmental and aquatic pollution have been addressed by a broader community and by governments, leading to national and

international agreements on the protection of our environment (Böcher & Töller, 2012; Rink, 2020; Uekötter, 2007). Some corresponding (German) political acts and regulations are listed in Table 1.1, and a more detailed overview can be found in the Appendix to Chapter 1. Particularly noteworthy are the first uniform national waste disposal act (Abfallbeseitigungsgesetz – AbfG) of 1972 and the federal immission control act (Bundesimmissionsschutzgesetz – BImSchG), which came into force in 1974. In combination with technical installations such as filters, desulfurization, and wastewater treatment plants, considerable improvements have been achieved in the 1970s and 1980s regarding different environmental problems (Rink, 2020).

For the current contamination of aquatic systems, the water framework directive (WFD) of 2000 is particularly relevant (UBA, 2023c). It aims at a comprehensive protection of surface waters and groundwaters to achieve a “good chemical” and “good ecological” respectively “good quantitative” status. Environmental awareness has also been deepened in non-legislative ways, in particular at the national executive level. The German Environment Agency (Umweltbundesamt – UBA) was founded in 1974 to achieve and protect a “healthy environment with clean air and water, free of pollutants to the greatest extent possible” (UBA, 2023b). Furthermore, several nature conservation organizations (e.g., the German Federation for the Environment and Nature Conservation / Bund für Umwelt und Naturschutz Deutschland - BUND) were founded and established during this period (BUND, 2023).

On a global scale, the first international conference on environmental concerns took place in Stockholm in 1972, followed by the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro in 1992 (Handl, 2012). In Rio, the concept of sustainable development was recognized as an international guiding principle, equating the protection of natural resources with economic efficiency and social justice (BMZ, 2023). Other important achievements and outcomes were the “Agenda 21”, a program of action to develop new strategies in the course of a sustainable development (e.g., new educational methods and new forms of participation), and three conventions on climate protection, the protection of biodiversity, and combating desertification that are binding under international law (BMZ, 2023; UN, 2023b). It is generally considered a milestone in global environment and development policy, and was followed by further important summits such as in Johannesburg in 2002 (World Summit on Sustainable Development), in Rio de Janeiro in 2012 (United Nations Conference on Sustainable Development) or in New York in 2015 (United Nations Sustainable Development Summit) (UBA, 2020; UN, 2023a).

1.2 Environmental Fate and Behavior of Organic Contaminants

Organic contaminants are used for a variety of applications in agriculture and industrial processes, as well as in personal care products or for military purposes. Accordingly, there are multiple emission sources and pathways of how these compounds can enter the environment. Particularly, river systems are a major recipient of organic contaminants (e.g., Loos et al., 2009; UBA, 2023c). In general, two types of emission sources can be defined: point sources (such as discharges from wastewater treatment plants or industrial facilities) and non-point or diffuse sources (such as from agriculture or traffic). Contaminants from the latter are typically introduced via groundwater exchange, (surface) erosion or immediately from the atmosphere, while point sources are mostly direct discharges into the rivers (e.g., Holt, 2000). A schematic overview of the emission sources in riverine systems is shown in Figure 1.1.

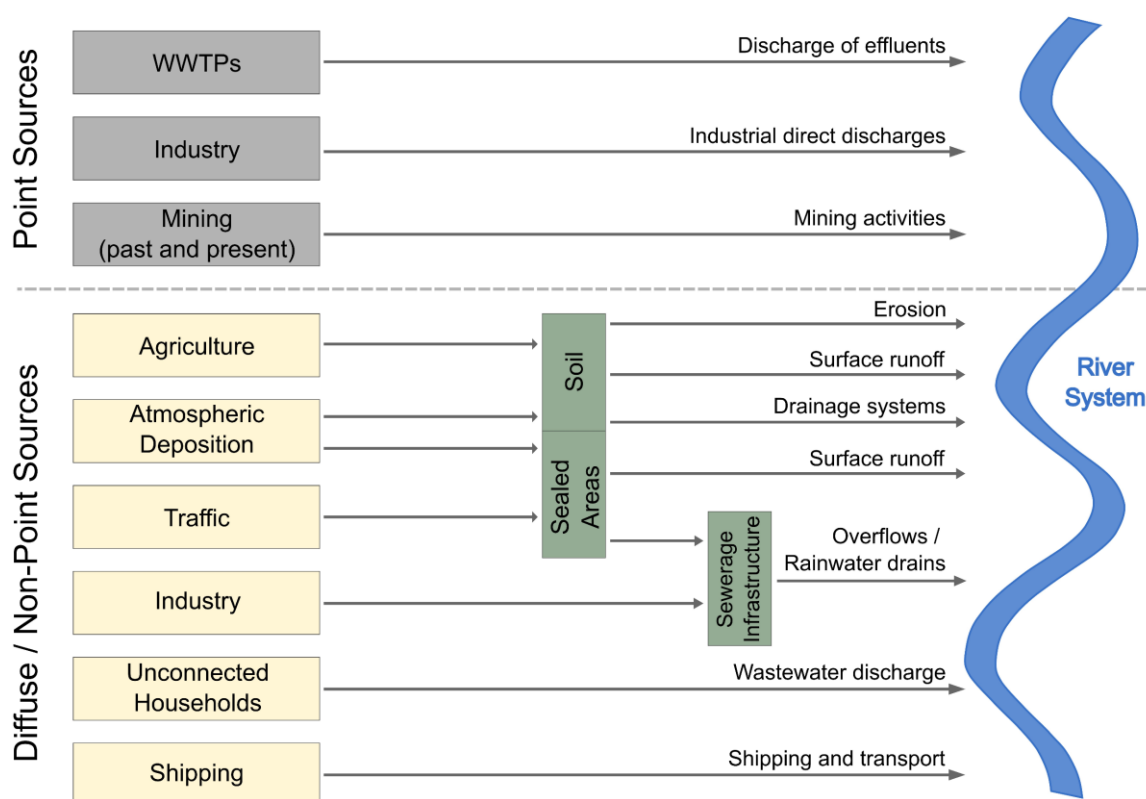


Figure 1.1 Schematic overview of relevant point and diffuse/non-point emission sources and corresponding main emission pathways into the aquatic environment (modified after KIT, 2023).

Once the organic compounds have entered a river system, their distribution and fate is mostly determined by their physicochemical properties and further parameters such as the interaction with abiotic and biotic components or the specific conditions of the river system (Kümmerer, 2011). Accordingly, transport and transfer processes determine the behavior of the individual compounds. The most relevant processes in surface water systems are highlighted in Figure 1.2.

Transport is the movement or spreading within a homogeneous phase. In the atmosphere, transport of contaminants takes place as gas or associated to dust, while in water it occurs as dissolved substances or in suspension (Reineke & Schlömann, 2023; Schwarzbauer & Jovančević, 2018). Other transport processes that determine the distribution patterns include diffusion, convection, or (ad)sorption (Cohen, 1986; Holt, 2000). Due to the high dynamics within a river system, transport is clearly important in the hydrosphere. Corresponding processes often occur in combination with degradation processes and therefore chemical transformations. The latter has to be considered for the environmental relevance of the contaminants in terms of toxicity and stability and thus for risk and hazard assessments (La Farré et al., 2008). For instance, the degradation of tetrachloroethane, a chlorinated hydrocarbon, can lead to the formation of vinyl chloride, which exhibits a higher toxicity than its parental compound (Lorah & Voytek, 2004).

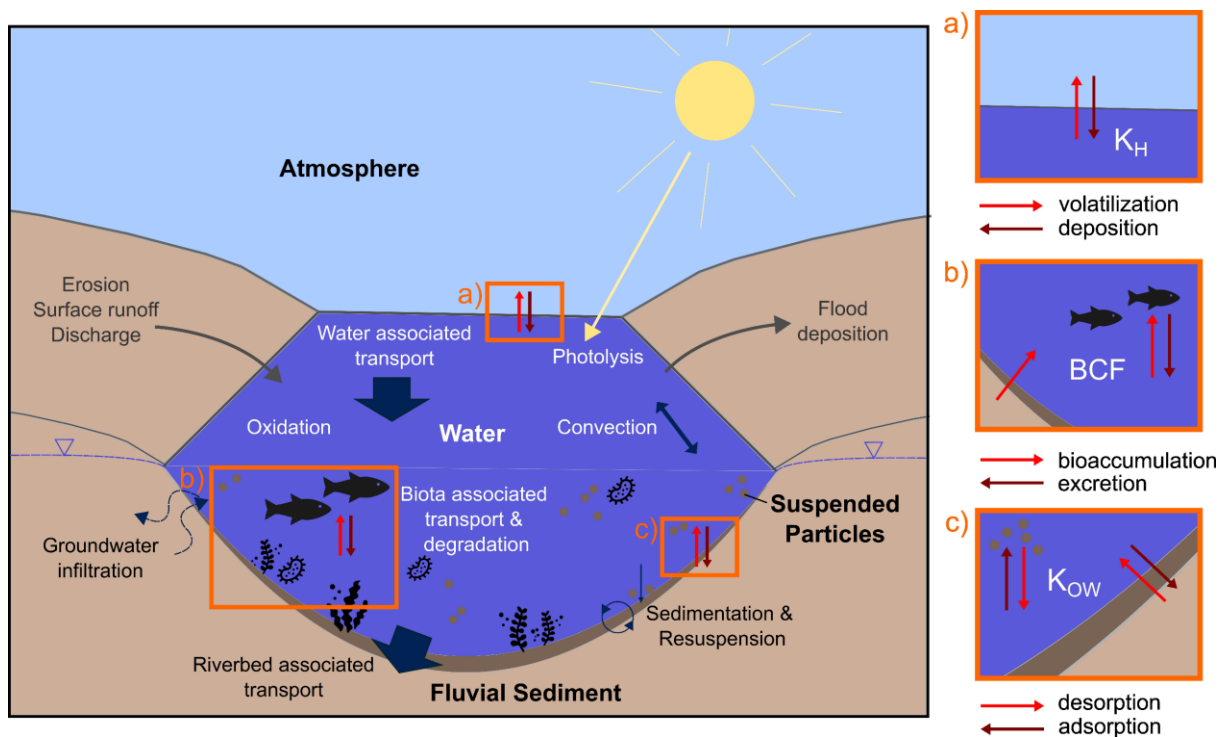


Figure 1.2 Overview of transport and transfer processes within the fluvial environment including a detailed consideration of partition processes between different environmental compartments in aquatic ecosystems (a – c).

Degradation pathways can be initiated by abiotic and biotic processes under anaerobic or aerobic conditions (Ibanez et al., 2007; Reineke & Schlömann, 2023). Abiotic degradation is determined by processes such as hydrolysis or radiation-induced photolysis. Accordingly, the latter pathway is mostly relevant in the atmosphere as well as the top layers of aquatic and soil systems (Schwarzbauer & Jovančević, 2018). However, biotic degradation processes, particularly those induced by

microorganisms, are generally more relevant (Schwarzenbach et al., 2003). In the aqueous compartment, aerobic biotic degradation pathways are decisive, while for the particulate phase (such as the riverbed), anaerobic microbial degradation is more important (Schwarzbauer & Jovančević, 2018). Aerobic conditions often result in a complete degradation or rather mineralization, while the conversion under anaerobic conditions is mostly incomplete and less efficient (Ibanez et al., 2007). Nevertheless, a complete degradation pathway typically involves several steps and processes (e.g., hydrolysis, oxidation, or reduction) and partly also changing conditions (Reineke & Schlömann, 2023; Schwarzbauer & Jovančević, 2018).

Furthermore, transfer processes lead to the distribution of substances between two different phases and are therefore more relevant in a long-term context (Schwarzbauer & Jovančević, 2018). Generally, each compound preferably accumulates in a specific compartment within the river system due to transfer processes such as dissolution, sorption, evaporation, or the uptake by biota (e.g., via the surface of the organisms such as the gills). Thus, a fundamental approach of a dynamic equilibrium with constant concentrations in both considered compartments can be used to assess the environmental fate of the investigated compounds (Schwarzenbach et al., 2003; Speight, 2017). The most relevant partition coefficients or equilibrium constants in aquatic environments are the Henry Laws constant (K_H) and the octanol-water coefficient (K_{OW}) (see Figure 1.2). However, under real environmental conditions, a clear equilibrium is generally not achieved (Reineke & Schlömann, 2023). Nevertheless, partition coefficients can be used to estimate the quantitative distribution of pollutants between different compartments.

The Henry Laws constant (K_H) indicates the tendency of a substance to accumulate more in the gas phase, while the K_{OW} value shows the ratio between the concentration of a substance in *n*-octanol and in water and thus reflects its tendency to adsorb on particulate matter (such as riverbed sediment or suspended material) (Harrad, 2001). High K_H values are associated with lower boiling points and polarities, while high K_{OW} values correlate with a high lipophilicity and low polarity. K_{OW} values and especially lipophilicity increase with molecular weight and increasing degree of chlorination, but decrease due to polar functional groups (Schwarzbauer & Jovančević, 2018). Furthermore, the bioconcentration factor (BCF) is an important parameter to assess the uptake of contaminants by biota, which is also depending on the lipid content of the organism (Harrad, 2001). The higher the BCF, the higher is also the potential for bioconcentration and biomagnification (Ibanez et al., 2007). In general, partition coefficients can be estimated based on the molecular structure and are mostly determined by the volatility and polarity (Reineke & Schlömann, 2023; Speight, 2017). Overall, air pollutants are characterized by a high volatility, while water pollutants have a low volatility combined with a high

polarity, and pollutants of the sedimentary compartment are defined by a high lipophilicity and lower volatility.

To cover the entire contamination of a river system, different compartments and matrices are of great relevance and need to be assessed (Figure 1.3). The fate and transport pathways generally depend on the flow dynamics of the river and, in particular, on the dynamics of the respective compartment:

1. *Aqueous compartment:*

The aqueous compartment within river systems is highly dynamic and mobile, depending on the flow discharges and behavior. Pollutants of the aqueous phase are typically hydrophilic and transported over long distances. However, they might undergo degradation and transformation along their way. In addition, extreme events such as droughts or floods can lead to an increase in pollutant concentrations or a dilution effect (Hrdinka et al., 2012; Wolff & van Vliet, 2021; Zhou et al., 2022). Fluctuations in discharges are highly relevant, so it is generally recommended to consider discharge-related loads rather than the concentrations of pollutants for this compartment. This also allows for better comparability with other riverine systems and thus different flow conditions.

2. *Particulate/Sedimentary compartments:*

Lipophilic, hydrophobic contaminants tend to accumulate in the particulate phase. The grain size and organic content of the sedimentary material are decisive here: the finer and more organic-rich the material is, the higher the adsorption capacity and the more likely the pollutants are to accumulate (Hilberg, 2022; Klamer et al., 1990). The transport and fate of these pollutants in a river system is therefore closely linked to the fluvial sediment transport, especially of suspended matter. This material and associated pollutants settle in areas of low flow velocity and low turbulence (Rhoads, 2020; Vercruyssen et al., 2017). Accordingly, there are different sedimentary compartments and accumulation areas that represent possible sinks for lipophilic pollutants:

- ***Riverbed:*** The riverbed or bed material load represents a subaquatic accumulation area within the channel bed. Depending on the hydraulic conditions, this accumulation area is generally temporary and can be easily resuspended and redeposited (Rhoads, 2020). In areas with higher flow velocities, coarser material such as gravel is deposited, while in areas with low flow velocities, finer material such as sand and especially silt accumulate. Therefore, areas such as meandering river segments or oxbows are potential (at least temporary) sinks for organic pollutants.
- ***Reservoirs:*** Reservoirs are based on the construction of dams. They artificially interrupt natural fluxes of water, sediment, and also chemical compounds (Schleiss et al., 2016). Based

on the low flow dynamics, the mostly undisturbed, continuous and homogeneous sedimentation of fine-grained material can result in a subaquatic long-term storage of sediments as well as contaminants (Ciszewski & Grygar, 2016; Heim & Schwarzbauer, 2013). Accordingly, reservoir sediments often reflect the sedimentation interval and pollution history of the catchment and can be used for geochronological investigations (Shotbolt et al., 2005).

- **Floodplains:** Geochronological approaches as mentioned for reservoir sediments are generally also applicable for floodplains (e.g., Gocht et al., 2001; Heim et al., 2004; Lorgeoux et al., 2016). Yet, the sedimentation and pollution interval of floodplains is not continuous, but closely related to floods, as floodplains are typically (re)activated during such events (Vrel et al., 2013). Nowadays, however, floodplains are often anthropogenically used for other purposes such as settlement, infrastructure development, and agriculture, disturbing the natural soil and sediment development (Patt, 2016). Hydraulic engineering measures and changes in flow regulation can also affect the geochronological suitability of floodplains.

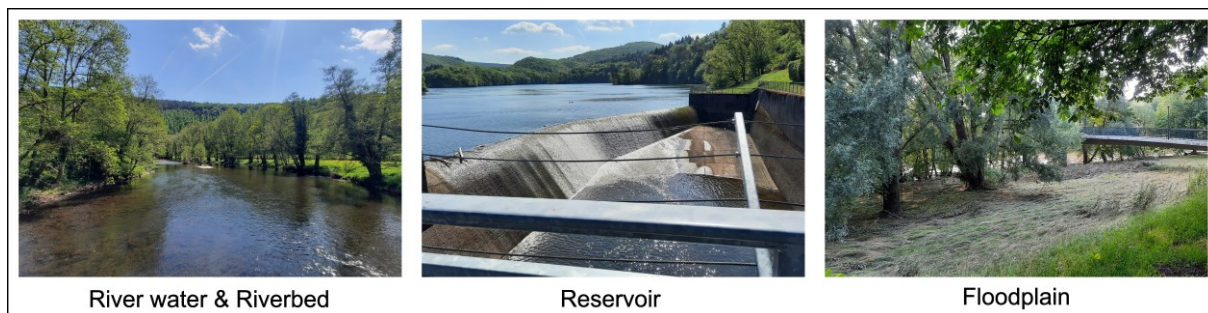


Figure 1.3 Overview of different environmental compartments at the Rur river. Images have been taken in July 2021 (floodplain) and May 2022 (river water & riverbed; reservoir).

1.3 Main Objectives

The overall aim of this doctoral thesis is to gain important insights and knowledge on the complex environmental behavior and fate of various organic pollutants in a highly anthropogenic affected river catchment. Despite a high number of studies focusing on aquatic pollution (cf. chapter 3), there is still a gap of a holistic and detailed understanding and consequently, comprehensive assessment of the dynamic and long-term impact of organic substances. This is also necessary as the introduction of emerging pollutants, coupled with increasingly advanced instrumental analytics, continues to increase the number of pollutants identified in the environment. Accordingly, in this thesis, the systematic qualitative and quantitative investigation of the Rur river is combined to determine the existing pollution situation as well as the environmental behavior and fate and corresponding processes of organic substances once they are released into the environment.

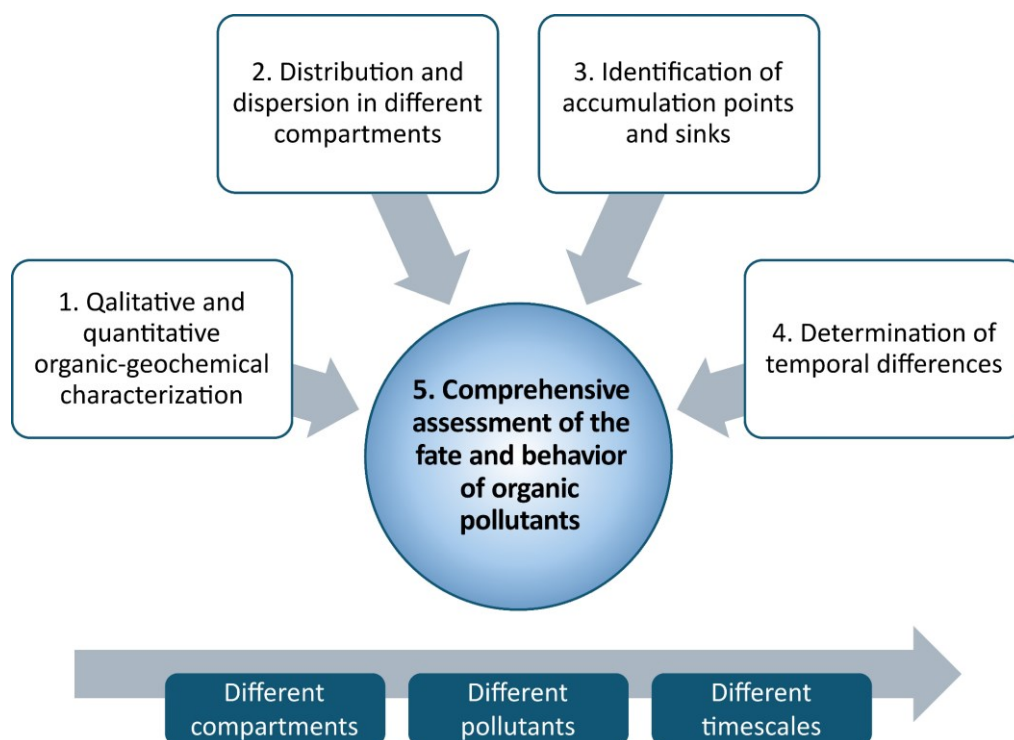
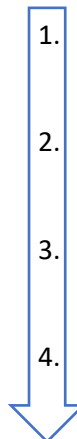


Figure 1.4 Overview of the main objectives of this doctoral thesis, considering different compartments and matrices, different organic pollutants, and different timescales.

To achieve this holistic understanding of the pathways and processes of a variety of organic contaminants, different Rur river compartments (including the river water, riverbed, floodplains, and reservoir sediments) have been sampled regularly or event-related after floods respectively drainage.

Following specific research objectives have been considered to achieve the comprehensive assessment of the environmental fate of organic pollutants:

- 
1. Qualitative determination of the structural diversity and quantification of organic pollutants as a basic organic-geochemical characterization of the catchment system
 2. Distribution and dispersion of organic pollutants in the different compartments of a dynamic river system
 3. Identification of potential accumulation points and sinks, including the effect of remobilization due to exceptional events such as floods
 4. Determination of temporal differences in the contamination situation, including the reconstruction of the pollution history
 5. Comprehensive assessment of the dynamic and long-term impact potential of organic substances in a complex river system and its different compartments

These objectives are also visualized in Figure 1.4. They were examined and analyzed across all studies to achieve a comprehensive assessment of the structural diversity, introduction, environmental behavior, and fate of diverse organic pollutants in the various compartments of the Rur river.

2 Study Area

Dynamic and thus rather small river systems are particularly well suited to analyze the general environmental behavior and fate of various organic contaminants. For these systems, the individual distribution processes, the influence of anthropogenic measures (e.g., structural or political) and the resulting effects on the ecosystem can be more easily identified, differentiated, and thus understood. In contrast, in larger river systems such as the Rhine river, complex pollutant mixtures are typically detected along the entire course of the river (Schäfer et al., 2011). This limits the ability to precisely identify individual distribution processes. Consequently, the dynamic river system of the Rur was chosen as a study area to evaluate the complex environmental fate of various organic contaminants. In particular, the diverse, but clearly distinguishable and definable emission sources make the Rur an ideal study area to determine the organic pollution, and thus also enable a transferability to other river systems.

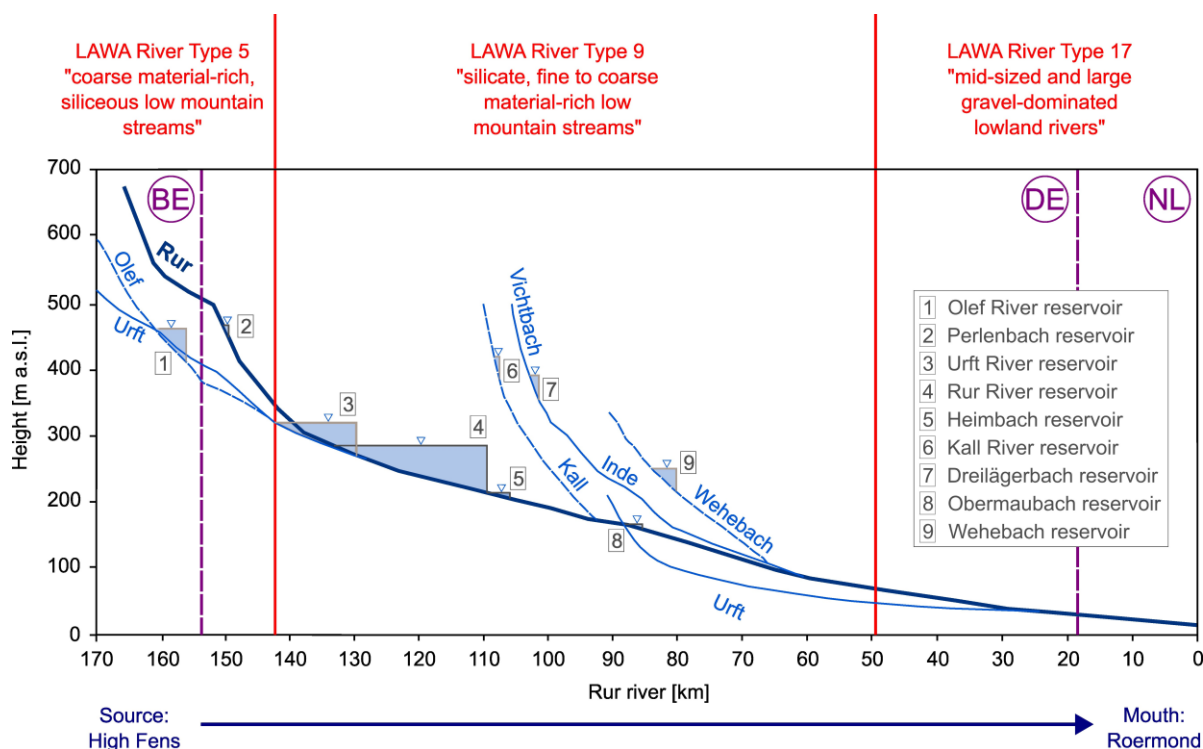


Figure 2.1 Longitudinal profile of the Rur river, corresponding main tributaries and the reservoirs within the catchment (modified after “WVER Steuerordnung” in Kufeld et al., 2010). The catchment covers parts in Belgium (BE), Germany (DE) and the Netherlands (NL). The subdivision into LAW A river types is shown as red lines (UBA, 2018).

2.1 Topographical and Climatological Context

The Rur belongs to the superordinate river catchment of the Meuse. It has a total flow length of about 163 km and covers a catchment area of about 2340 km² (MKULNV NRW, 2005). It originates in the high moorland and peat bog area of the High Fens in Belgium (approx. 660 m a.s.l.) and then flows through the typical low mountain range landscape of the Eifel in western Germany. In this area, several dams and weirs determine the flow and discharge pattern (cf. Figure 2.1 and Figure 2.2). At Kreuzau, south of Düren, the Rur merges into its middle course and from Linnich to its confluence with the Meuse at Roermond (approx. 30 m a.s.l.), the Rur corresponds to a classic lowland watercourse (MKULNV NRW, 2005). The downstream and lowland area generally belongs to the Lower Rhine embayment and is highly anthropogenically dominated due to the straightening and channelization of the water course as well as the construction and installation of numerous artificial river junctions (Kufeld et al., 2010). The LAWA river type classification divides the river into type 5 (coarse material-rich, siliceous low mountain streams) at the beginning, type 9 (silicate, fine to coarse material-rich low mountain streams) in its middle section, and type 17 (mid-sized and large gravel-dominated lowland rivers) at its lower course from Linnich to Roermond (UBA, 2018). Table 2.1 also summarizes the river types of the most important tributaries (Urft, Inde, and Wurm) in the order of their confluence with the Rur river. In total, the Rur catchment consists of 50 natural and 5 artificial surface water bodies with a specific catchment area of more than 10 km² (MKULNV NRW, 2005). The latter are mostly so-called mill ditches and were mostly constructed for the continuous water supply of the local industry (see chapter 2.3).

The separation into a mid-mountain (northern Eifel) and a lowland part (Lower Rhine embayment) is also recognizable from a climatological perspective. Principally, the catchment is located within the climatic zone of the westerly wind drift, and the cool, moderate climate is attributable to its proximity to the Atlantic Ocean (Kufeld et al., 2010). Nevertheless, there are clear differences in average annual temperature and precipitation between the mid-mountain and the lowland part. The average annual temperature (1991 to 2020) in Monschau in the Eifel is 8.3 °C with an annual precipitation of more than 1130 mm/a (LANUV, 2023). The latter is generally lower in the northern part of the catchment with values around 700 mm/a (Düren 660 mm/a; Jülich: 701 mm/a; Hückelhoven: 696 mm/a). In contrast, temperatures are higher, such as in Düren with an average of 10.7 °C between 1991 and 2020 (LANUV, 2023). These differences are based on the prevailing general weather conditions, as the westerly winds are pushing against the Eifel/Ardennes mountain ranges, causing increased precipitation on the windward side (Kufeld et al., 2010). Therefore, less precipitation is recorded on the leeward side facing away from the wind, e.g., in Vettweiß near Düren with an average precipitation of only 636 mm/a (LANUV, 2023). Furthermore, summer precipitation is most relevant for the northern part of the catchment area, while the main precipitation in the Eifel region occurs in winter. Prior to the

construction of the dam system (starting in 1900), this winter precipitation often led to flooding, as evaporation processes are also limited during this period. In contrast, summer discharges were often very low and insufficient for industrial applications (Kufeld et al., 2010; Polczyk, 1999).

Table 2.1 Overview of the LAWA typology of the Rur river and the three main tributaries Urft, Inde, and Wurm (MUNV NRW, 2023; UBA, 2018).

River		River km	LAWA river type	Description
Rur river	Source to Widdau (downstream of Monschau)	163.1 – 141.8	Type 5	coarse material-rich, siliceous low mountain streams
	Widdau to Rurdorf (upstream of Linnich)	141.8 – 49.4	Type 9	silicate, fine to coarse material-rich low mountain streams
	Downstream of Rurdorf	49.4 – 0	Type 17	mid-sized and large gravel-dominated lowland rivers
Confluence with the Rur river at river km 124.8				
Urft river	Source to Nettersheim	47.1 – 29.6	Type 5	coarse material-rich, siliceous low mountain streams
	Nettersheim to Kall	29.6 – 18.5	Type 7	coarse material-rich, carbonate low mountain streams
	Downstream of Kall	18.5 – 0	Type 9	silicate, fine to coarse material-rich low mountain streams
Confluence with the Rur river at river km 62.2				
Inde river	Source to Friesenrath (upstream of Walheim)	54.1 – 46.0	Type 5	coarse material-rich, siliceous low mountain streams
	Friesenrath to Vichtbach confluence (in Stolberg)	46.0 – 28.3	Type 7	coarse material-rich, carbonate low mountain streams
	Vichtbach confluence to Eschweiler Patternhof	28.3 – 21.4	Type 9	silicate, fine to coarse material-rich low mountain streams
	Downstream of Eschweiler Patternhof	21.4 – 0	Type 17	mid-sized and large gravel-dominated lowland rivers
Confluence with the Rur river at river km 26.4				
Wurm river	Source to Übach-Palenberg	57.6 – 26.7	Type 5	coarse material-rich, siliceous low mountain streams
	Downstream of Übach-Palenberg	26.7 – 0	Type 17	mid-sized and large gravel-dominated lowland rivers

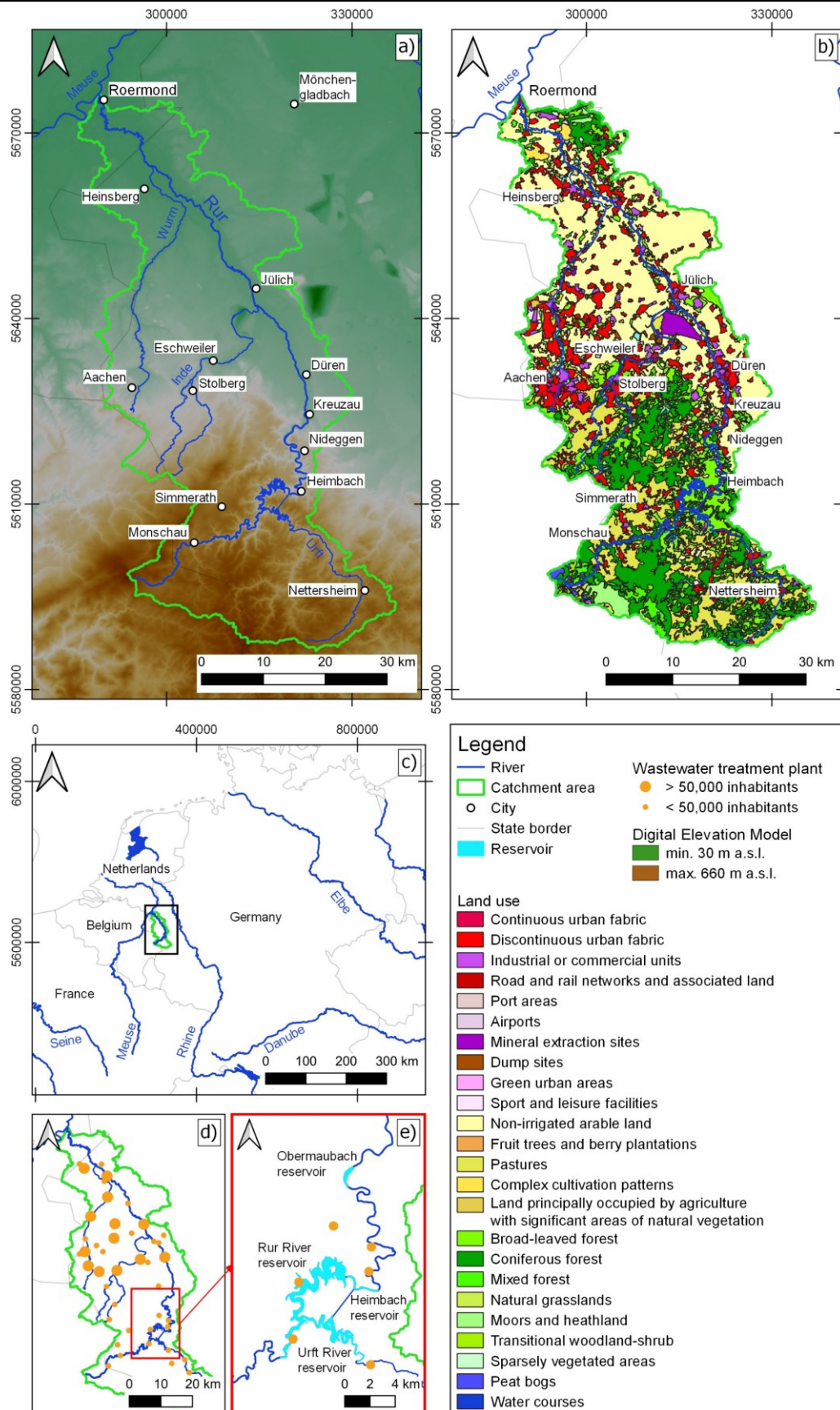


Figure 2.2 Overview of the Rur catchment a) shows the Rur river and its main tributaries, cities within the catchment and elevations (meters above sea level, m a.s.l.); b) shows the land use according to Corine Landcover (2018) data; c) shows the location of the Rur catchment in an European context; d) and e) show the location of wastewater treatment plants, while e) also shows four reservoirs in the upper course of the Rur river; Coordinate system: ETRS89 / UTM zone 32N.

2.2 Geological Context

The separation between the mid-mountain and the lowland part is also observed in the geological as well as hydrogeological features. The bedrock area of the northern Eifel is a part of the Rhenish Massif and was formed in the Upper Carboniferous by the Variscan orogeny. Today, mainly argillaceous shales from the Lower Devonian are exposed due to erosion processes (Kufeld et al., 2010). Devonian shales dominate the region between Kalterherberg and Kreuzau, while there are also highly weathered Ordovician and Cambrian quartzites and argillaceous shales present near the source of the river in the High Fens (Ribbert et al., 1992). Due to their low water permeability, peat bogs were formed in this area. In between are also magmatic rocks from volcanic activity, and in the region around Nideggen, red sandstone and shell limestone are present as a consequence of global sea level rise and the subsequent flooding of the area (Ribbert et al., 1992). Generally, the Eifel has been repeatedly covered by the sea, but nevertheless it has been rising since the Permian. This rise has led to stronger depth erosion and steep valleys, e.g., caused by the Rur river system since the Mesozoic era (Kufeld et al., 2010). The corresponding eroded material is then transported to the lowland part in the north of the Rur catchment. This part of the catchment is dominated by loose, unconsolidated sediments based on the gravel banks of the Rhine and Meuse rivers (Klostermann et al., 1990). They are mostly covered by Holocene fluvial deposits and, in the area of Jülich, by aeolian loess deposits of the Weichsel glacial stage (Kufeld et al., 2010). Accordingly, river terraces are predominant, but partly there are also older formations and outcrops (e.g., along the Rurand fault). Overall, particularly the upper geological layers are directly connected to the Rur river system and are therefore highly important during erosion processes and the associated sediment transport. They are also relevant for the prevailing land use and development (e.g., agriculture on the fertile loess in the area of Jülich).

From a hydrogeological point of view, the groundwater flow in the bedrock area is mainly characterized by joint and partly karstified aquifers, while porous aquifers are present in the lowland part (MKULNV NRW, 2005). The dominant groundwater flow direction is from south to north, as is the general flow direction of the Rur river.

2.3 Land and Water Use

The entire river course of the Rur shows a complex picture with a highly variable land cover and land use. Throughout the catchment, about one third of the area is used for agriculture and one tenth for urban settlements, while grassland accounts for almost one fifth and forests account for just under one third of the total area (MKULNV NRW, 2005). However, there is no uniform distribution of the different land covers in the Rur catchment. The mid-mountain part of the Eifel is predominantly used for forestry, with pastures on the plateaus. To a minor extent, there are also agriculturally used areas, but this has decreased significantly in the past centuries (Nilson, 2006). In contrast, agriculture is of high relevance in the lowland part, reflecting the morphologic and geologic bipartition. A detailed assessment of the land cover in the Rur catchment is based on the Corine Landcover data (2018) and is shown in Figure 2.2.

Table 2.2 Overview of the 10 largest wastewater treatment plants in the Rur catchment according to their treated annual wastewater volume of 2016 with the directly receiving river system; operated by and according to the Water Board Eifel-Rur (WVER, 2017c).

Wastewater treatment plant	Receiving river system	Treated annual wastewater volume in 2016 [m ³ /a]
Aachen – Soers	Wurm	27,796,097
Düren – Merken	Rur	21,020,943
Eschweiler	Inde	9,383,323
Stolberg – Steinfurt	Inde	8,453,188
Jülich	Rur	4,978,128
Heinsberg – Kirchhoven	Rur (via Flutgraben & Kitschbach)	4,682,326
Aachen – Eilendorf	Wurm (via Haarbach)	4,595,586
Aachen – Süd	Inde	4,512,598
Hückelhoven – Ratheim	Rur (via Mühlenbach)	3,586,229
Schleiden	Urft (via Olef)	3,123,826

The largest German cities in the catchment area are Aachen (251,000 inhabitants in 2023), Düren (93,000 inhabitants in 2023), Stolberg (56,000 inhabitants in 2023), Eschweiler (56,000 inhabitants in 2023), and Heinsberg (44,000 inhabitants in 2023) (IT.NRW, 2023a). In addition, Roermond (60,000 inhabitants in 2023) is located in the Netherlands at the confluence of Rur and Meuse (Gemeente Roermond, 2023). All mentioned cities are situated in the northern part of the catchment system, whereas only Düren is located directly on the course of the Rur river. The southern catchment part in

the Eifel is only sparsely populated and the most relevant urban agglomerations are Monschau (12,000 inhabitants in 2023) and Simmerath (16,000 inhabitants in 2023) on the Rur river as well as the municipality of Schleiden (13,000 inhabitants in 2023) on the tributaries Urft respectively Olef (IT.NRW, 2023a).

The largest wastewater treatment plants (WWTPs) are in these urban areas (see Table 2.2). The overall largest one is situated in the city of Aachen (WWTP Aachen-Soers) and discharges its treated effluents into the Wurm tributary. However, the largest ones discharging directly into the Rur river are the WWTP Düren-Merken and the WWTP Jülich. In general, there are more than 40 WWTPs in the catchment area and especially in the more urban, lowland part, these plants mostly treat municipal as well as industrial influents (WVER, 2017c).

The most important industrial areas are also located close to the urban agglomerations, some of which even discharge directly into the Rur or its tributaries. Particularly, the paper industry is of high relevance, but there are also metal and textile processing industries (e.g., Lang, 2023; Pappenfabrik Nierfeld, 2023). Historically, past and present mining activities have influenced the landscape in the catchment system (Bode et al., 2009; Reinartz, 1952). While in the past there has been underground mining of hard coal (especially in the Wurm catchment) and of different ores like copper, lead, and zinc (especially in the Urft catchment), open-pit mining of lignite still occurs in the middle part of the catchment close to Jülich and the confluence of Inde and Rur. The current lignite mining has a direct impact on the river system due to the groundwater lowering and the drainage into the Rur and its tributaries, as well as the withdrawal of cooling water for the associated power plants (RWE Power, 2023).

In general, the surface waters and groundwaters of the Rur catchment are largely used and partly modified for different anthropogenic activities. As already mentioned, they are among others important for industrial processes, mining activities, and the discharge of treated wastewater effluents. In particular, the construction of various mill ditches (“Mühlenteiche”) and of the dam system in the Eifel region had a major impact on the flow characteristics and discharge situation of the Rur river (Figure 2.1). Due to previous highly variable flow conditions and the increased water demand of the local industry, but also for flood protection, energy generation and for drinking water supply, a sum of 9 dams with a total reservoir capacity of about 300 million m³ has been built from 1900 onwards (MKULNV NRW, 2005; Polczyk, 1999). The so-called “Rurtalsperre” is still one of the largest reservoirs in Germany and is also used for recreational purposes (WVER, 2017a).

3 State of the Art

3.1 Research on the Organic Pollution of River Systems

First pioneering studies on organic pollution of aquatic systems focused, for example, on wastewater discharges from the chemical industry and the associated transport and accumulation of corresponding pollutants into river sediments (e.g., Jungclaus et al., 1978; Lopez-Avila & Hites, 1980). For river systems, persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), or linear alkylbenzenes (LABs) have been regularly identified for decades (e.g., Cerniglia, 1993; Safe, 1994; Takada & Eganhouse, 1998; Zhang et al., 2007). Due to their physicochemical properties and associated lipophilicity and hydrophobicity, these POPs mostly accumulate on particulate matter and therefore represent the contamination of the sedimentary compartment. As mentioned in chapter 1.2, there are different accumulation areas of lipophilic pollutants corresponding to sedimentary and thus also to pollution sinks.

Sediment cores from floodplains and reservoirs are regularly investigated using geochronological approaches, with a particular focus on well-studied POPs (cf. Bigus et al., 2014; Buchty-Lemke et al., 2019; Fikarová et al., 2018; Heim & Schwarzbauer, 2013). For instance, Franců et al. (2010) detected historical changes in organic pollution in sediment cores from the Brno reservoir in the Czech Republic. The analyzed spectrum consisted of PCBs and PAHs, but also metabolites of dichlorodiphenyl-trichloroethane (DDT) and hexachlorobenzene (HCB). They were able to divide the sedimentation and pollution interval into three major sections, representing the different flooding sequences of the reservoir, and showing the highest contamination towards the younger strata. In fact, sediment cores taken from reservoirs typically show the entire sedimentation and pollution interval since the construction of the specific dam, while floodplain accumulations are more variable and dependent on flood events (Ciszewski & Grygar, 2016; Vauclin et al., 2021). For this reason, not only sediment cores, but also surface samples are often collected from floodplains immediately after such events, usually to investigate the flood-induced transport of various pollutants (e.g., Hilscherova et al., 2007; Maliszewska-Kordybach et al., 2012; Stauch et al., 2023b). In recent years, the focus has increasingly shifted to the remobilization of existing contaminated sites and old burdens or legacy pollutions in river systems and the associated risk assessment (Crawford et al., 2022).

Another, more temporary, pollutant sink are river sediments or the riverbed itself. Sedimentation processes of suspended particulate matter and associated pollutants depend mainly on flow velocities within the river as well as particle sizes (Rhoads, 2020; Vercruysse et al., 2017). Accordingly, riverbed sediments can be easily mobilized and resuspended (Cofalla et al., 2012). They are also regularly analyzed for common pollutants such as PCBs and PAHs (e.g., David et al., 2012; Dsikowitzky et al.,

2020; Lv et al., 2015; Net et al., 2015; Wang et al., 2014; Zhang et al., 2010). In some cases, a parallel sampling of the riverbed and the river water has been performed (e.g., Da Silva et al., 2011; Gorga et al., 2015; Khim et al., 2001). Khim et al. (2001) focused mainly on the occurrence of the aforementioned standard compounds (PAHs, PCBs, etc.) in Ulsan Bay and its discharging rivers in Korea, while Da Silva et al. (2011) and Gorga et al. (2015) analyzed the occurrence and distribution of different pharmaceuticals and endocrine disruptor compounds (EDCs) in the Ebro river basin or other Iberian rivers. In addition, pesticides have been studied in the sedimentary compartment of various river systems worldwide, especially in regions with a high agricultural relevance (e.g., Doong et al., 2002; Neamtu et al., 2009; Villaverde et al., 2008).

For the aqueous compartment, contaminations originating in municipal and industrial discharges have been examined in particular, including compounds such as pharmaceuticals (e.g., Hughes et al., 2013; Wang et al., 2010; Wiegel et al., 2004), pesticides (e.g., Dahshan et al., 2016; Konstantinou et al., 2006; Stone et al., 2014), constituents of personal care products (e.g., Archer et al., 2017; Balakrishna et al., 2017; Boyd et al., 2003), or different industrial substances, for example, plasticizers or flame retardants (e.g., Andresen et al., 2004; Wang et al., 2015; Wolschke et al., 2015). However, most studies are limited to one or two of these pollutant groups. Only a few studies are based on a non-target or extensive screening and have detected a large variety of organic substances. For instance, Ccancapa-Cartagena et al. (2019) assessed a Mediterranean river basin and combined suspected, target as well as non-target screening to evaluate the contamination of the Turia river in the central-eastern part of Spain. Similar studies have also been carried out for the Lippe river and the Rhine river in western Germany (Dsikowitzky et al., 2004a; Dsikowitzky et al., 2004b; Ruff et al., 2015). Though, in larger river systems such as the Rhine, there is often a complex pollutant mixture resulting in a cumulative detection over the entire river profile (Schäfer et al., 2011). Accordingly, it is more difficult to understand the pollutant introduction and inputs, and to determine specific emission sources and pathways. Nevertheless, most studies of riverine contamination focus on such large systems, or, conversely, on a more local scale, such as urban surface waters (e.g., Gasperi et al., 2009; Ruff et al., 2015; Shi et al., 2016; Široká et al., 2005).

Although treatment technologies and efficiencies are increasingly improved and water protection is now of high priority in environmental legislation, the introduction of new and unknown (“emerging”) pollutants is still taking place from multiple and diverse emission sources (Morin-Crini et al., 2021; Petrovic et al., 2016). In fact, xenobiotics are continuously detected in every monitored stream in Germany (UBA, 2023c). The self-purification capacity of many river systems is insufficient, and remediation processes are often very complex and expensive, so that there is still a great need for research on aquatic pollution in general (González et al., 2014; Ostroumov, 2005). This also includes

the determination of toxicity and other adverse effects on humans and the environment, which allows the estimation of potential risks to aquatic systems and ultimately to humans. Mainly POPs are the focus of such studies because they are often ubiquitously distributed in our environment and show a highly bioaccumulative behavior (e.g., Alharbi et al., 2018; Li et al., 2006). Accordingly, studies are mostly related to human health and even differentiate effects on selected population groups, such as children (Damstra, 2002) or women (Grindler et al., 2015; Wahlang, 2018), or on different apparatuses or systems within the human body, e.g., on respiratory and immune systems (Gascon et al., 2013) or the liver (Kumar et al., 2014). However, there is still a limited amount of chemical and toxicological information in databases, so that risk assessment of these substances is quite limited (Du et al., 2022). Furthermore, as the (aquatic) contamination is generally composed of a mixture of different organic compounds, even low-level exposure to specific pollutants can lead to adverse effects (Le Magueresse-Battistoni et al., 2018; Vasquez et al., 2014). Thus, there is an ongoing need to identify and evaluate the composition of such mixtures or “pollution cocktails”, particularly in highly dynamic riverine systems (Du et al., 2022).

3.2 Research and Monitoring of the Organic Pollution of the Rur River

Regarding the Rur river, specific analyses and monitoring was mainly conducted by different authorities on the basis of German environmental legislation. According to the water framework directive (WFD), an initial surveying of the European river systems was performed in 2005. The main objectives were to analyze and review the past and present human impacts (including associated contaminations) and the economic value of water uses (MKULNV NRW, 2005; UBA, 2023c). Therefore, the inventory for the Rur river has also been assessed. The survey included an initial measurement of selected organic pollutants (e.g., PAHs, PCBs, and some pesticides) and the identification of relevant direct and indirect dischargers. Since then, regular monitoring has been carried out under the frame of the WFD and the corresponding results are also published in a qualitative form via ELWAS-WEB (MUNV NRW, 2023). However, the regular measurements and monitoring by the authorities mostly focus on a very limited number of substances within the aqueous compartment. Rarely, biota and suspended sediments are or have been analyzed as additional compartments. In contrast, sediment samples from the riverbed and the floodplains are not included in the WFD monitoring program.

In addition to the official investigations, scientific research on the Rur river has mostly focused on morphodynamics and anthropogenic influences on the transport of sediment and inorganic pollutants (e.g., Wolf et al., 2021; 2022; 2023). Other studies concentrated on the simulation of the aquatic fate of selected detergent and cleaning agent ingredients or pharmaceuticals (Schowanek & Webb, 2002; Schulze & Matthies, 2001), as well as on drought governance and climate change effects (Pyka et al., 2016; Vidaurre et al., 2016). In addition, some studies have compared the Rur river and other river systems, regarding, for example, the occurrence of the industrial substance 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) and further organic contaminants in the water compartment (Guedez & Püttmann, 2014; Schwarzbauer & Ricking, 2010). Guedez & Püttmann (2014) analyzed and quantified TMDD concentrations, while the approach of Schwarzbauer & Ricking (2010) was more qualitative and aimed on the identification of the diversity of organic pollutants for monitoring activities. More detailed studies were conducted for the tributaries Inde and Wurm in the northern part and the Urft in the southern part of the Rur catchment. Hagemann et al. (2018; 2020) as well as Buchty-Lemke et al. (2019) investigated the sedimentary pollution within the river corridor of the Wurm and examined corresponding geochronological approaches, while Esser et al. (2020) were looking at pollution profiles of different trace elements in the riverbed sediments of the Inde and Wurm. Stauch et al. (2023a) analyzed the sediment deposition in the Urft reservoir by detailed mapping and the creation of digital elevation models based on several topographic maps.

4 Structural Diversity of Organic Contaminants in a Meso-Scaled River System

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Abstract

Due to intensive anthropogenic usage, a complex mixture of inorganic and organic contaminants entered and still enters freshwater systems, released by various activities and emission sources. However, because of the highly dynamic nature of rivers, the individual occurrence, fate, and behavior especially of organic contaminants are highly complex and not fully understood. Here, a GC/MS non-target screening was applied to identify and determine the chemical diversity in the aqueous phase of the meso-scaled Rur river and to categorize indicative and relevant contaminants according to their load profiles for a distinct emission characteristic. Besides very well-known or widespread lipophilic to semi-polar contaminants, also so far unknown or only sporadically identified substances have been detected. In particular, wastewater treatment plants and the paper industry have been identified as major emission sources. Additionally, temporal variations in organic contamination were investigated over three sampling campaigns (2004, 2015, and 2020). Within this timespan, the overall composition of the contamination in the Rur has changed slightly, but nevertheless, the high chemical diversity remained. A detailed consideration such as that undertaken in this study is necessary as the occurrence of substances in a river system depends on many different factors. For a holistic assessment of environmental behavior, not only the sampling locations and associated development of emission profiles must be considered but also temporal variations and mitigation measures. Such a multi-parameter scenario provides an important basis for the mitigation and reduction of organic pollutants in our environment.

Keywords: GC/MS non-target screening, Pollution pattern, River water, Organic contaminants, Fluvial transport

4.1 Introduction

Particularly in the 20th century, anthropogenic activities such as changing of watercourses, increasing pollution, and thus, rapid degradation impacted the river systems worldwide (e.g. Dsikowitzky et al., 2004a; 2004b; Lin et al., 2017; Wang et al., 2012). Due to the highly dynamic nature of rivers, a complex mixture of inorganic and organic contaminants entered and still enters freshwater systems, released by various activities and emission sources (Lin et al., 2017; Schwarzbauer, 2006). As a first rough classification, the sources of anthropogenic contaminants can be divided into point sources (industrial and municipal effluents, single incidents as, e.g., industrial disasters) and diffuse sources (agricultural or shipping activities), leading to direct respectively indirect contamination of freshwater systems (Heim & Schwarzbauer, 2013; Morin-Crini et al., 2021; Petrovic et al., 2016).

Low-molecular weight organic contaminants are used for various purposes in industry and urban applications (e.g., as pesticides, plasticizers or pharmaceuticals) so that they show an extremely high diversity and structural variety (Bernhardt et al., 2017; Botalova et al., 2009; Lorenzo et al., 2018). Depending on their chemical and physical behavior and the dynamic nature in this compartment, the distribution processes in the aqueous phase are very short-term and complex, which makes their determination quite challenging. Only a few substances (like PCBs, PAHs, or DDT) and their environmental behavior in water systems are already well studied (e.g., Cerniglia, 1993; Safe, 1994; Turusov et al., 2002; Zhang et al., 2007). But mostly specific fates and complex behaviors are still largely unexplored, posing unknown risks to ecosystems and water safety.

This is of raising concern as surface waters are largely used as drinking water and human beings are thus highly interested in their respective conditioning and protection (Benotti et al., 2009; Houtman, 2010; Petrovic, 2003; Schwarzbauer, 2006; Vulliet et al., 2011). For instance, in North Rhine-Westphalia (Germany), around 60% of the raw water for drinking is taken from surface waters (esp. from dams), bank filtrate, and enriched groundwater (IT.NRW, 2019).

Furthermore, even though wastewater treatment involves increasingly efficient processes, and policy and environmental legislation are focusing more and more on water protection and renaturation, new, unknown pollutants are still entering the environment (Morin-Crini et al., 2021; Petrovic et al., 2016). Our existing conventional treatment plants are not designed to eliminate these “emerging contaminants”, and there are currently no regulations regarding monitoring or public reporting of their presence in water supply and effluents (e.g., Lorenzo et al., 2018; Mohapatra & Kirpalani, 2019; Patel et al., 2019; Tang et al., 2019).

To determine the behavior and fate of contaminants and for risk assessment, it is therefore crucial to be able to assign identified substances to possible sources. Thus, especially dynamic and rather small

river systems are well suited to show the general environmental behavior. Individual distribution processes, influences of anthropogenic measures, as well as resulting impacts on the ecosystem are easier to identify and differentiate. In contrast, in larger river systems such as the Rhine, complex mixtures of pollutants are often identified, resulting in a cumulative detection over the entire course of the river (Ruff et al., 2015; Schäfer et al., 2011). In this study, the Rur river as a meso-scaled catchment system was chosen to assess the longitudinal contamination status of the river water. Within this river system, heterogeneous emission sources as industrial and municipal wastewater effluents can be identified and considered. This also enables transferability to other river systems.

Up to now, only a few comparable studies are available regarding, for example, the Lippe river in Germany (Dzikowitzky et al., 2004a; Dzikowitzky et al., 2004b) or the Turia and Henares rivers in Spain (Ccanccapa-Cartagena et al., 2019; Gómez et al., 2012). These studies involved extensive screening and detection of a variety of organic substances in a diverse but distinguishable emission situation. However, the timeframe investigated is usually very limited and does not fully cover temporal developments. Schwarzbauer & Ricking (2010) investigated several different-sized European rivers to show the high structural diversity of organic contaminants. As part of their studies, they have also revealed that each river has unique contaminations patterns and structures. Especially river-specific contaminants are promising candidates for monitoring programs. Thus, individual and fundamental investigations of single freshwater systems, as in this study, are a crucial precondition.

Consequently, the overall aim of the present study was to determine the chemical diversity of organic contaminants in the Rur river system regarding its aqueous phase. This river system can be considered as a typical and representative meso-scaled Central European catchment in terms of flow and emission sources. In general, as the inventory in the aqueous compartment is very dynamic, the determination of the distribution and fate of various substances is challenging. However, it is indispensable to fill the general lack of knowledge of the behavior of organic pollutants in complex environmental systems and their impact on corresponding ecosystems and freshwater resources. A gas chromatography-mass spectrometry (GC/MS) non-target screening was applied to identify both well-known organic pollutants and emerging contaminants as such screenings have been proven to be effective for the identification of various organic pollutants in aquatic systems (e.g., Grigoriadou & Schwarzbauer, 2011; Köppe et al., 2020; Ruff et al., 2015; Schwarzbauer & Ricking, 2010). Additionally, indicative and relevant contaminants are categorized according to their load profiles for a distinct emission characteristic. Furthermore, temporal variations in organic contamination between 2004, 2015, and 2020 were investigated to achieve a holistic assessment of emission sources and environmental fate and behavior of organic contaminants.

4.2 Experimental

4.2.1 Study Area and Sampling

The Rur river is a tributary to the superordinate river basin of the Meuse. In total, the Rur has a flow length of 163 km and covers a catchment area of about 2340 km², so that it is classified as a meso-scaled catchment system. It can be divided into two geologic respectively physiographic parts: The southern part is the mountain range landscape of the Eifel that contributes to the Rhenish Massif, and the northern lowland part belongs to the Lower Rhine Embayment (MKULNV NRW, 2005). The upper course of the Rur river is close to a natural state, whereby the transition to its middle course is determined by various dams and water reservoirs. These are partly used for drinking water supply, as, for example, the “Rurtalsperre” which is one of the largest reservoirs in Germany (WVER, 2017a). The middle course, starting at Kreuzau (south of Düren), is clearly more urban and less natural. Particularly, the influence of local industry (paper, metal, and textile processing) and lignite mining are noteworthy here. From Linnich to its confluence with the Meuse at Roermond, it corresponds to a classic, but unnatural lowland watercourse, which is predominantly used for agricultural purposes.

In total, the river flows through three different countries (Belgium, Germany, and Netherlands), showing a highly dynamic river course with multiple anthropogenic impacts. The most relevant discharges are considered to be two wastewater treatment plants (WWTP) in the lower parts, the WWTP Düren and the WWTP Aachen-Soers (tributary Wurm) (Schröder, 1995; Schulze & Matthies, 2001). Their treatments include municipal as well as industrial influents. However, overall, there are more than 40 WWTPs in the Rur catchment area influencing the river and its water quality (WVER, 2017c).

Grab water samples (1 L) were collected at 21 locations on three different times over the entire course of the Rur river (as shown in Figure 4.1). Not all localities could be sampled at all times. The width of the river is ranging from 2 m at the first sampling location to about 20 to 25 m at locations further downstream. Each water sample was scooped from midstream approximately 1 m below the water surface. The samples were filled into pre-cleaned glass flasks and sealed free of air bubbles. Prior to extraction, they were stored in the darkness at 4 °C. Samples were processed within 2 to 3 weeks after collection and then measured directly. The extraction and measurement procedure was the same for all sampling campaigns. The analysis of all datasets was extended in 2020/2021 to include further organic contaminants.

The first sampling campaign was performed from November 30 to December 2, 2004. The second sampling was done on March 23-24, 2015, and the third sampling was done on November 23-24, 2020.

At the upstream sampling points, the mean flow over all sampling campaigns ranged from 1 to 4 m³/s, while further downstream, it increased to 9 to 27 m³/s.

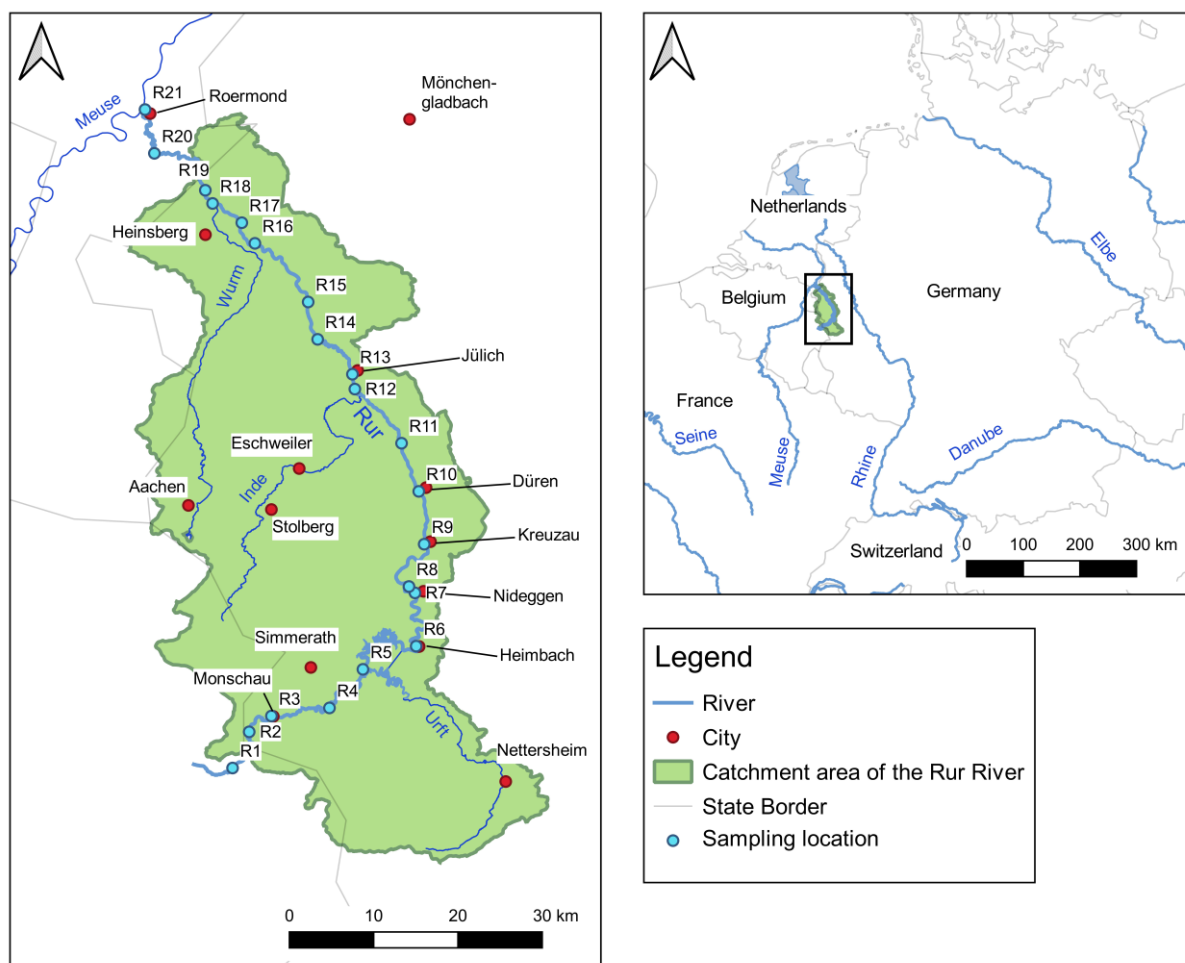


Figure 4.1 Overview of the Rur catchment (North-Rhine Westphalia, Germany) and the location of the sampling sites R1 to R21.

4.2.2 Chemicals, Blanks, and Recovery Experiments

Only equipment made of glass, metal, and Teflon/PTFE was used in the laboratory to minimize sample contamination. Prior to usage, the equipment was ultrasonically cleaned in detergent-containing water (Extran, Merck, Germany) and rinsed with high-purity acetone and *n*-hexane. All solvents used were acquired from Merck, Germany, and distilled over a 0.5 m packed column (reflux ratio approximately 1:25). The purity of the solvents was checked by gas chromatographic analyses. Anhydrous granulated sodium sulfate (Merck, Germany) and hydrochloric acid (Merck, Germany) required for the analytical procedure were cleaned with pure solvents. Blank analyses (*n*=4) were carried out to determine possible background contaminations. They revealed the presence of different plasticizers as phthalates,

acetyl tributylcitrate, and triacetin. Recovery rates ($n=4$) were determined by spiking 1 L of high-purity water (Rotisolv, Roth, Germany) with 4 μg of the respective reference compounds (Sigma-Aldrich, Germany) and then applying the same analytical procedure as described in the following for the environmental samples. The determined recovery rates are presented in Supplementary Information (Appendix to Chapter 4).

4.2.3 Sample Extraction

Sample treatment and analysis followed well-established and previously described methods (e.g., Dsikowitzky et al., 2002; Grigoriadou et al., 2008). Prior to the extraction, the water samples were filtered through pre-cleaned GF/F filters (Macherey-Nagel, Düren, Germany) to remove suspended particulate matter from the aqueous phase. Afterwards, a liquid-liquid extraction was carried out to approximately 1 L samples. For this purpose, sequentially, 50 mL each of *n*-pentane (1st fraction), dichloromethane (2nd fraction), and dichloromethane after acidification to pH 2 (3rd fraction) were used for the extraction in a separatory funnel. The sample was shaken for 5 min each, and after separation, fractions 1 and 2 were spiked with 50 μL of a surrogate standard solution containing the reference compounds fluoroacetophenone (5.8 ng/ μL), benzophenone- d_{10} (6.3 ng/ μL), and hexadecane- d_{34} (6.0 ng/ μL). All fractions were then concentrated to approximately 2 mL by rotary evaporation and dried with anhydrous granulated sodium sulfate. Acidic compounds present in the third fraction were methylated by the addition of a methanolic diazomethane solution. Afterwards, a surrogate standard (200 μL) containing fluoroacetophenone (14.4 ng/ μL) was added to the third fraction. Prior to injection, all fractions were concentrated to final volumes of 10 to 50 μL (first two fractions) and 200 μL (third fractions).

4.2.4 Gas Chromatography- Mass spectrometry

GC/MS analyses of the extracts were performed with a quadrupole ThermoQuest Trace MS mass spectrometer linked to a ThermoQuest Trace GC (ThermoQuest, Germany). The gas chromatograph was equipped with a ZB-5 fused silica capillary column (Phenomenex, Aschaffenburg, Germany; 30 m $\times$ 0.25 mm ID $\times$ 0.25 μm film thickness) and carrier gas velocity (helium) was ca. 40 cm/s. A 1 μL split/splitless injection (injector temperature of 270 $^{\circ}\text{C}$) was carried out at 60 $^{\circ}\text{C}$ with a splitless time of 60 s. After 3 min at initial temperature, the oven was programmed to 310 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C}/\text{min}$ and 20 min isothermal time. Mass spectrometer operation took place in electron impact ionization mode (EI^+ , 70 eV) using a source temperature of 200 $^{\circ}\text{C}$, scanning from 35 to 700 amu at a

rate of 2.5 scan/s in low-resolution mode. Further details of chromatographic conditions and quantification procedures are given in Dsikowitzky et al. (2004b) and Grigoriadou et al. (2008).

4.2.5 Compound Identification and Quantification

Individual compounds were identified by comparison of EI+ mass spectra with those of mass spectral databases (NIST, Wiley) and published information. Furthermore, the identification was verified with mass spectra of purchased reference compounds to consider also specific gas chromatographic retention times and elution orders. Quantification was based on the integration of characteristic ion chromatograms extracted from the total ion current. In Supplementary Information (Appendix to Chapter 4), all characteristic ions used for substance quantification are given. Response factors were obtained from four-point linear regression functions based on external calibration measurements with compound concentrations between 4 ng/ μ L and 40 ng/ μ L (injection of 1 μ L). These concentrations ranged within the expected values of the compounds in the samples and within the linear detection range. If reference compounds were not commercially available, response factors of substances with a similar structure were used for quantification. The inaccuracies of injection and sample volume were corrected with the surrogate standard. The limit of detection (LOD) was in the range of 1 ng/L, and the limit of quantification (LOQ) in the range of 5 ng/L.

4.3 Results and Discussion

4.3.1 Structural Diversity of Organic Contaminants in the Rur River

One main objective of this study was to determine the structural diversity of organic contaminants in the meso-scaled river system of the Rur river. Besides very well-known or widely distributed contaminants, also so far unknown or only sporadically identified substances have been detected.

In detail, the GC/MS based non-target screenings over all sampling campaigns revealed the presence of more than 70 lipophilic to semi-polar substances. They were dominantly xenobiotic and therefore of anthropogenic origin. As summarized in Table 4.1, the substances can be divided into different categories based on their technical application or their chemical structures.

Table 4.1 Concentration ranges (ng/L) of organic compounds detected in Rur river water samples (taken in November 2020, March 2015, and November/December 2004).

No.	Compounds	Detected concentrations [ng/L]		
		November 2020	March 2015	November 2004 December 2004
	<i>Pharmaceuticals</i>			
1	Carbamazepine	n.d. - 160	n.d. - 190	n.d. - 400
2	Oxcarbazepine	n.d. - 30	n.d.	n.d.
3	Caffeine	n.d. - 150	< 5 - 70	n.d. - 170
4	Chlorobutanol	n.d.	n.d.	n.d. - 1600
5	Iminostilbene	n.d.	n.d.	n.d. - 30
6	Lidocaine	n.d. - 210	n.d.	n.d. - 110
7	Acetylsalicylic acid	n.d.	n.d.	n.d. - < 5
8	Diclofenac	n.d.	n.a.	n.d.
9	Tocopheryl acetate	n.d. - 250	n.d. - 20	n.d. - 170
	<i>Personal care products</i>			
10	N,N,N',N'-Tetraacetylenediamine, TAED	n.d. - 80	n.d. - 200	n.d. - 80
11	4-Methoxycinnamic acid 2-ethylhexylester	n.d. - < 5	n.d. - 10	n.d. - 220
12	Drometrizole	n.d. - < 5	n.d.	n.d. - 50
13	Galaxolide	n.d. - 70	< 5 - 100	10 - 170
14	Tonalide	n.d. - 6	< 5 - 9	< 5 - 30
15	4-Oxoisophorone	< 5 - 20	< 5 - 50	20 - 120
16	Lilial	n.d. - < 5	n.d. - 30	n.d. - 10
17	Viridine	n.d.	n.d.	n.d. - < 5
18	Dihydromethyljasmonate	6 - 40	< 5 - 70	n.d. - 20
19	Cineol	n.d.	n.d. - 40	n.d. - 160
20	Coumarin	n.d. - 30	n.d. - 10	n.d.
21	4-tert-Butylcyclohexanone	n.d. - 10	n.d.	n.d. - 20
22	Benzophenone	< 5 - 30	n.d. - 100	10 - 280
23	Isopropylaurate	60 - 330	1100 - 16900	20 - 500
24	Isopropylpalmitate	10 - 70	n.d. - 3800	90 - 370
25	Methyl dehydroabietate	280 - 3800	290 - 17700	n.d. - 280
	<i>Pesticides and biocides</i>			
26	N,N-Diethyltoluamide, DEET	n.d. - 50	n.d. - 10	n.d. - 20
27	4,4'-Dichlorobenzophenone, DBP	n.d.	n.d.	n.d. - 240
	<i>Technical additives, plasticizers and other industrial compounds</i>			
28	Di-iso-propylnaphthalenes, DIPN	n.d. - < 5	n.d. - 110	10 - 30
29	N-Butylbenzenesulfonamide, NBBS	n.d. - 110	n.d. - 10	n.d. - 50
30	2,4,4-Trimethylpentane-1,3-dioldi-iso-butyrate, TXIB	10 - 70	n.d. - 3700	5 - 30
31	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	20 - 23600	100 - 24600	10 - 1700

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No.	Compounds	Detected concentrations [ng/L]		
		November 2020	March 2015	November 2004 December 2004
32	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	n.d. - 110	20 - 1500	n.d. - < 5
33	Triethylcitrate	< 5 - 120	n.d. - 540	n.d. - 40
34	Acetyl tributylcitrate	n.d. - 340	n.d. - 540	< 5 - 40
35	Triacetin	300 - 11800	n.d. - 1900	n.d. - 100
36	Triethylphosphate	n.d. - 220	n.d. - 210	n.d. - 160
37	Tributylphosphate	n.d. - 20	n.d. - 4300	10 - 730
38	Tris(2-chloroethyl)phosphate, TCEP	n.d. - 10	n.d. - 70	n.d. - 60
39	Tris(chloropropyl)phosphate, TCP	< 5 - 110	n.d. - 1200	n.d. - 40
40	Triphenylphosphate	n.d.	n.d. - 160	< 5 - 10
41	Triphenylphosphine oxide	n.d. - 260	n.d. - 60	n.d.
42	Dimethyl phthalate	10 - 70	30 - 1000	n.d. - 10
43	Diethyl phthalate	50 - 220	120 - 2500	180 - 700
44	Di-iso-butyl phthalate	30 - 460	170 - 3900	< 5 - 120
45	Di-n-butyl phthalate	70 - 1200	210 - 2600	130 - 620
46	Benzyl butyl phthalate	n.d. - 40	n.d. - 150	n.d. - 360
47	Bis(2-ethylhexyl) phthalate, DEHP	230 - 1400	180 - 4400	n.d. - 760
48	2,2-Dimethoxy-1,2-diphenylethanone, DMPA	n.d. - 40	n.d.	n.d.
49	Diphenoxyethane	n.d. - 10	n.d. - 90	n.d. - 40
	<i>Miscellaneous contaminants</i>			
	<i>Halogenated compounds</i>			
50	Dichloroaniline	n.d. - 8	n.d.	n.d. - 10
51	1,1,2,2-Tetrachloroethane	n.d. - 370	n.d. - 6	n.d. - 20
52	4-Bromoanisole	n.d.	n.d.	< 5 - 180
53	2,4-Dibromoanisole	n.d.	n.d.	n.d. - 20
54	2,4,6-Tribromoanisole	n.d.	n.d.	< 5
	<i>S-containing compounds</i>			
55	Diphenylsulfone	n.d. - 20	n.d. - 80	n.d.
56	Methylphenylsulfone	n.d. - 40	n.d.	n.d. - 20
57	Benzothiazole	n.d. - 8	n.d. - 20	< 5 - 20
58	2-Methylthiobenzothiazole	n.d. - 70	n.d. - 50	n.d. - < 5
59	N-Phenylbenzenesulfonamide	n.d. - 40	n.d. - 10	n.d. - 10
60	N-Ethyl-o-toluenesulfonamide	n.d. - 180	n.d. - 20	n.d. - 30
61	N-Ethyl-p-toluenesulfonamide	n.d. - 250	n.d. - 90	n.d. - 120
62	2-Aminodiphenylsulfone	n.d.	n.d.	n.d. - 10
	<i>N-containing compounds</i>			
63	2-Methylbenzotriazole	n.d. - 290	n.d. - 10	n.d. - 30
64	Quinoline	n.d. - 20	n.d. - 9	< 5 - 10
65	Quinoxaline	n.d.	n.d.	n.d. - < 5
66	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d. - < 5	n.d. - < 5	n.d. - 170

No.	Compounds	Detected concentrations [ng/L]		
		November 2020	March 2015	November 2004 December 2004
67	Phenylisocyanate	n.d. - 140	n.d.	n.d.
68	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile (TMSN)	n.d. - 1300	n.d. - 120	n.d. - 70
69	N,N-Dibutylformamide	120 - 560	7 - 750	20 - 160
	<i>O-containing compounds</i>			
70	2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone	n.d. - 40	10 - 100	n.d. - 10
71	Butylated hydroxytoluene, Ionole	5 - 20	n.d. - 330	10 - 40
72	1,3,3-Trimethyloxindole	n.d. - 30	n.d. - 10	n.d.

n.d. (not detected) means the concentration was below the detection limit (< 1 ng/L); < 5 means the concentration was below the limit of quantification and above the detection limit (1–5 ng/L); n.a. means not analyzed

4.3.1.1 Pharmaceuticals

Pharmaceuticals as emerging contaminants have gained intensive scientific attention worldwide over the last two decades. They are widely used in both human and veterinary medicine and have been identified in various studies of different aqueous compartments as wastewater, surface water, groundwater, and recently also drinking water (e.g., Patel et al., 2019; Vulliet et al., 2011). However, since specific compounds target specific activities and, thus, have different effects on a target organism, this group is very heterogeneous. The substances show a high variety of chemical, physical, structural, and biological properties and, therefore, different environmental behaviors. Among others, caffeine, carbamazepine, diclofenac, and acetylsalicylic acid have been detected in the Rur river, which are known to be ubiquitous and frequently detected compounds (Hughes et al., 2013). Acetylsalicylic acid was only detected below limit of quantification, but the detected concentrations of carbamazepine (up to 400 ng/L) and caffeine (up to 170 ng/L) were similar to other studies (Brezina et al., 2017; Hughes et al., 2013; Zhang et al., 2007).

However, also some uncommon and less-frequently detected pharmaceuticals were identified. The amino compound lidocaine is a local anesthetic and antiarrhythmic agent that was firstly synthesized in the 1950s, and since then, it has been used extensively for medical applications. In high doses, it can have a neurotoxic effect (Holmdahl, 1998). However, even though lidocaine is widespread used, it has only sporadically been noted as an environmental contaminant. Rúa-Gómez & Püttmann have investigated its presence in German wastewater treatment plants and the corresponding impact on surface water quality (2012a, 2012b). They have shown that lidocaine is constantly discharged by WWTP effluents as our conventional wastewater treatment does not remove it. At this point, Rúa-Gómez & Püttmann recognized a direct relationship between the amount of connected population and

discharge levels. Its maximum concentration in the Rur river was 210 ng/L, which is comparable to other German rivers (max. 176 ng/L) that have been investigated by Rúa-Gómez & Püttmann (2012a). Besides lidocaine, also chlorobutanol (sedative hypnotic and local anaesthetic), oxcarbazepine (anticonvulsant, derivate of carbamazepine), and iminostilbene (metabolite of carbamazepine) have been detected as noteworthy pharmaceuticals with maximum concentrations between 30 ng/L and 1.6 µg/L.

4.3.1.2 Personal care products

Similar to pharmaceuticals, personal care products (PCPs) are also a very diverse group of compounds and are typically released via municipal wastewater effluents. Both substance classes are consumed by humans in rather large quantities. The group of PCPs typically includes constituents of lotions, detergents, deodorants, toothpaste, or cleaning products. Compounds that are frequently detected in various surface waters include, e.g., fragrances or synthetic musk compounds as galaxolide or tonalide (Dsikowitzky et al., 2002). They have been identified in the Rur river with concentrations up to 170 ng/L and 30 ng/L respectively. However, several further fragrances have been also identified in this catchment area in a wide range of concentrations between LOQ and 160 ng/L (lilial, cineol, dihydromethyljasmonate, viridine, coumarin). Most of them have only been rarely documented as water contaminants so far (Klaschka et al., 2013; Matamoros et al., 2012). Some can be of both natural and artificial origin; hence, an exclusive anthropogenic emission cannot be assumed (e.g., coumarin). However, lilial (or butylphenyl methylpropional) is a synthetic aromatic aldehyde that has a floral scent and no known natural source (Bolek & Kümmerer, 2010). It is considered a contact allergen and must therefore be labeled in cosmetic products according to the EU Directive 2003/15/EC (European Parliament and Council, 2003). Godayol et al. (2015) have shown that it cannot be efficiently removed in WWTPs by conventional activated sludge treatments, where they even refer to Lilial as the most persistent fragrance allergen. Since it can be easily oxidized, metabolization might be of relevance and requires further investigations (Klaschka et al., 2013).

The substance 4-oxoisophorone is also used in the perfume and fragrance industry. It has been detected ubiquitously in the Rur river with concentrations between LOQ and 120 ng/L. Similar results in terms of occurrence and concentrations have been obtained in other studies, such as in the German rivers Lippe and Rhine (Dsikowitzky et al., 2004a; Dsikowitzky et al., 2004b; Schwarzbauer & Heim, 2005). Nevertheless, it has not received much attention beyond that. Of emerging interest is also the fragrance compound 4-*tert*-butylcyclohexanone that was only detected with low concentrations up to 20 ng/L. According to ECHA, it is toxic to aquatic life with long-lasting effects. However, to the author's

knowledge, 4-*tert*-butylcyclohexanone has only been reported in individual studies, so that the fate and behavior in the environment remains mainly unknown (Johnstone et al., 2020; Jüttner, 1999).

Besides fragrances, PCPs also include other substances and substance groups present in the Rur river. For instance, UV-filters (benzophenone, drometrizole, 4-methoxycinnamic acid 2-ethylhexylester) or tetraacetythylenediamine (TAED), a bleaching activator in laundry detergents, have been detected in concentrations up to 280 ng/L. TAED has been detected in surface water systems in only a few studies (Schwarzbauer & Ricking, 2010), and due to its high biodegradability and good photolysis in the presence of Fe(III) only at low concentrations (Brand et al., 1997; Schwientek et al., 2016; Sýkora et al., 2001).

4.3.1.3 Pesticides and biocides

N,N-Diethyl-m-toluamide (DEET) is mainly used as an insect repellent and has been detected in the Rur river with a maximum of 50 ng/L comparable to several surface waters worldwide (Aronson et al., 2012). It is commonly found in the aquatic environment, but its probability for adverse risks is low (Aronson et al., 2012; Weeks et al., 2012). In this study, DEET occurs only downstream of the WWTP Düren, which shows that wastewater effluents, in general, are an important input pathway for this substance. Nowadays, DEET is standardly considered in several surveys and offers a high potential as a molecular marker (Dsikowitzky et al., 2014b; Weeks et al., 2012). Eventually, benzothiazole (BT) and 2-methylthiobenzothiazole (MTBT) can also be assigned to this group as they are known degradation products of the fungicide 2-(thiocyanomethylthio)benzothiazole (Reemtsma et al., 1995). However, substances based on benzothiazole have widespread applications in industrial processes, e.g., in the tire and rubber manufacturing industry (Fiehn et al., 1994; Kloepper et al., 2004). Nevertheless, BT and MTBT are of concern because of their limited biodegradability and potential aquatic toxicity, and they have been identified as environmental pollutants in several studies (Asimakopoulos et al., 2013; Hidalgo-Serrano et al., 2019; Reemtsma et al., 1995). In this study, the maximum concentrations were rather low, with 20 ng/L (BT) and 70 ng/L (MTBT) (cf. Dsikowitzky et al., 2017).

4.3.1.4 Technical Additives, Plasticizers and Other Industrial Compounds

This group includes many and very diverse substances with different molecular structures as well as chemical and physical properties. Compounds that have been detected in the Rur river include well-known water contaminants such as organophosphate flame retardants respectively plasticizers (TCPP, TCEP, TBP, TEP, TPP) (e.g., Cristale et al., 2013; Kim & Kannan, 2018; Regnery & Püttmann, 2010). They

have been found in a wide range of concentrations from LOQ up to 1.2 µg/L, with high concentrations of TCPP comparable, e.g., to those found in Iberian rivers (Gorga et al., 2015). Due to their high production volumes and extensive usage, there is growing concern about their fate and behavior in the aquatic environment (Cristale et al., 2013; Pantelaki & Voutsas, 2019). Earlier studies have determined that some of them can have toxic effects on living organisms (Cristale et al., 2013; Reemtsma et al., 2008; van der Veen & Boer, 2012). Since they are typically highly water-soluble, drinking water contamination is also of significant and current interest (Kim & Kannan, 2018; Reemtsma et al., 2008; van der Veen & Boer, 2012).

However, one substance that has only been recognized as an indicative marker for industrial effluents in recent years is the synthetic intermediate triphenylphosphine oxide (TPPO) (Botalova et al., 2009). Since then, it has been recognized as an environmental contaminant in a few studies (Bollmann et al., 2012; Wang et al., 2015). Nevertheless, according to Wang et al. (2015), TPPO is harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Thus, special attention should be given to corresponding contaminations. In the Rur river, this phosphorous-containing compound has been detected at all sampling locations downstream of the WWTP Düren with up to 260 ng/L. Furthermore, several other plasticizers (e.g., phthalate-based plasticizers, NBBS, TXIB) and citrate esters have been detected with maximum concentrations between 110 ng/L (NBBS) and 12 µg/L (triacetin). For instance, due to its properties (lack of odor, low toxicity), acetyl tributylcitrate (ATBC) is commonly used as a phthalate substitute in pharmaceutical drugs or cosmetics (Takeshita et al., 2011). Nevertheless, Takeshita et al. (2011) suggest handling ATBC products with care as they may lead to altered metabolism of endogenous steroid hormones and prescription drugs.

Especially the paper industry is quite specific for the emission situation of the Rur so that the identification of corresponding industrial substances as triacetin, 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD), DIPN, or Irgacure 184 with partly high concentrations up to 25 µg/L is not surprising. However, the surfactant TMDD and the photoinitiator Irgacure 184 have been detected in several different river systems, so that these substances are recommended for international high-scale monitoring programs rather than for regional approaches intended to cover the real state of pollution (Schwarzbauer & Ricking, 2010). Botalova et al. (2011) suggested triacetin as a potential marker for paper production and printing inks because it has been detected in the effluent of an industrial plant specialized in the manufacture of paper, special cosmetic and pharmaceutical products, as well as materials for printing inks. Furthermore, according to Dsikowitzky et al. (2015), 2,2-dimethoxy-2-phenylacetophenone (DMPA) and diphenoxyethane are characteristic compounds of wastewaters from modern paper production sites. However, they are only reported in German wastewater influents but were not detected in the receiving water. Nevertheless, in the Rur catchment, both substances were

found with concentrations up to 40 ng/L (DMPA) and 90 ng/L (diphenoxyethane) downstream of the WWTP Düren, questioning the input of insufficiently treated wastewaters of the paper industry. Generally, data on behavior and fate is still missing as these compounds have only scarcely been identified in the aquatic environment.

4.3.1.5 Miscellaneous contaminants

In addition, further halogenated and sulfur-, nitrogen-, or oxygen-containing compounds have been detected in the Rur river with maximum concentrations between LOQ and 1300 ng/L that were not able to be assigned to specific emission sources. Some of them have been already described as emerging or even common contaminants of the aquatic environment (e.g., 2-methyl-2H-benzotriazole or quinoline). The N-heterocyclic quinoline is used in several industrial processes but also occurs naturally in the environment (Felczak et al., 2016). It is widely distributed and frequently detected in water and soil, but nevertheless, it shows a high ecotoxic potential (Felczak et al., 2016; Neuwoehner et al., 2009). However, the maximum concentration of quinoline in the Rur river was only 20 ng/L.

2,6-Di-*tert*-butyl-*p*-benzoquinone (BHT-quinone) is an oxidant and polymerization catalyst and also known as a transformation product of 2,6-di-*tert*-butyl-4-methylphenol/butylated hydroxytoluene (BHT) (Liu & Mabury, 2020; Ma et al., 2006). These substances have been detected with maximum concentrations of 330 ng/L (BHT) and 100 ng/L (BHT-quinone) (cf. Moldovan et al., 2018). BHT is a synthetic phenolic antioxidant that is extensively used and has gained much attention. Recently, however, there has been growing concern about toxic effects, environmental pollution, and challenges for water reuse due to its metabolite BHT-quinone (Liu & Mabury, 2020; Wu et al., 2019). Earlier studies have shown that it can cause DNA damage even at low concentrations (Nagai et al., 1993). However, further knowledge about sources, fates, and behavior is still lacking.

Finally, a nitrogen-containing substance was detected in the Rur river with a maximum concentration of around 1.3 µg/L. It has been identified as azobisisobutyronitrile (AIBN) or its degradation product tetramethylsuccinonitrile (TMSN). AIBN is a well-known and widely used radical initiator for various polymer and organic syntheses (Malow et al., 2015; Yamashina et al., 2014). By releasing elemental nitrogen N₂, AIBN generates organic radical species (Yamashina et al., 2014). Since this can be a thermally introduced process, the mass spectra of AIBN and TMSN obtained by GC/MS cannot be differentiated, as the hot gas chromatographic injection may produce the derivative from the original compound. However, these substances have different effects on the environment as TMSN shows acute toxic properties (Johannsen & Levinskas, 1986). Nevertheless, to the authors' knowledge, up to now,

both have not been identified as environmental contaminants. Thus, there is no information available regarding their behaviors and fates, and further research is required.

4.3.2 Emission Profiles and Spatial Distribution of Selected Contaminants

Another major objective of this study was to determine emission characteristics and patterns of the diverse contaminants to determine their specific environmental behaviors. Therefore, emission profiles showing the load over the entire longitudinal section of the river were calculated and categorized. In this context, loads are clearly more informative than concentrations as changing river runoffs affect the compound concentrations, but not the loads. Thus, spatial distributions along the river course can be assessed in detail. In principle, increasing loads indicate the input of a substance, e.g., by wastewater effluents, whereas decreasing loads show a removal from the water phase. Possible processes here are partitioning into other phases (e.g., as volatilization or adsorption to particulate matter) or degradation of the substance in the aquatic environment. Depending on the physicochemical properties of the compounds, this results in emission profiles that allow an estimation and assessment of the environmental behavior and fate.

According to the input of the individual substances, a general distinction was made between profiles showing local point and multiple to diffuse sources. As the data from 2020 shows the current exposure situation and variety of organic contaminants, the profiles are based on this campaign, while the next section provides a more detailed look on temporal variations. According to Dsikowitzky et al. (2004b), the load (g/d) was calculated with the compound concentration in water, C (ng/L), and the median river runoff, MQ (m³/s), as follows:

$$L = C \times MQ \times (3600 \times 24/10^6).$$

Further river data used for calculation are given in Supplementary Information (Appendix to Chapter 4). An overview of the detected concentrations and loads can be found in Table 4.1 and Table 4.2, respectively.

Table 4.2 Span of minimum and maximum loads (g/d) of organic compounds detected in Rur river water samples (taken in November 2020, March 2015, and November/December 2004).

No.	Compounds	Detected loads [g/d]		
		November 2020	March 2015	November 2004 December 2004
	<i>Pharmaceuticals</i>			
1	Carbamazepine	0 - 124	0 - 225	0 - 935
2	Oxcarbazepine	0 - 17	0	0
3	Caffeine	0 - 110	1 - 87	0 - 410
4	Chlorobutanol	0	0	0 - 3235
5	Iminostilbene	0	0	0 - 71
6	Lidocaine	0 - 125	0	0 - 259
7	Acetylsalicylic acid	0	0	0 - < 24
8	Diclofenac	0	0	0
9	Tocopheryl acetate	0 - 48	0 - 11	0 - 348
	<i>Personal care products</i>			
10	N,N,N',N'-Tetraacetylenediamine, TAED	0 - 59	0 - 247	0 - 164
11	4-Methoxycinnamic acid 2-ethylhexylester	0 - < 8	0 - 20	11 - 450
12	Drometrizole	0 - 1	0	0 - 126
13	Galaxolide	0 - 56	< 1 - 113	3 - 401
14	Tonalide	0 - 5	< 1 - 12	< 1 - 71
15	4-Oxoisophorone	1 - 12	1 - 63	6 - 204
16	Lilial	0 - < 8	0 - 41	0 - 24
17	Viridine	0	0	0 - < 24
18	Dihydromethyljasmonate	3 - 29	3 - 92	0 - 55
19	Cineol	0	0 - 55	0 - 377
20	Coumarin	0 - 19	0 - 14	0
21	4-tert-Butylcyclohexanone	0 - 9	0	0 - 41
22	Benzophenone	< 1 - 18	0 - 113	2 - 305
23	Isopropylaurate	22 - 271	116 - 24231	3 - 593
24	Isopropylpalmitate	3 - 48	7 - 2372	9 - 745
25	Methyl dehydroabietate	122 - 3078	76 - 25386	0 - 36
	<i>Pesticides and biocides</i>			
26	N,N-Diethyltoluamide, DEET	0 - 27	0 - 12	0 - 47
27	4,4'-Dichlorobenzophenone, DBP	0	0	0 - 477
	<i>Technical additives, plasticizers and other industrial compounds</i>			
28	Di-iso-propylnaphthalenes, DIPN	0 - < 8	0 - 105	1 - 54
29	N-Butylbenzenesulfonamide, NBBS	0 - 67	0 - 13	0 - 118
30	2,4,4-Trimethylpentane-1,3-dioldi-iso-butyrate, TXIB	3 - 42	25 - 419	2 - 66
31	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	4 - 14294	32 - 83863	1 - 4027

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No.	Compounds	Detected loads [g/d]		
		November 2020	March 2015	November 2004 December 2004
32	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	0 - 16	8 - 1967	0 - < 24
33	Triethylcitrate	1 - 70	0 - 351	0 - 94
34	Acetyl tributylcitrate	0 - 48	0 - 774	< 1 - 82
35	Triacetin	234 - 6579	39 - 2474	0 - 197
36	Triethylphosphate	0 - 158	0 - 281	0 - 366
37	Tributylphosphate	0 - 13	0 - 5638	2 - 1717
38	Tris(2-chloroethyl)phosphate, TCEP	0 - 8	0 - 43	0 - 130
39	Tris(chloropropyl)phosphate, TCP	< 1 - 68	0 - 769	0 - 74
40	Triphenylphosphate	0	0 - 105	< 1 - 12
41	Triphenylphosphine oxide	0 - 206	0 - 73	0
42	Dimethyl phthalate	2 - 52	5 - 995	0 - 24
43	Diethyl phthalate	12 - 117	0 - 3233	45 - 1644
44	Di-iso-butyl phthalate	19 - 370	51 - 3375	8 - 165
45	Di-n-butyl phthalate	33 - 970	47 - 1562	29 - 850
46	Benzyl butyl phthalate	0 - 12	0 - 143	7 - 386
47	Bis(2-ethylhexyl) phthalate, DEHP	105 - 1060	56 - 6245	0 - 827
48	2,2-Dimethoxy-1,2-diphenylethanone, DMPA	0 - 24	0	0
49	Diphenoxyethane	0 - 6	0 - 18	0 - 104
	<i>Miscellaneous contaminants</i>			
	<i>Halogenated compounds</i>			
50	Dichloroaniline	0 - < 8	0	0 - 24
51	1,1,2,2-Tetrachloroethane	0 - 253	0 - < 14	0 - 45
52	4-Bromoanisole	0	0	1 - 197
53	2,4-Dibromoanisole	0	0	0 - < 24
54	2,4,6-Tribromoanisole	0	0	< 1 - < 24
	<i>S-containing compounds</i>			
55	Diphenylsulfone	0 - 14	0 - 104	0
56	Methylphenylsulfone	0 - 25	0	0 - 45
57	Benzothiazole	0 - 6	0 - 18	< 1 - 47
58	2-Methylthiobenzothiazole	0 - 42	0 - 63	0 - < 24
59	N-Phenylbenzenesulfonamide	0 - 25	0 - < 14	0 - 24
60	N-Ethyl-o-toluenesulfonamide	0 - 111	0 - < 14	0 - 80
61	N-Ethyl-p-toluenesulfonamide	0 - 149	0 - 93	0 - 288
62	2-Aminodiphenylsulfone	0	0	0 - < 24
	<i>N-containing compounds</i>			
63	2-Methylbenzotriazole	0 - 217	0 - 18	0 - 71
64	Quinoline	0 - 15	0 - 15	< 1 - 24
65	Quinoxaline	0	0	0 - < 20
66	2,3-Diethyl-2,3-dimethylsuccinonitrile	0 - < 8	0 - < 14	0 - 389

No.	Compounds	Detected loads [g/d]		
		November 2020	March 2015	November 2004 December 2004
67	Phenylisocyanate	0 - 129	0	0
68	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile (TMSN)	0 - 756	0 - 155	0 - 172
69	N,N-Dibutylformamide	26 - 432	3 - 989	7 - 363
	<i>O-containing compounds</i>			
70	2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone	0 - 10	1 - 118	0 - 31
71	Butylated hydroxytoluene, Ionole	1 - 13	0 - 435	2 - 75
72	1,3,3-Trimethyloxindole	0 - 16	0 - 16	0

4.3.2.1 Emission Profiles Showing One Local Main Emitter

In general, cities and their corresponding WWTPs are often local hotspots resulting in higher concentrations and increasing loads at the specific location. Located directly on the Rur river, Düren (91,000 inhabitants in 2020) is the biggest and most important agglomeration. However, regarding the entire catchment, Aachen (249,000 inhabitants in 2020) represents the biggest city, located at the Wurm tributary which flows into the Rur river north of Heinsberg close to the Dutch-German border. Thus, these cities hold also the largest WWTPs in this area with treated annual wastewater volumes of 28 million m³ (Aachen) and 21 million m³ (Düren) (WVER, 2017c). Especially, the WWTP Düren has an enormous influence on the river contamination as it discharges its effluents directly into the Rur itself. Many substances have only been identified at the corresponding sampling location (R11) and downstream. Nevertheless, they show differences in their environmental behavior and stability. For some, the loads decrease rapidly after this point source, while for others, they remain constant or even increase.

Significant Increase due to WWTPs and Subsequently Decreasing Loads

The sulfur-containing compound methylphenylsulfone shows a clear increase in both concentrations and loads at the sampling location downstream of the WWTP Düren (R11). At this location, loads of 25 g/d were determined while it was not detected earlier (cf. Figure 4.2). Furthermore, directly at the next location R12 (9.5 km downstream of WWTP), the values were close to the quantification limit again. Another increase at sampling location R14 can be traced back to the input of the WWTP Jülich (treated annual wastewater volumes of 5 million m³ in 2016). In this case, too, concentrations and loads quickly decrease again. This indicates a dynamic environmental behavior, characterized by local emissions and rapid elimination as the result of, e.g., low stability, partitioning into other phases or

rapid degradation. However, methylphenylsulfone is only rarely documented as a riverine contaminant, and corresponding studies are lacking. While Schwarzbauer & Heim (2005) also mentioned, among others, the emission pathway as a metabolite of the herbicide planavin, the present emission profile implies either industrial or municipal sources. Similar emission profiles occurred for phenyl isocyanate, oxcarbazepine, or TPPO. For all of them, the WWTP Düren is the local main emitter. The inflow of smaller WWTPs or the Wurm and, thus, the effluents of the WWTP Aachen did not lead to any significant increases in loads. This could be attributed to the low environmental stability of the specific compounds that got obvious within the emission profiles. In particular, after the long flow path from the discharge of the WWTP Aachen into the Wurm to the confluence with the Rur (around 45 km), no additional high loads are thus to be expected.

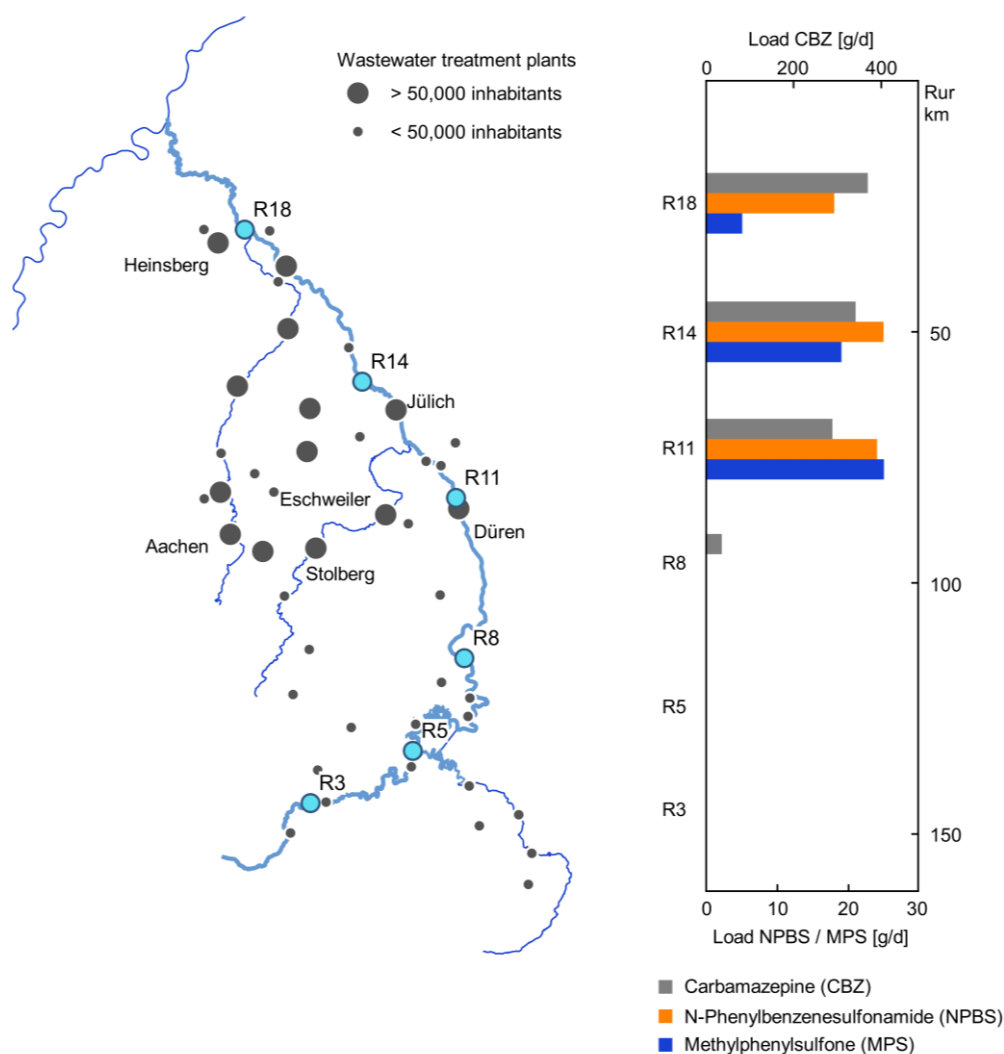


Figure 4.2 Wastewater treatment plants in the Rur catchment and spatial distribution of carbamazepine, N-phenylbenzenesulfonamide, and methylphenylsulfone loads (g/d) at six monitoring stations on the Rur. Sampling took place in November 2020.

Significant Increase due to WWTPs and Subsequently Constant Loads

This type of substances also shows a local main emitter (generally the WWTP Düren) and subsequently almost constant loads. Similar to methylphenylsulfone, the emission profile of N-phenylbenzenesulfonamide clearly shows inputs from wastewater treatment plants. As shown in Figure 4.2, the loads remain about the same, which indicates higher stability and the relative persistence of this substance in the water phase. However, this substance is also practically unknown as an environmental contaminant.

Better-known examples of this emission type are organophosphate flame retardants. Detected compounds included TCEP, TCPP, and TEP, which all show similar profiles having the WWTP Düren as the most important emission source. These three substances all exhibit a high water solubility (TCEP: 7 g/L, TCPP: 1.2 g/L, TEP: 50 g/L) and a rather low $\log K_{OW}$ (TCEP: 1.63, TCPP: 2.89, TEP: 0.39). Thus, they are commonly detected in the aqueous phase (Kim & Kannan, 2018; Pantelaki & Voutsas, 2019). Furthermore, TCEP and TCPP show a high persistence and do not degrade during wastewater treatment (Kim et al., 2017; Reemtsma et al., 2006). This clarifies both their introduction and the associated emission profiles. Similar conclusions also apply to TMDD (water solubility 1.7 g/L, $\log K_{OW}$ 2.8), which, however, was detected with significantly higher concentrations and loads (up to 24 µg/L and 14 kg/d in 2020). Such high concentrations have already been attributed to its use in the paper industry which also occurs along the Rur river (Dsikowitzky et al., 2015; Guedez & Püttmann, 2011). Guedez & Püttmann (2011) have also shown that its removal efficiency during wastewater treatment varies from 33% to 68% and that its biodegradability was only 25.4% during 57 days using the OECD Tests Guideline 302 A. These properties, therefore, also indicate certain stability and transport in river water.

4.3.2.2 Emission Profiles Showing Multiple Anthropogenic Emitters

Emission Profile with Increasing Loads

This type includes emission profiles of substances that show various emission sources with strong variations of concentrations but increasing loads with the course of the river. In particular, many of the detected fragrances show a corresponding environmental behavior (galaxolide, dihydromethyljasmonate, 4-oxoisophorone, 4-*tert*-butylcyclohexanone, coumarin). The main emitter here is again the WWTP in Düren, but there are also other emission sources. In the case of dihydromethyljasmonate, the highest concentrations (up to 40 ng/L at R1) were detected in the upper reaches of the river. In this area, there are smaller WWTPs discharging directly into the Rur and tributary streams. However, the associated loads are very low due to the low river runoff in this area (6 g/d at R1). Schwarzbauer &

Ricking (2010) identified dihydromethyljasmonate in several German and European rivers with the same multiplicity as the common synthetic musk compound galaxolide. According to its widespread distribution and the emission profile in the Rur river itself, dihydromethyljasmonate shows elevated stability and low degradation potential in the aqueous environment. Nowadays, it is therefore confirmed as a present environmental contaminant (Dey et al., 2019).

As visible in Figure 4.2, increasing loads were also detected for the antiepileptic drug carbamazepine. The two largest emission sources can be assigned to the WWTPs Düren and Aachen. Here, the influence of the large volume of wastewater from Aachen can be seen despite its longer flow distance to the sampling point (Wurm tributary). This leads to conclusions about the stability of carbamazepine in the water phase. It exhibits a low removal efficiency at WWTPs as well as a low degradation potential and high persistence in the environment so that it has been detected in numerous studies worldwide (Clara et al., 2004; Durán-Álvarez et al., 2015; Leclercq et al., 2009). Interestingly, the structurally similar oxcarbazepine shows steadily decreasing loads after its first introduction at the WWTP Düren, indicating a lower stability, degradation, or partitioning into other compartments. According to Leclercq et al. (2009), oxcarbazepine shows higher removal efficiencies in WWTPs than carbamazepine, and according to Kaiser et al. (2014), it is biodegradable. Furthermore, the toxicological evaluation suggested a reduced (geno-)toxicity compared to carbamazepine (Brezina et al., 2017). Thus, the environmental behavior of these structurally similar substances can be well differentiated.

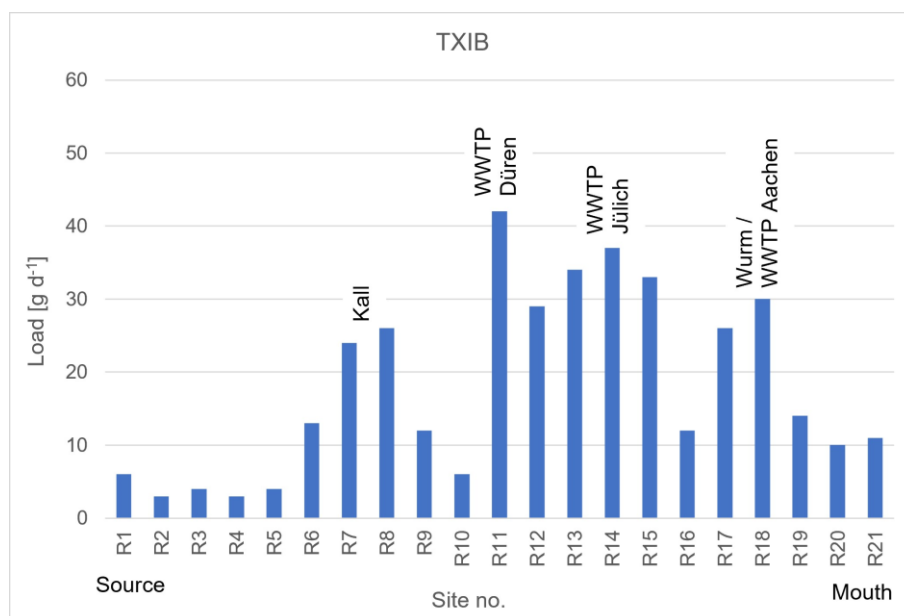


Figure 4.3 Spatial distribution of TXIB loads (g/d) over the entire river course with peak values at various wastewater treatment plant discharges (Düren, Jülich, Aachen) and tributaries (Kall, Wurm). Sampling took place in November 2020. The sampling sites are indicated in Figure 4.1.

Emission Profile with Varying Loads

In contrast to the previously mentioned substances, there is no clear increase of the loads of the plasticizer 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) along the river course. Nevertheless, it shows multiple emission sources. TXIB was also identified in a high multiplicity in the European rivers investigated by Schwarzbauer & Ricking (2010). The emission profile of the Rur river shows a ubiquitous presence with varying loads, but peaks that can clearly be assigned to wastewater treatment plants of different dimensions (cf. Figure 4.3). While the large plants in Düren and Jülich also treat industrial wastewater, the smaller ones treat mainly municipal wastewater revealing a municipal origin of TXIB. Also, according to Dsikowitzky et al. (2014a), it is a typical constituent of municipal sewage and is not readily biodegradable. However, overall, it can be assigned to a non-specific and diffuse origin as it was present at every sampling location. Very similar profiles with varying loads, but assignable main emission sources, were also observed for isopropyl laurate and N,N-dibutylformamide.

4.3.2.3 Emission Profiles Showing No Specific Emitters

Many substances of this profile type show a ubiquitous appearance. In contrast to the previously described profiles of, e.g., TXIB, no clear emission sources can be assigned. Examples of substances showing these emission profiles are various phthalates. These were detected at all sampling locations in varying concentrations and loads without any clear trend being identifiable. Comparable dynamic profiles were also found in earlier investigations from the Rhine river (Schwarzbauer & Heim, 2005). As phthalates are well-known environmental contaminants, there are several studies on their introduction, fate, and toxicity (Fromme et al., 2002; Staples et al., 1997). Due to their high production volume and wide distribution, they are nowadays ubiquitous and are among the most common compounds that humans come in contact with (Net et al., 2015). Even if their exposure does not lead to bioaccumulation, some phthalates are of concern due to their developmental and/or reproductive toxicity (Heudorf et al., 2007).

The emission profile of the plasticizer triacetin also shows no clearly recognizable trend. Very high concentrations were detected in both the upper and middle course (12 µg/L and 8.1 µg/L, respectively), with the associated loads only showing a peak in the middle course. This peak is located near to the cities of Düren and Jülich and could possibly be attributed to the paper industry located there. However, due to the ubiquitous occurrence in this river system, the substance is not suitable as a marker for the paper industry at the Rur river.

Quinoline also shows a highly interesting emission profile having no clear emission sources. Its concentrations and loads are continuously increasing along the river's longitudinal section. This suggests a biogenic input.

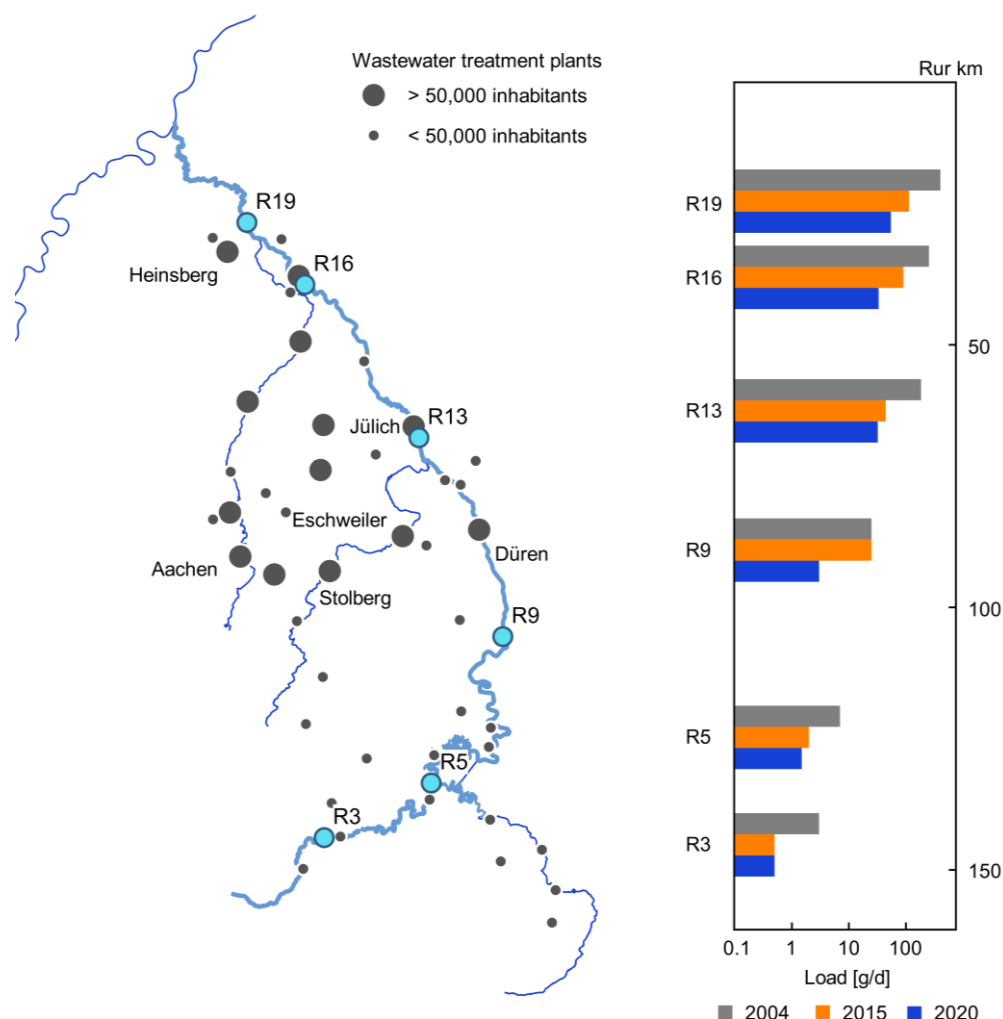


Figure 4.4 Wastewater treatment plants in the Rur catchment and temporal as well as the spatial distribution of galaxolide loads (g/d) at six monitoring stations on the Rur over three different sampling campaigns (please note the logarithmic illustration of the x-axis).

4.3.3 Temporal Variations

Another objective of this study was to investigate temporal variations in organic contamination and to determine whether it has decreased in recent decades. The general conditions regarding population development, water demand and effluent production have remained almost the same over the period under consideration. Nevertheless, since the water compartment, in particular, is highly dynamic, these samplings are only to be understood as snapshots of contamination. Nevertheless, general trends can be derived if, for example, a substance shows similar emission profiles over several campaigns. This is

the only way to make reliable statements about environmental behavior and fate. Overall, 64 contaminants were identified in 2004, 54 contaminants in 2015, and 59 contaminants in 2020. Thus, the detected contaminants show a high structural diversity in all sampling years. Due to new developments, but also new findings regarding the resistance and toxicity of the contaminants, the overall pollution load of the river changes, but nevertheless, the high diversity remains.

Especially brominated and some chlorinated compounds (e.g., bromoanisole or chlorobutanol) were not detected in recent campaigns of 2015 and 2020. Due to their partly high environmental relevance, this can possibly be attributed to restrictions on use or even bans (Huang et al., 2014; Reemtsma et al., 2008). Furthermore, for a large number of substances, significantly lower loads were determined in 2020 than in the previous samplings. These include, for example, the substances galaxolide, tonalide, lilial, 4-methoxycinnamic acid 2-ethylhexylester, 2,3-diethyl-2,3-dimethylsuccinonitrile, and DIPN. While in 2004, galaxolide loads of up to 401 g/d were found; the maximum load in 2015 was 113 g/d, and in 2020 it was even only 56 g/d. Nevertheless, due to its persistence, the emission profiles are very similar with relatively constantly increasing loads (cf. Figure 4.4). This indicates a lower input into the water body, either due to a reduced use or higher removal efficiencies of the respective WWTPs. The other before-mentioned substances were no longer detected beyond doubt in 2020. While in 2015, they were detected only sporadically and mostly with concentrations below the limit of quantification (except for DIPN); in 2004, they appeared in part with significantly higher concentrations and loads (4-methoxycinnamic acid 2-ethylhexylester: 450 g/d; 2,3-diethyl-2,3-dimethylsuccinonitrile: 389 g/d; tonalide: 71 g/d). DIPN was detected frequently in both 2004 and 2015 (maximum loads of 54 g/d and 99 g/d), but only sporadically and below the limit of quantification in 2020.

In addition to substances with lower loads, nearly constant (e.g., for carbamazepine, caffeine, and triethyl citrate) or even higher loads also occurred for some substances (e.g., for TMDD, triacetin, and AIBN/TMSN). For TMDD, the values were significantly higher both in 2015 and 2020. In 2015, the maximum load was reached after the discharge of the WWTP Jülich (84 kg/d) and in 2020 after the WWTP Düren (14 kg/d). Thus, the local main emitter differs, but in both locations, it can be traced back to the paper industry located there. In general, the booming online trade and the associated increase in the volume of packaging have led to an increase in the production capacity of the paper producers in the catchment area (Kaleß et al., 2020). Therefore, this explains higher loads and increased detection of substances from paper production in the river water.

2-Methylthiobenzothiazole was also detected more frequently in both recent campaigns. In 2004, it was only found at sampling locations close to the mouth and below quantification limit. In 2015 and

2020, the WWTP Düren was the main emitter resulting in loads of 40 g/d and 42 g/d, respectively. In 2015, however, the inflow of the Wurm also led to a high load (63 g/d), which was not the case in 2020.

Moreover, the substances DMPA, phenyl isocyanate, and oxcarbazepine have only been detected in 2020. They all occur only downstream of the WWTP Düren and are thus discharged by industrial (DMPA, phenyl isocyanate) and municipal (oxcarbazepine) wastewater effluents there. DMPA, oxcarbazepine, and phenyl isocyanate occurred with loads of 24 g/d, 17 g/d, and 129 g/d, respectively. Oxcarbazepine was first approved in Germany in 2000 (Flesch, 2004). However, studies on tolerability only followed in subsequent years, so the detection in 2020 may be due to an increased usage of this pharmaceutical (Freidel et al., 2007; Steinhoff, 2009).

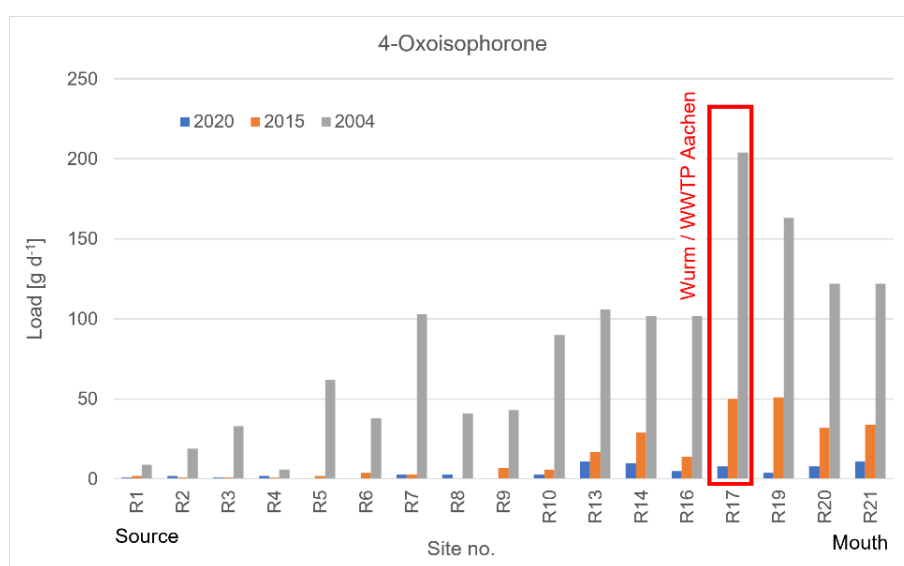


Figure 4.5 Temporal and spatial distribution of 4-oxoisophorone loads (g/d) over the entire river course with peak values at the confluence of the Wurm tributary, into which the effluents of the wastewater treatment plant in Aachen are discharged. This influence declined from 2004 (gray) to 2015 (orange) and is no longer discernible in 2020 (blue). The sampling sites are indicated in Figure 4.1.

Looking specifically at the courses of the emission profiles and not just the loads, the greatest variations were noticeable for the influence of the Wurm tributary. Although the largest WWTP in the catchment area discharges into it, the inflow of the Wurm did not lead to any significant increase in concentration and load in 2020 for most of the identified substances. In 2004 and 2015, this tributary had the character of a main point source. For example, when considering the entire emission profile, the inputs of 4-oxoisophorone were highest at this location, with loads of 204 g/d in 2004 and 57 g/d in 2015. As shown in Figure 4.5, this influence was no longer evident in 2020. However, the detected concentrations and loads of 4-oxoisophorone were generally significantly lower in 2020 (max. 12 g/d), but its ubiquitous presence remained. A reason for the reduced influence of the Wurm could be the

large-scale ozone plant at the WWTP Aachen, which has been in operation since 2018. Initial investigations as well as the previous pilot operation already showed promising results regarding the elimination of trace substances (on average 80%) and the formation of transformation products (Brückner et al., 2018). However, a final report on the effects and optimization of this plant in operation is still pending.

It is important to include such concrete measures in consideration of organic contamination as well as temporal and spatial changes per se because the occurrence of substances in a river system depends on many different factors and parameters. Only with such detailed consideration of changing emission profiles and behaviors, a holistic assessment and evaluation is possible.

4.4 Conclusions

GC/MS non-target screenings revealed the presence of a wide spectrum of low-molecular-weight organic compounds showing a high structural diversity as well as a high diversity in environmental behaviors. Many contaminants are of anthropogenic origin and used as, e.g., pharmaceuticals, personal care products, or in industrial processes. Based on the emission profiles, initial assessments are made about the stability and environmental behavior of the contaminants. These largely coincide with previously published research results. For some substances, however, further investigations are still necessary, as they have rarely been considered as environmentally relevant contaminants (e.g., AIBN/TMSN, BHT-quinone, oxcarbazepine, or methylphenylsulfone).

Their environmental pathways were mainly traced back to effluents of wastewater treatment plants. Especially the treatment plant in Düren showed a high input and influence on the chemical diversity in the river system as the diversity and loads of organic contaminants are clearly higher downstream of this WWTP than in the river upstream. However, this can be attributed to the diverse influents of the wastewater treatment plant which collects municipal as well as industrial wastewaters. The paper industry plays a major role here so that corresponding contaminants as TMDD or diphenoxyethane were also detected, partly with very high loads. Interestingly, the effluents of the even larger wastewater treatment plant in Aachen (which discharges into the Wurm tributary) no longer have a major impact on the contamination of the Rur river in 2020 compared to earlier investigations (2004 and 2015). This is probably due to an improved removal performance from a new ozonation system. In general, many decreases in loads and concentrations were observed over the three sampling campaigns and the corresponding 16-year time window. However, higher loads were also detected in individual cases, which indicate increased consumption (e.g., in the paper industry). Over the years, the overall composition of the contamination load in the Rur river has changed slightly, but

nevertheless, the high chemical diversity and structural variety remained. This also shows that regular surveys of river systems are necessary to identify current contamination and take appropriate action if necessary.

Overall, a detailed consideration such as that undertaken in this study is necessary as the occurrence of substances in a river system depends on many different factors. For a holistic assessment of environmental behavior, however, not only the sampling locations and associated development of emission profiles over the course of the river must be considered but also temporal variations as well as associated measures (e.g., technical, and technological development of WWTPs or bans on certain substances). Such a multi-parameter scenario of changing emission profiles and environmental behavior provides an important basis for the mitigation and reduction of organic pollutants in our environment.

5 Distribution, Remobilization and Accumulation of Organic Contaminants by Flood Events in a Meso-Scaled Catchment System

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Abstract

Background: Extreme weather events and natural disasters such as floods can cause severe damage and impacts on catchment systems covering natural as well as urban, industrial or agricultural areas. Thus, floods often lead to the acute and unusual release of organic pollutants, as well as the remobilization of legacy contaminations or old burdens. Floodplains are then of major relevance for the accumulation of pollutants. Accordingly, various floodplains distributed throughout the course of the Rur river were sampled immediately after two flood events in January/February and July 2021. The main objective was to address the general lack of knowledge on indirect effects of flooding and the corresponding distribution and accumulation of organic pollutants regarding different dimensions and dynamics of flood events.

Results: Gas Chromatography/Mass Spectrometry (GC/MS) based non-target screenings revealed the presence of several lipophilic to moderate polar organic pollutant groups, including PAHs (polycyclic aromatic hydrocarbons), hopanes, PCBs (polychlorinated biphenyls), LABs (linear alkylbenzenes) and various other industrial substances. These substances are indicators of petrogenic pollution, historical and current industry in the catchment area, and of wastewater and urban pollution, respectively. In general, concentrations detected after the extreme summer flood were higher than in winter. This points to additional emission sources due to substantially higher discharges and consequently more severe flooding in July. The main tributaries also had a major influence on the input and concentrations of organic pollutants at the receiving Rur river. Further on, structural features such as dams and reservoirs, but also (re)naturalized areas were clearly recognizable in the flood-related dispersion of

organic pollutants. Interestingly, LAB contamination was similar after both flood events regardless of the specific dimension.

Conclusions: Flood dimension and frequency are of great relevance for the distribution, remobilization and accumulation of organic contaminants. However, special attention should be given to the introduction of wastewater pollutants for any flood extent. Overall, organic indicators are therefore very useful to obtain information on specific distribution patterns and the influence of tributaries or structural measures, providing an important basis for the assessment of short- and long-term environmental risks and hazards.

Keywords: Flood events, Organic pollution, Remobilization, Vulnerability, Hazard

5.1 Background

In recent years, the number of extreme weather events and natural disasters has increased worldwide, which has also led to an increase in flooding. To mention just a few recent examples, in the twenty-first century major floods occurred on European rivers in 2002, 2005, 2007, 2010 and 2013 (Kundzewicz et al., 2013; Raynaud et al., 2015). Due to global climate change, severe flood events like these are likely to occur more frequently and also with higher intensities in the coming decades (Hirabayashi et al., 2013; Kundzewicz et al., 2013; Wilby & Keenan, 2012). In addition to infrastructural and economic damage, flood events have a direct and indirect impact on humans, animals and the environment. It is particularly important to consider the ecological damage due to the discharge of pollutants and toxic substances into river systems by a flooding of industrial sites, landfills, agricultural areas as well as urban areas including wastewater treatment plants. The resulting release of substances leads to an increased environmental contamination and can affect formerly unpolluted sites. In return, in many catchments, there is also a risk that contaminated sediments and old burdens will be remobilized during floods (Crawford et al., 2022). In particular, this effect has been scarcely studied to date.

Generally, different inorganic and organic substances tend to be enriched in sediments due to their mainly hydrophobic and lipophilic character. These substances include heavy metals and a variety of organic contaminants such as PAHs, LABs, PCBs or pesticides. In particular, the input and distribution of metals and PAHs have been intensively studied in flood deposits (e.g., Maliszewska-Kordybach et al., 2012; Martínez-Santos et al., 2015; Vulava et al., 2017). Nevertheless, there are several further pollutants that need to be investigated to assess risks for human health and environmental protection. These include substances that are generally difficult to be degraded in wastewater treatment plants or the aquatic environment. In addition, substances of high production or emission rates but principally

degradable also enter water bodies and possess therefore also environmental relevance. This can locally result in a cumulative contamination potentially posing a significant risk to environmental quality as well as human and animal health (Crawford et al., 2022).

Especially floodplains are an important sink for sedimentary material and accumulated pollutants. Their natural functions include aspects such as water, sediment and nutrient retention, flood protection, groundwater recharge as well as the self-purification of water bodies. However, nowadays people use these areas for various other purposes such as agriculture, settlement or infrastructure (e.g., for the construction of rail- or motorways). Due to these impacts and associated large losses of floodplains in the past, only about one-third of the former floodplain areas on rivers in Germany can still be inundated during large flood events (Koenzen et al., 2021). Nevertheless, the existing floodplains are important accumulation areas for particulate matter and organic contaminants as POPs (persistent organic pollutants), which is why they are also referred as the river's memory of contamination (Heim et al., 2004; Klös & Schoch, 1993).

Due to extreme precipitation and runoff during the period 12 to 15 July 2021, severe flooding occurred in Germany and other neighboring countries (Kreienkamp et al., 2021; Szönyi et al., 2022). Within a very short period of time, an extreme amount of precipitation fell over the low mountain ranges in Rhineland-Palatinate and North Rhine-Westphalia in Germany. This amount was partly more than twice as high as the average for the entire month of July (Ionita et al., 2021; Schäfer et al.). Furthermore, the soils were saturated by previous rain events and therefore could not absorb the water masses (BMI, 2022; Kreienkamp et al., 2021). Particularly in low mountain ranges such as the Eifel, this led to rapid rises in water levels as the water was channelled and collected in the river courses. Overall, the severe weather event and flooding had extreme impacts in terms of great damage to infrastructure (including houses, roads, rail- and motorway lines, bridges and communication), but also in terms of more than 200 fatalities (BMI, 2022; Kreienkamp et al., 2021; Szönyi et al., 2022). In addition to these direct impacts, it is also important to study longer-term or indirect impacts such as the input and accumulation of pollutants in river systems.

Therefore, different floodplains distributed throughout the course of the Rur river were sampled immediately after two flood events in January/February and July 2021. The main objectives were to determine pollutant concentrations, (re)distribution, and accumulation, as well as to understand the dimension and corresponding impacts of different floods on a meso-scaled catchment system. This was all done under the framework of risk assessment and pollutant mitigation during and after flood events.

5.2 Methods

5.2.1 Study Area and Sampling

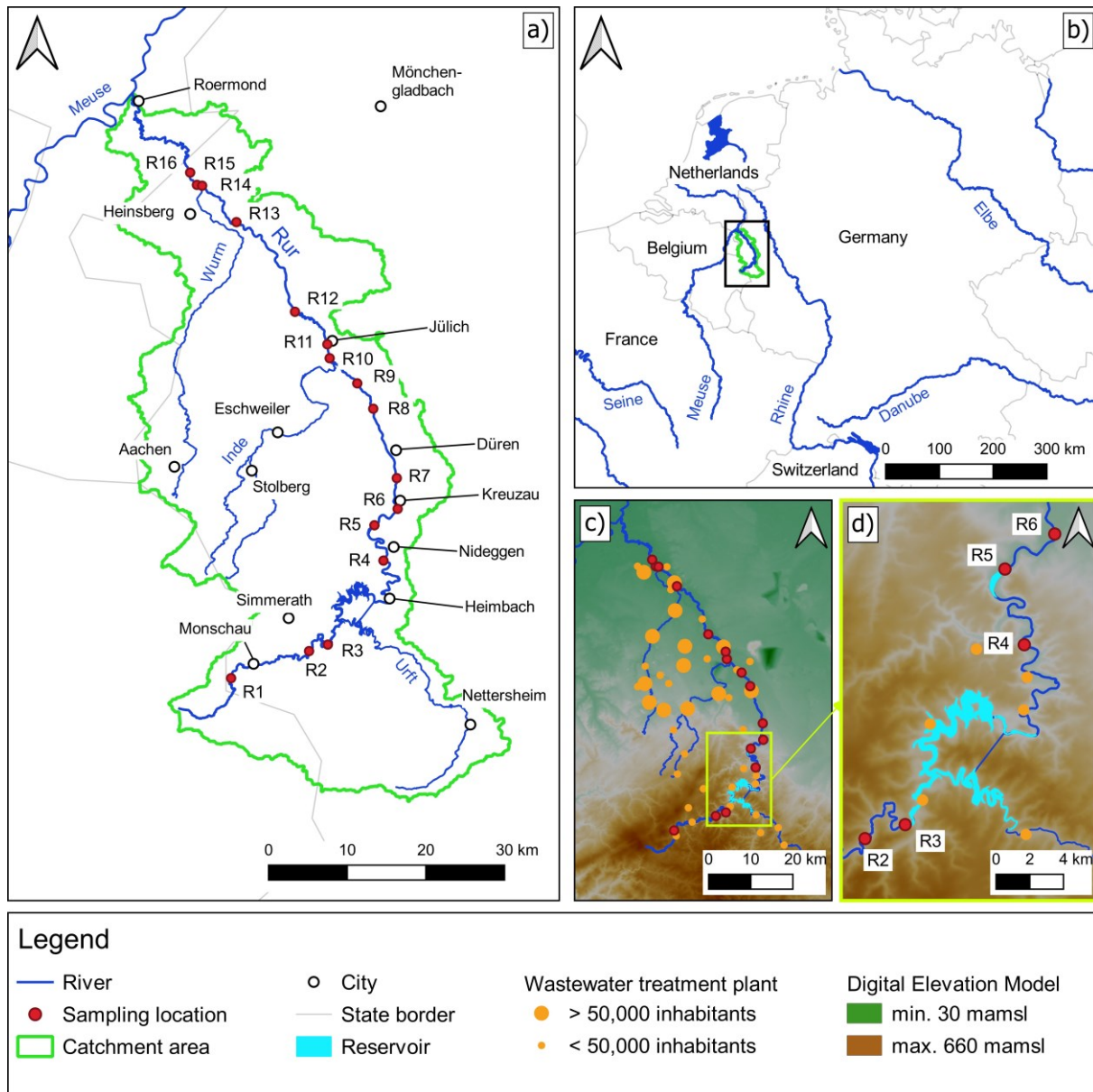


Figure 5.1 Overview of the Rur catchment. *a)* Rur catchment with sampling locations and important tributaries, *b)* Location of the Rur catchment in an European context, *c)* Wastewater treatment plants and elevations (meters above mean sea level, mamsl), *d)* Reservoirs in the upper course of the Rur.

The 163-km-long Rur river runs from the High Fens in Belgium through the typical low-mountain range landscape of the Eifel to the lowland part of the Lower Rhine Embayment in western Germany to its confluence with the Meuse in Roermond (Netherlands) (MKULNV NRW, 2005). The catchment covers various land uses and has natural river sections, immediate urban settlement, several industries (e.g.,

paper processing) and agriculture. Furthermore, the region is historically characterized by centuries of underground mining and nowadays by lignite mining. Overall, there are more than 40 wastewater treatment plants (WWTPs) in the Rur catchment area, mostly located in the lower parts and the corresponding tributaries (especially Inde and Wurm). Together with the tributary Urft, Inde and Wurm are also the most relevant tributaries in terms of discharge.

Sediment samples were taken on July 22, 2021, as well as on February 5, 2021, shortly after corresponding flood events in July, respectively, January/February. In detail, samples were taken at 16 (July), respectively, 13 sites (February) throughout the entire course of the river (Figure 5.1). Sampling was done after the flood had subsided at the floodplains and prior to the next rain event. Hence, the material was not subject to any washing out or relocation. The material was taken near the surface (at a depth of 0 to 3 cm) as a composite sample from an area of about 1 m² at the respective floodplain. The samples with a total weight of 200 to 300 g were stored in solvent-cleaned glass flasks at 4 °C in the dark prior to analysis. Besides organic geochemical analysis, all samples were also analyzed for grain size and total organic carbon (TOC).

5.2.2 Standard Parameters

Grain sizes were determined using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer (Beckman Coulter GmbH, Krefeld, Germany) on the fraction < 2 mm. Sediments were treated with 30% H₂O₂ to remove organic matter and with 1.25 mL Na₄P₂O₇ in an overhead shaker for 12 h to prevent particle agglutination (Pye & Blott, 2004). According to Schulte et al. (2016), the device was equipped with an aqueous liquid module and a Polarization Intensity Differential Scatter unit. The grain size distribution was calculated using the Mie theory (Fluid RI: 1.33; Sample RI: 1.55; Imaginary RI: 0.1; cf. Schulte & Lehmkuhl, 2018) and is given as percentage size frequency of 116 classes within a size range of 0.04–2000 µm. Furthermore, the content of total organic carbon (TOC), total carbon (TC) and total inorganic carbon (TIC) of each sample was determined by loss on ignition (LOI) using the liquiTOC II (Elementar Analysensysteme GmbH, Langenselbold, Germany). Dried sample aliquots of 0.1 g were heated and ashed at 550 °C (TOC) and 1000 °C (TIC) and the following difference in mass was used to calculate the (in)organic content. Finally, TOC concentrations were used to normalize the concentration of organic compounds to allow a comparability between different samples and sampling campaigns.

5.2.3 Organic Geochemical Analysis

5.2.3.1 Sample Extraction

Aliquots of around 20 g of untreated sediment were extracted using accelerated solvent extraction (Dionex ASE 150, Thermo Fisher Scientific, Waltham, MA, USA). Samples were extracted sequentially with approximately 30 mL of acetone, acetone/*n*-hexane 1:1 (v/v) and *n*-hexane. During each extraction step, the extraction cell was held at a temperature of 100 °C and a pressure of 10 MPa for a period of 5 min for static extraction. After each step, the extracts were collected and combined. Following the separation and disposal of the aqueous phase, the sample extract was concentrated to a volume of 5 mL by rotary evaporation and then dried with anhydrous granulated sodium sulfate (Na₂SO₄). Again, the extract was concentrated to a volume of 0.5 mL and activated copper powder was added to remove elemental sulfur when ultrasonically treated for 15 min.

5.2.3.2 Fractionation

According to the polarity of the organic contaminants, the extract was separated into six fractions by column chromatography. Columns were filled with 2 g activated silica gel and conditioned over night at 200 °C. Mixtures of *n*-pentane, dichloromethane and methanol were used as eluents with increasing polarity (Schwarzbauer et al., 2000):

- Fraction B1: 5 mL *n*-pentane,
- Fraction B2: 8.5 mL *n*-pentane/DCM 95/5,
- Fraction B3: 5 mL *n*-pentane/DCM 90/10,
- Fraction B4: 5 mL *n*-pentane/DCM 40/60,
- Fraction B5: 5 mL DCM,
- Fraction B6: 5 mL methanol.

The acidic compounds in the sixth fraction (B6) were methylated by adding Bf₃-methanol. The resulting extract was then evaporated and fractionated by column chromatography into two further subfractions using 3 mL of *n*-pentane/DCM 40/60 plus 6 mL of DCM (fraction B6K1) and 5 mL of methanol as eluents (B6K2). An internal standard (5.8 ng/μL fluoroacetophenone, 6.3 ng/μL d₁₀-benzophenone and 6.0 ng/μL d₃₄-hexadecane) was added to fractions B1 to B5 (50 μL) as well as fraction B6K1 (200 μL). Prior to injection, all fractions were concentrated to final volumes of 50 to 200 μL (fractions B1 to B5) and 200 to 800 μL (fractions B6).

5.2.3.3 Gas Chromatography – Mass Spectrometry Analyses

GC/MS analyses were performed on a quadrupole ThermoQuest Trace MS mass spectrometer linked to a ThermoQuest Trace GC equipped with a ZB-5 fused silica capillary column (Phenomenex, Aschaffenburg, Germany; 30 m × 0.25 mm ID × 0.25 µm film thickness). Carrier gas flow was 1.5 mL/min. For all fractions, a 1 µL split/splitless injection (injector temperature of 270 °C) was carried out at 60 °C with a splitless time of 60 s, 3 min hold, then programmed at 3 °C/min to 310 °C with 20 min isothermal time. Operation took place in full-scan mode (EI⁺, 70 eV) using a source temperature of 200 °C, scanning from 35 to 700 amu at a rate of 1.5 scans/s.

5.2.3.4 Compound Identification and Quantification

Organic compounds were identified by comparison with mass spectral databases (NIST, Wiley) and published information. Verification was achieved by comparison of specific gas chromatographic and mass spectral parameters (e.g., retention times and elution orders) with those of purchased reference material. Quantification was based on peak integration of characteristic ion chromatograms and an external four-point calibration with reference material. A surrogate standard was used to correct inaccuracies of injection and sample volume. The detection limit was in the range of 1 ng/g_{TOC} (calculated based on signal-to-noise ratios in real sample matrix) and therefore, no attempts were made to quantify concentrations lower than 5 ng/g_{TOC}. Recovery rates for the analytes in this study ranged between 70 and 100% (with exception of naphthalene and DIPNs with values around 50%). Blank analyses (n=2) were done to identify possible background and laboratory contaminations and revealed neglectable concentrations of a few PAHs, DIPNs and BHT.

5.3 Results

Since the TOC content plays a major role in pollutant distribution and accumulation, all concentration values were normalized to the TOC content for better comparability between different locations as well as campaigns. The TOC content varied between 0.2 and 7.6% in July and 0.7 and 6.8% in February 2021. The highest TOC levels occurred in the middle course of the Rur in both campaigns. A similar pattern was also found for the grain size distribution with the finest samples in the middle course. The samples from the Eifel region were mainly very coarse sands and in the lower reaches silty medium to coarse-grained sands were present.

GC/MS-based non-target screenings revealed the presence of a wide spectrum of organic compounds covering different groups of organic pollutants (cf. Table 5.1). Particularly, petrogenic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and geohopanes were identified, but also various compounds attributable to urban (e.g., LABs) and industrial emission sources (e.g., DPE, DIPN, PCBs).

Table 5.1 Maximum concentrations [$\mu\text{g/g}_{\text{TOC}}$] and corresponding sampling locations of different pollutants/pollutant groups.

Pollutant (group)	Maximum concentration [$\mu\text{g/g}_{\text{TOC}}$]	
	February	July
LABs	6.9 (R15)	4.4 (R15)
PAHs (EPA16)	247 (R4, R12)	500 (R2)
Hopanes	0.4 (R3)	11.5 (R15)
PCBs		
6 congeners	6.1 (R12)	13.7 (R6)
total	30.7 (R12)	68.8 (R6)
DIPN	4.1 (R12)	14.2 (R9)
DPE	0.01 (R2)	0.8 (R15)
Mesamoll®	0.75 (R8)	1.3 (R6)
BHT	< 0.005 (R2)	2.3 (R11)
N-Benzylformamide	< 0.005 (R11)	0.05 (R15)
Methyltriclosan	0.02 (R16)	0.08 (R14)

Many of the identified compounds were PAHs with concentrations up to $103 \mu\text{g/g}_{\text{TOC}}$ in July and up to $50.2 \mu\text{g/g}_{\text{TOC}}$ in February. ΣEPA16 PAH exposure occurred mainly in the high $\mu\text{g/g}_{\text{TOC}}$ range (July: 69 to $500 \mu\text{g/g}_{\text{TOC}}$; February: 31 to $247 \mu\text{g/g}_{\text{TOC}}$). Further identified substances were so-called hetero-PAHs, which have one or more heteroatom (N, S, O) in their aromatic moieties. As a result, they exhibit increased water solubility compared to the generally lipophilic PAHs. They occurred with concentrations up to $32.4 \mu\text{g/g}_{\text{TOC}}$ in July and up to $4.5 \mu\text{g/g}_{\text{TOC}}$ in February. Overall, PAHs are common environmental pollutants and identified in several studies regarding environmental and flood pollution (e.g., León et al., 2017; Maliszewska-Kordybach et al., 2012; Vulava et al., 2017). They can originate from fossil fuels (e.g., due to seepage or oil spills) or be a result of incomplete combustion processes of organic matter. Therefore, PAHs also occur naturally and do not necessarily indicate anthropogenic input, but, nevertheless, they show a high biological and chemical stability in the environment and many PAHs are carcinogenic, mutagenic or toxic for reproduction (Abdel-Shafy & Mansour, 2016; Haritash & Kaushik, 2009).

Geohopanes as diagenetic products of biohopanes can additionally indicate petrogenic contaminations and thus anthropogenic or urban emissions (e.g., from oil heating systems or vehicles). For instance, the ratio $Ts/(Ts+Tm)$ and the quantitative distribution of (22S)- and (22R)-homohopanes can indicate thermally mature organic material introduced into the river system by contamination from, e.g., fossil fuels (Farrimond et al., 1998; Gao et al., 2007; Yunker & Macdonald, 2003). The homologous series of C_{29} - to C_{35} -hopane stereoisomers was detected with total concentrations up to $11.5 \mu\text{g/g}_{\text{TOC}}$ in July and $0.4 \mu\text{g/g}_{\text{TOC}}$ in February.

Linear alkylbenzenes (LABs) are alkylated benzenes with linear C_{10} to C_{13} alkyl chains (phenyldecanes, phenylundecanes, phenyldodecanes and phenyltridecanes). They were identified in the samples of the Rur floodplains with maximum concentrations of $4.4 \mu\text{g/g}_{\text{TOC}}$ in July and $6.9 \mu\text{g/g}_{\text{TOC}}$ in February. LABs are common detergent residues with an enhanced lipophilicity and environmental stability and can therefore be used as anthropogenic markers of wastewater pollution. Furthermore, the abundance of specific LAB isomers or systematic changes in their composition can be used as indicator to determine the degree of (microbial) degradation (Takada & Ishiwatari, 1990).

Another well-known group of pollutants are polychlorinated biphenyls (PCBs). PCBs are man-made and thus, artificial and were once widely used in industrial applications as for instance in electrical insulation or hydraulic equipment (Waid, 1986; Walker et al., 2019). Manufacturing and usage of PCBs is banned for more than 30 years, but they are still ubiquitously distributed in the aquatic environment as they have a high persistence and are not easily degradable. As a consequence of their lipophilicity and low vapor pressure, PCBs have a tendency to accumulate in soils, sediments and also in biota (Schwarzbauer & Jovančević, 2018; Walker et al., 2019). However, they are carcinogenic to humans and have further adverse effects in terms of endocrine disruption and neurotoxicity. Representative congeners as PCB 28 (Cl_3 -PCB), PCB 52 (Cl_4 -PCB), PCB 101 (Cl_5 -PCB), PCB 138 (Cl_6 -PCB), PCB 153 (Cl_6 -PCB) and PCB 180 (Cl_7 -PCB) were detected with maximum concentrations up to $4.7 \mu\text{g/g}_{\text{TOC}}$ in July and $2.1 \mu\text{g/g}_{\text{TOC}}$ in February. To quantify the total PCB contamination, the sum of the representative PCBs has been multiplied by 5. As recommended by the German Environment Agency (UBA), this value reflects their constant relative proportion. Consequently, the total contamination was estimated to be maximum $68.8 \mu\text{g/g}_{\text{TOC}}$ in July and $30.7 \mu\text{g/g}_{\text{TOC}}$ in February.

Furthermore, different compounds suggesting an industrial origin were detected in the floodplains such as alkylsulfonic acid phenyl esters (Mesamoll®), di-*iso*-propylnaphthalenes (DIPNs) or 1,2-diphenoxyethane (DPE). Mesamoll® is a mixture of various alkylsulfonic acid phenyl esters that is used as an alternative for phthalate-based plasticizers. Its ability to sorb to sedimentary material indicates a wide distribution in the environment (Fromme et al., 2017). As a second relevant group, DIPNs are

highly persistent and bioaccumulative and have several industrial applications (e.g., as PCB substitutes). Among others, they are used as technical agents to produce specialty papers and have therefore also been detected in recovered papers and packaging made from recycled paper (Boccaccio Mariani et al., 1999; Franke et al., 2007). Further on, DPE is a characteristic compound of wastewaters from modern paper production sites, and both were already found in the water of the Rur river (Schwanen & Schwarzbauer, 2022). For the investigated floodplains, the maximum concentrations for Mesamoll® were 1.3 $\mu\text{g/g}_{\text{TOC}}$ in July and 0.75 $\mu\text{g/g}_{\text{TOC}}$ in February, for DIPN 14.2 $\mu\text{g/g}_{\text{TOC}}$ in July and 4.1 $\mu\text{g/g}_{\text{TOC}}$ in February and for DPE 800 ng/g_{TOC} in July and 13 ng/g_{TOC} in February.

5.4 Discussion

To understand the levels of pollution, to identify possible emission sources and to determine specific environmental behaviors of organic contaminants as the result of floods, the concentration trends were assessed over the entire river course (see Figure 5.2). A special focus is placed on different dimensions and dynamics of the respective flood events and the varying extent of the impacts. This will also include an assessment to which degree remobilization and further relocation of the pollutants has taken place.

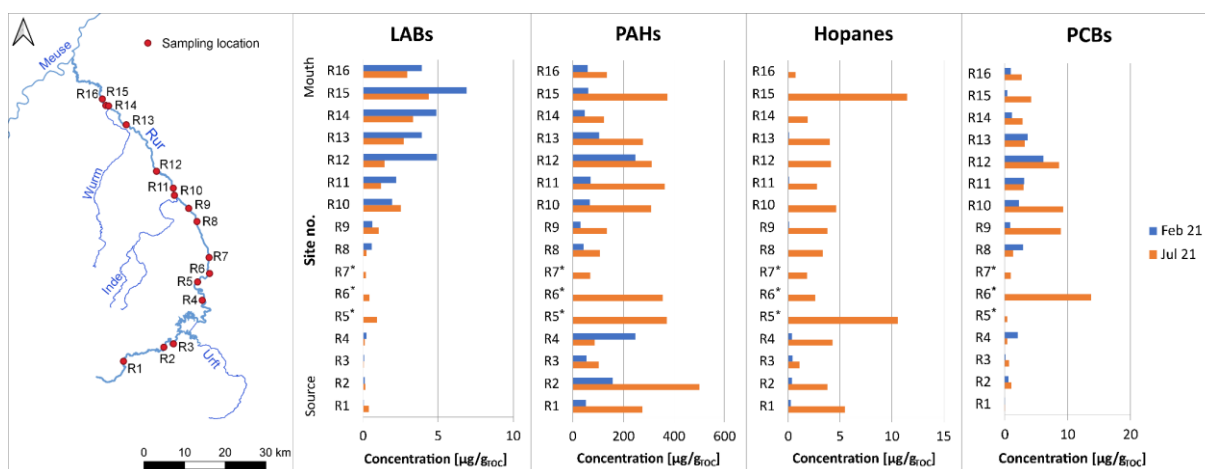


Figure 5.2 Spatial distribution of LABs, PAHs, hopanes and PCBs over the Rur river course. Samples have been taken after two flood events in January/February and July 2021. (*) R5 to R7 were not sampled in February.

Both flood events differ in particular in water level and discharge. The normal mean water level at Jülich (close to R11), at the transition from the middle to the lower course of the Rur river, is 1.24 m and the average discharge of the Rur is 16.2 m³/s (ELWAS-WEB, 2022; Stadt Jülich, 2021). The winter flood had a maximum water level of 2.43 m and a maximum daily mean value of 73.2 m³/s, while the summer

flood at the same location even caused a water level over 4 m and a maximum discharge of 207 m³/s (ELWAS-WEB, 2022; Stadt Jülich, 2021; WVER, 2021b). The values in January did not exceed flood events with an annularity of 5 years and can therefore be considered as a regular event. However, the discharge in July was high above the previous measured maximum discharge of 173 m³/s in 1947 indicating the extreme dimension of this flood event (ELWAS-WEB, 2022).

Wolf et al. (2022) have shown that the concentrations of suspended sediment in the Rur river are increased with higher discharge. They have been especially high due to the extreme flood event in summer. As the dispersion of lipophilic to semi-polar organic pollutants is strongly dependent on sediment transportation, an increased environmental contamination after the flood is assumed. This effect and the different flood dimensions are reflected in the measured concentrations of various substances. In general, concentrations detected after the July flood were mainly higher than in February. However, for some substances no considerable differences in concentrations occurred between both flood events (cf. Figure 5.2). These differences and possible causes are discussed in more detail in following. Particular attention will be paid to tributary inflows and structural features of the river system, as these can also play a significant role in flood events.

5.4.1 Compounds with no considerable differences in concentrations

Specific pollutants that are quantitatively not affected by the different intensities of both flood events are LABs. They are indicative for domestic wastewater and, as shown in Figure 5.3, occurred at high concentrations in the Rur floodplains downstream of Düren (R8). The city of Düren is the first big agglomeration with the largest WWTP in the catchment that is discharging its effluents directly into the Rur. In general, the largest WWTPs are located in the lower reaches of the Rur including its northern tributaries. This is well reflected in the concentration profiles of LABs determined in this study. For both flood events, the concentrations showed a clear increase downstream, which matches well with urban and industrial settlements. Particularly, the Inde and Wurm tributaries were clearly evident in the LAB emission patterns (R10 and R15). Several large WWTPs located on both tributaries consistently represent emission sources for LABs and thus explain the steady inputs. In fact, the highest overall concentrations occurred after the Wurm tributary inflow (Feb.: 6.9 µg/g_{TOC}; Jul.: 4.4 µg/g_{TOC}). The largest WWTP (Aachen-Soers) in the entire catchment area is located on this tributary.

Interestingly, in the more heavily polluted lower river, the cumulative concentrations of LABs in July were comparable and partly even lower than in the February samples. Perhaps, the volumes of wastewater (influent and effluent) were simply decreased in July, so that less LABs could be introduced to the Rur river. However, higher concentrations of LABs were detected in the upper reaches

in July. In particular, a concentration increase was evident behind the Obermaubach reservoir (R5), where possibly an enrichment takes place due to altered flow characteristics. The overall increase in the contamination upstream could be due to additional flooding of smaller wastewater treatment plants in the Eifel area documented for the summer flood (Eifeler Presse Agentur, 2021; WVER, 2021c). Nonetheless, compared to the inputs in the more urbanized lower reaches, the relevance of the upper reaches to the total contamination is very low.

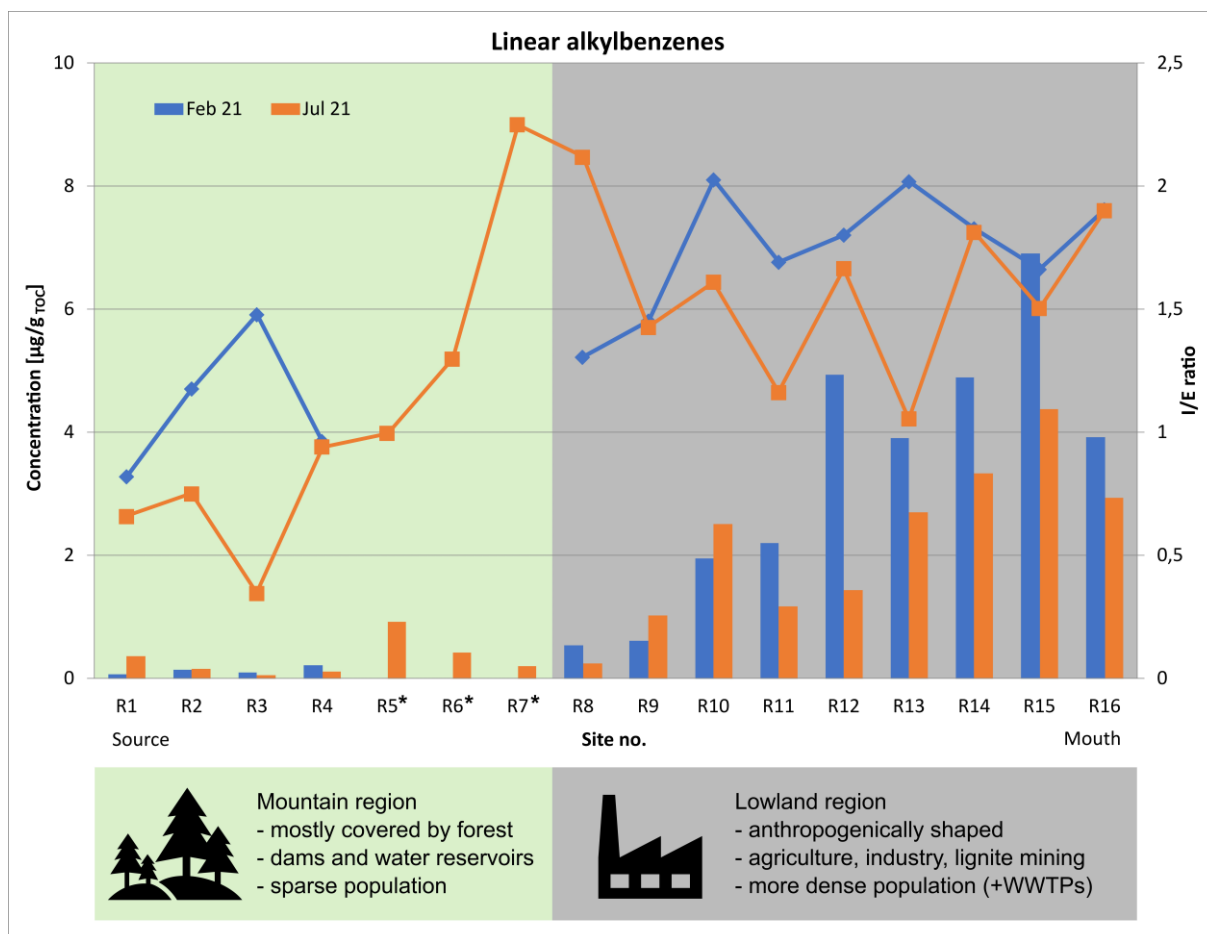


Figure 5.3 Spatial distribution of LAB concentrations and I/E ratios [$\mu\text{g/g}_{\text{TOC}}$] over the Rur river course. I/E ratios close to 0.7 represent untreated wastewater, while higher values up to 7 represent ongoing microbial degradation according to Takada & Eganhouse (1998). (*) R5 to R7 were not sampled in February.

Depending on the position of the phenyl substitution, LABs can be distinguished in external substituted isomers (E) and internal substituted isomers (I). According to Takada & Ishiwatari (1990) external substituted isomers are more readily biodegraded. Thus, the I/E ratio and therefore the changes of the isomer pattern of LABs can be used as indicator for the degree of microbial degradation. Ratios in untreated wastewater are typically close to 0.7, while higher values up to 7 represent ongoing microbial

degradation (Takada & Eganhouse, 1998). For the Rur floodplains, the I/E ratios were between 0.4 and 2.3 in July and between 0.8 and 2.0 in February. This likely indicates a recent input of undegraded LABs from untreated sewage by the flood events, as these also inundated wastewater treatment plants along the river course (WVER, 2021c). In both campaigns, there is a very slight increase of I/E ratios from the upper to the lower reaches, possibly indicating initial degradation processes. Nevertheless, the values downstream were still comparable to those of barely treated sewage effluents.

In general, LABs have been introduced during both flood events. Thus, the dimension of the flood event does not seem to play a major role in their introduction, probably due to the direct spatial proximity of WWTPs and the receiving river. Therefore, an additional flood-induced LAB contamination should be regularly considered for any flood extent and dimension.

5.4.2 Compounds with enriched concentrations

After both flood events, PAHs occurred ubiquitously and mainly in high $\mu\text{g}/\text{g}_{\text{TOC}}$ ranges (cf. Figure 5.2). However, these contaminants generally show a diffuse emission, as there can be both petrogenic and pyrogenic sources. In the catchment area of the Rur river, lignite mining is a specific emission source of fossil matter derived contamination. However, in the case of natural disasters such as a flood, other input sources are also of key importance (e.g., stormwater runoff). Interestingly, in July the maximum EPA16 concentration of over $500 \mu\text{g}/\text{g}_{\text{TOC}}$ already occurred in the near-natural Eifel region (R2). There is a low settlement density and only limited industry. However, the sampling site is located directly on a so-called state road, which could be a pollution source due to its runoff. Elevated concentrations also appeared downstream of the Obermaubach reservoir (R5) and the Inde and Wurm tributaries (R10, R15). These two tributaries have themselves caused flooding and extreme damage along their courses, so they probably also discharged pollutants into the Rur (WVER, 2021c). The Obermaubach reservoir potentially collects pollutants from the upper reaches of the river because the flow velocity is highly reduced by the dam, allowing particulate material to settle and thus possibly be transported in higher concentrations during floods. According to Wolf et al. (2022), there were also increased Cu- and Pb-concentrations at this location after the July flood highlighting the relevance of anthropogenic measures on the dispersion of different pollutants. At all three of the aforementioned sampling locations, the cumulative concentration of PAHs was above $300 \mu\text{g}/\text{g}_{\text{TOC}}$. This is of high importance, because especially in the lower reaches, many areas adjacent to the river are used for agriculture.

In February, the maximum of nearly $250 \mu\text{g}/\text{g}_{\text{TOC}}$ occurred at a near-natural area close to Floßdorf (R12). In this area there is a nature reserve, which reflects the natural flow pattern of the Rur (wide meanders, almost unobstructed floodplains). Due to the reduced flow velocity, an increased flooding of the

surrounding floodplains and thus the deposition of sedimentary material is very likely and thus explains the concentration peaks. Although the PAH concentration in Floßdorf was higher in July, the surrounding sampling locations also showed very high concentrations in summer, while in February the strong contamination occurred only locally. This again indicates a partial remobilization, but also additional emission sources in July. Similar high concentrations were detected in winter downstream of Abenden (R4: 247 $\mu\text{g/g}_{\text{TOC}}$) and thus, downstream of the Rurtalsperre. This reservoir also influences and changes the flow behavior, which may have led to sedimentation and relocation of the pollutants. However, the PAH sum at the corresponding sampling point decreased from February to July. Presumably, a remobilization of the contaminants took place there due to the considerable increase in the reservoir discharge of the Rurtalsperre caused by the flood. While the discharge in dry periods is about 5 m^3/s , it was up to 41.5 m^3/s in January and even 97.7 m^3/s in July (WVER, 2021b). This large increase in discharge occurred within a short period of time and thus may have displaced sediments and soils, including accumulated pollutants, further downstream.

In July, benzo[b]fluoranthene, fluoranthene, pyrene and chrysene accounted for the largest contribution to the PAH pollution. Similarly, in February, fluoranthene, pyrene, phenanthrene and benzo[b]fluoranthene made up the largest shares. However, all of them suggest particularly a pyrogenic origin (Akpambang & Akpoesiri, 2016; Bellanova et al., 2020; Sicre et al., 2008). Further on, PAH diagnostic ratios were used to differentiate pollution emission sources such as combustion, petroleum or mixed sources. The ratios used in this study were anthracene and phenanthrene ($\text{An}/(\text{An}+\text{Ph})$), benz[a]anthracene and chrysene ($\text{BaA}/(\text{BaA}+\text{Ch})$), indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene ($\text{IP}/(\text{IP}+\text{Bghi})$) plotted against the ratio of fluoranthene and pyrene ($\text{Fl}/(\text{Fl}+\text{Py})$). Further on, C_1 phenanthrenes and anthracenes ($\text{C}_0/(\text{C}_0+\text{C}_1) \text{ Ph}+\text{An}$) as well as C_1 fluoranthenes and pyrenes ratios ($\text{C}_0/(\text{C}_0+\text{C}_1) \text{ Fl}+\text{Py}$) have been applied.

Most of the floodplain samples plot in the area of combustion, including petroleum combustion as well as grass, wood, or coal combustion (see Figure 5.4). Pyrogenic emissions initially released into the air indicate a diffuse origin. According to Ahrens & Depree (2010), asphalt pavements out of coal tar can also shift the compositional signature of PAHs towards a pyrogenic origin. Thus, PAHs could also have been introduced through damage to infrastructure and surface runoff. An exception to the identified pattern was the sampling point downstream of Düren (R8) in July, which plots in the mixed area of petroleum and combustion. Düren is the largest city and an urban as well as industrial agglomeration directly on the Rur river (~94,000 inhabitants). It is possible that petrogenic emissions from flooded industrial plants or urban areas were also introduced here. Generally, the scatter of points is larger for the samples of the summer flood indicating more and diverse emission sources.

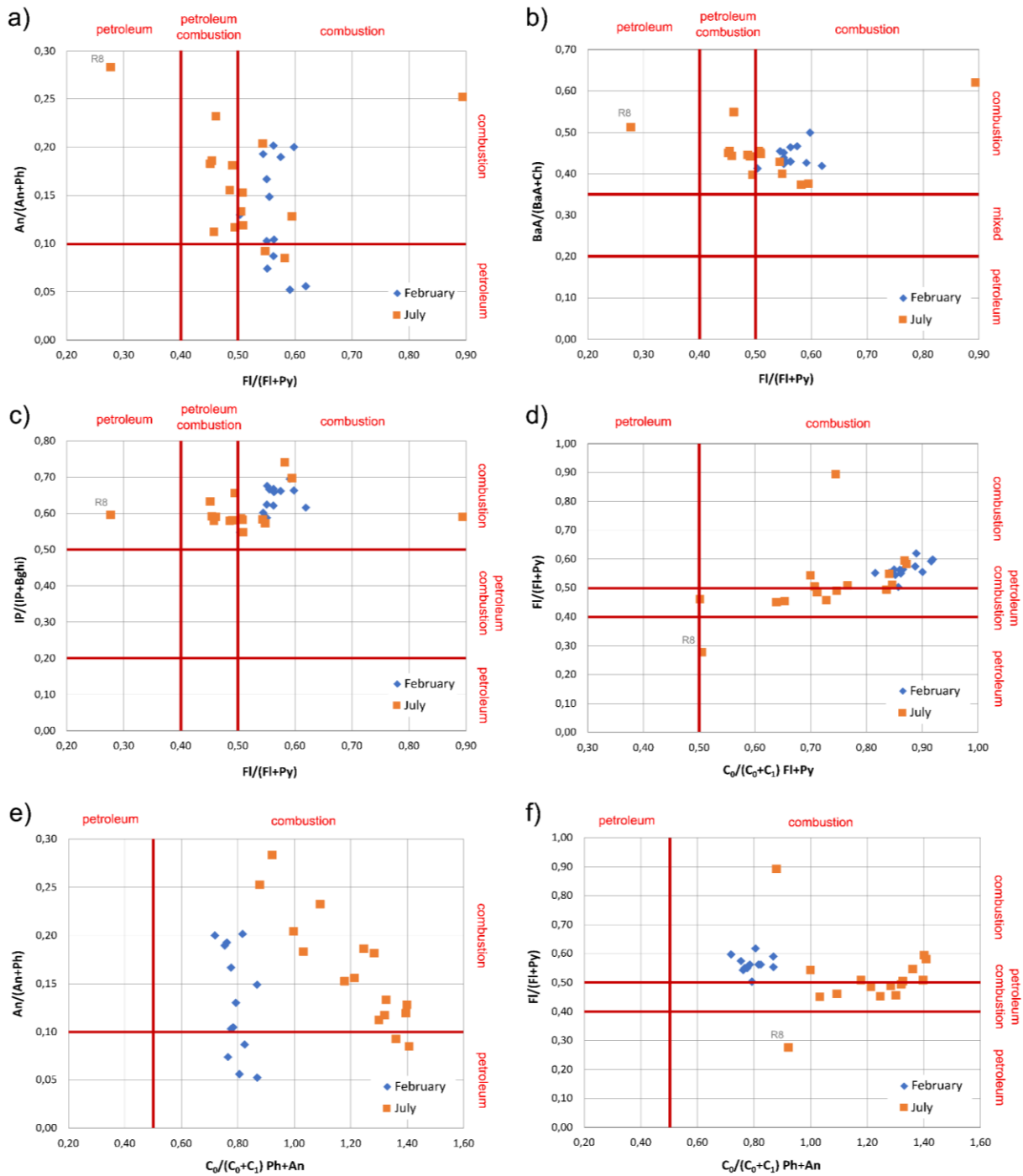


Figure 5.4 PAH diagnostic ratios to differentiate and classify emission sources (petrogenic vs pyrogenic). Cross plots of a) $An/(An+Ph)$ vs. $Fl/(Fl+Py)$, b) $BaA/(BaA+Ch)$ vs. $Fl/(Fl+Py)$, c) $IP/(IP+Bghi)$ vs. $Fl/(Fl+Py)$, d) $Fl/(Fl+Py)$ vs. $C_0/(C_0+C_1) Fl+Py$, e) $An/(An+Ph)$ vs. $C_0/(C_0+C_1) Ph+An$ and f) $Fl/(Fl+Py)$ vs. $C_0/(C_0+C_1) Ph+An$ according to Yunker et al. (2002).

Similar to PAHs and as shown in Figure 5.2, geohopanes were also present in all samples. However, there were remarkable differences in concentrations depending on the different dimensions of the floods. The maximum cumulative concentration of C_{29} - to C_{35} -hopanes in July was $11.5 \mu g/g_{TOC}$ and

occurred at the Wurm tributary in the lower reaches (R15). Another considerable peak was caused by the Obermaubach reservoir (R5: 10.5 $\mu\text{g/g}_{\text{TOC}}$). As with PAHs, hopanes were probably retained and then released by the altered flow behavior (Obermaubach) or introduced by the damage caused at the tributary (Wurm). However, concentrations at the other sites also averaged more than 4 $\mu\text{g/g}_{\text{TOC}}$. This is more than ten times higher than the maximum hopane concentration in February, which was lower than 0.4 $\mu\text{g/g}_{\text{TOC}}$ and occurred at the head of the reservoir Rurtalsperre (R3). The lower reaches showed hardly any contamination in February indicating additional emission sources in summer. Thus, it cannot be clearly determined whether remobilization has taken place. Overall, the July flood resulted in remarkable petrogenic inputs due to industrial or urban flooding or the direct introduction of fossil fuels.

The maturity-dependent $T_s/(T_s+T_m)$ ratio was nearly the same in both campaigns: between 0.23 and 0.49 in July and between 0.22 and 0.50 in February. This value is dependent both on maturity and source as it varies with organic matter inputs and source facies (Farrimond et al., 1998; Gao et al., 2007; Peters et al., 2007). The ratios detected in this study are similar to those found in Middle East oils as well as some heavy oils from Venezuela, Canada and the USA (Volkman et al., 1997; Wang et al., 2006). Typically, heavy oils are used for plastics, petrochemicals or road surfacing. Thus, the hopanes were probably introduced by remobilization and flooding of industrial or urban areas rather than fuels (as gasoline or diesel). Nevertheless, the $T_s/(T_s+T_m)$ ratios indicate a petrogenic contamination with fossil material of enhanced maturity. The values were also similar to riverine samples from the Guilan province (Iran), which are also characterized by inputs of oil and its derivatives (Shirneshtan et al., 2016). The ratio of 22S/(22S+22R) C_{31} -hopanes ranged from 0.47 to 0.72 in July and from 0.45 to 1.00 in February. These ranges also point to enhanced maturities of fossil material with a predominance of 22S compared to the 22R epimer (Jeanneau et al., 2006). Possibly, petrogenic contamination took place as a consequence of flooding and destruction of, e.g., oil heating systems, industrial sites or vehicles. Again, similar results were obtained for riverine sediments in Iran highlighting the general distribution of fossil fuels in river systems (Shirneshtan et al., 2016).

However, PAH ratios are less indicative of relevant petrogenic contamination. Nevertheless, hopane concentrations and maturity parameters clearly show petrogenic inputs raising the question of the applicability of PAH and hopane markers in the field of environmental or flood pollution. According to Tobiszewski & Namieśnik (2012), there are some limitations and PAH diagnostic ratios should be applied cautiously, as their values may change during the environmental fate of the corresponding substances. Some compounds are more sensitive to biodegradation, seasonal and other environmental changes, so that multiple authors recommend applying several diagnostic PAH ratios to confirm the results (Biache et al., 2014; Tobiszewski & Namieśnik, 2012; Yunker et al., 2002). Low molecular weight PAHs

in particular are less stable and should only be used with caution in diagnostic ratios (Zhang et al., 2005). Nonetheless, as shown in Figure 5.4, all PAH cross plots showed mostly a pyrogenic contamination. However, PAHs from asphalt pavements also tend to indicate pyrolytic origins, although road surfaces are often made from heavy oils or bitumen and can accordingly be attributed to a petrogenic origin when considering hopane distribution. Generally, it must be taken into account that both pollutant groups are likely introduced from more than one source during flood events which cannot be clearly differentiated by diagnostic ratios. In addition, concentrations of PAH contaminants were at least 20 times higher than hopane concentrations. Probably, contaminants of pyrogenic origin were just more present than petrogenic compounds, which, however, were clearly identified by hopanes and hopane maturity indicators. As a result of severe flooding, both (diffuse) pyrogenic and petrogenic contaminants are likely to be emitted into river systems. Therefore, different pollutant groups as well as different molecular ratios should always be considered and compared with the prevailing land use and industries.

PCBs are a very significant pollutant group to assess the remobilization potential of floods, because their use is now banned worldwide (in Germany since 1989). As with many other identified substances, the strongest pollution was present in the middle to lower course of the river with much higher concentrations in July. After the summer flood, the sampling location at Winden at the beginning of the Rur's middle course (R6) showed the cumulative maximum concentration of the representative congeners (PCB6) with almost 14 $\mu\text{g/g}_{\text{TOC}}$. Thus, the total PCB contamination at this location is estimated to be around 69 $\mu\text{g/g}_{\text{TOC}}$. The concentrations of the surrounding sampling points were very low, so this maximum is likely the result of a point source. One possible explanation is the flooding of the paper factory located at this site. As shown in Figure 5.5, mainly high-chlorinated PCBs were detected (esp. Cl₆- and Cl₇-PCBs), which are more stable and resistant to degradation. However, the composition of PCBs also depends on the area of application and the decade of usage (Hagemann et al., 2018). Higher chlorinated types were typically used as additives, e.g., in transformer oils, while low molecular weight products were frequently used in mining equipment (Friege et al., 1989; Schettgen et al., 2018). Thus, Cl₆- and Cl₇-PCBs at this site have been probably introduced by flooding of production sites and facilities or from contaminated sites in this industrial area.

In July, high cumulative PCB concentrations also occurred at Schophoven (R9), downstream of the Inde tributary (R10), and at Floßdorf (R12). Until 1944, the Inderevier was a former mining region for the extraction of hard coal (Voncken, 2020). It is possible that the July flood remobilized PCBs from corresponding mining sites and carried them into the Rur. The concentrations of low-chlorinated PCBs, which have often been used in underground mining processes, have also increased slightly (esp. Cl₃- and Cl₄-PCBs). They are 1.5 (Cl₃) respectively nearly 2 times (Cl₄) as high as on the previous sampling

location R9. However, these low-chlorinated congeners were not used for open-pit mining and since their usage is now generally banned, the current lignite mining at the Inde river does not seem to have an influence on PCB introduction. The sampling point at the nature reserve Floßdorf (R12) was remarkable in July as well as February 2021. In winter, it showed the maximum summed PCB concentration of 6.1 µg/g_{TOC} (in July: 8.6 µg/g_{TOC}). The surrounding sampling locations had much lower concentrations that were almost the same in February and July, so remobilization processes in summer were probably not relevant. Instead, only an additional accumulation of pollutants in the floodplains at Floßdorf took place. Interestingly, concentrations at two monitoring sites were higher in February than in July. At Abenden (R4), downstream of the Rurtalsperre and downstream of Düren (R8), the concentrations were thus decreasing from February to July, possibly due to remobilization (e.g., by increased reservoir discharge).

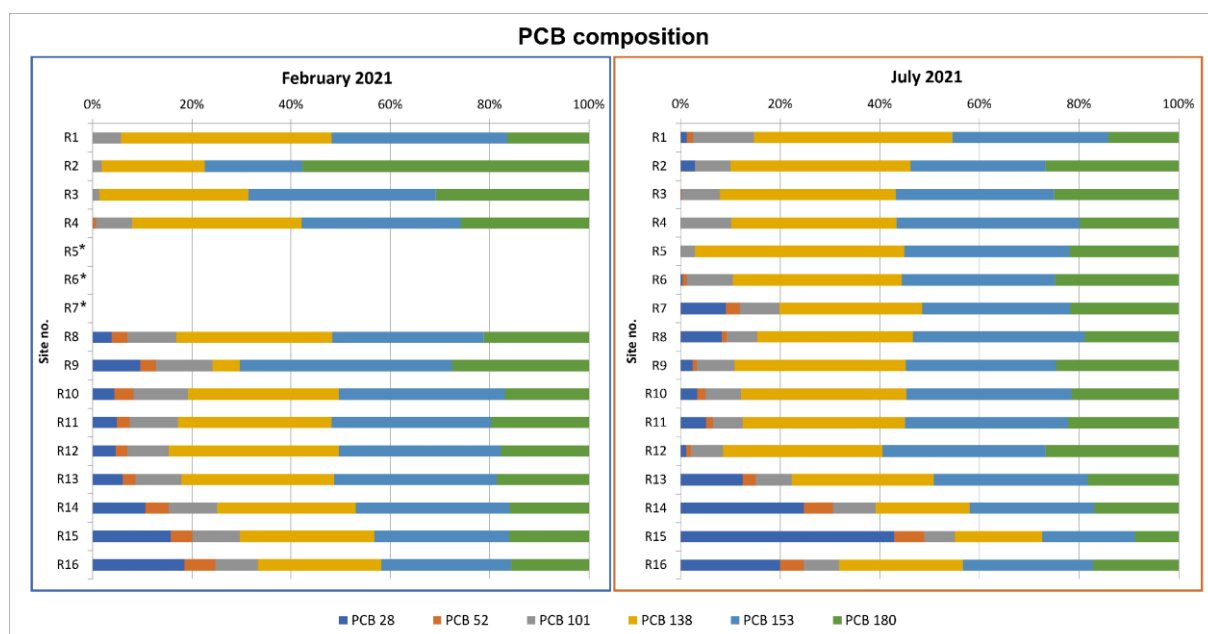


Figure 5.5 Composition of the PCB mixtures divided into 6 representative congeners. Representative congeners are PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180. (*) R5 to R7 were not sampled in February.

Another remarkable feature regarding the PCB distribution pattern was that the proportions of higher-chlorinated PCBs decrease downstream and those of lower-chlorinated PCBs (esp. Cl₃-PCB 28) increase in July and slightly in February as well (see Figure 5.5). Since the low-chlorinated PCBs show less environmental stability and have other typical applications (e.g., in mining), this indicates different emission sources than in the upper reaches. In July, high concentrations of the low-chlorinated PCB 28 were found after the Wurm tributary inflow (R15). In the Wurm catchment, underground mining of coal took place up to the end of the twentieth century, whereby the Wurm area was much more relevant than the aforementioned Inde region (Voncken, 2020). As the underground mining happened

mainly at shallower depths, a flooding of respective sites and thus a remobilization of old mining burdens is quite likely (Maaß & Schüttrumpf, 2018). However, there was probably no PCB input of these specific emission sources in February. Generally, the varying PCB proportions after the July flood indicate a more diverse input with additional and different emission sources.

As a last representative group of contaminants, the identified industrial additives generally showed higher concentrations in the lower reaches. The main contamination with DIPN occurred in the middle to lower reaches in both sampling campaigns. Again, the maximum value appeared in February at the natural river course near Floßdorf (R12: 4.1 µg/g_{TOC}). The maximum in July was further upstream next to a weir at Schophoven (R9: 14.2 µg/g_{TOC}). Emission sources are likely to be from the industrial sector around Düren, e.g., from flooding and damaging of corresponding facilities. The effect of the near-natural area of Floßdorf was no longer recognizable in July. Instead, there was a large concentration increase due to the Wurm tributary (R15: 10.0 µg/g_{TOC}) indicating damage to industrial areas or facilities on the Wurm itself. In February, the influence of the Rurtalsperre was also recognizable with an enriched accumulation of DIPN at the head of the reservoir (R3: 1.0 µg/g_{TOC}). The importance of such structural measures for pollutant distribution was also evident in July. Compared to the surrounding sampling locations, the site downstream of the Obermaubach reservoir showed increased concentrations of 2.6 µg/g_{TOC} (R5).

Interestingly, the main contamination with Mesamoll® shifted upstream. In July, the highest concentrations (between 570 and 1300 ng/g_{TOC}) occurred downstream of the Rur and Obermaubach basins at R4 to R6 and at Schophoven (R9). Latter concentration peak could be a result of remobilization as the maximum concentration in February occurred at the previous location in the industrial center of Düren (R8: 750 ng/g_{TOC}). The second highest concentration in February was also attributed to urban settlement and the associated industry in Jülich (R11: 400 ng/g_{TOC}). However, locations R5 to R7 were not sampled in February, so a direct comparison of the maxima is difficult.

In July, DPE showed concentration peaks in Jülich (R11: 220 ng/g_{TOC}) and after the inflow of the Wurm tributary (R15: 800 ng/g_{TOC}). Jülich itself (34,000 inhabitants) is an industrial center for paper production, which is probably the main emission source of DPE in this river system. However, the paper industry is also important in the Düren area, where no considerably increased DPE concentrations occurred. In February, DPE was only found in the Eifel with much lower concentrations (max. 13 ng/g_{TOC}). As shown in Table 5.1, further (industrial) substances (e.g., butylated hydroxytoluene (BHT)) were also detected in July at higher concentrations and at more monitoring sites. While they were only detected sporadically or not at all in February, they were identified at most of the sites in July indicating additional emission sources from the industrial sector.

5.4.3 Influences of the river course, its structural adjustments as well as tributaries

As shown in Figure 5.6, the sampling site near Floßdorf and the associated Rur meanders were particularly remarkable in connection with the winter flood, as the highest concentrations of many substances were detected there. In general, the Rur meanders influence the flow behavior and velocity, so that sedimentation of material occurs at the corresponding floodplains. In addition, this site is located downstream of the large urban and industrial areas of Jülich and Düren. The urban areas themselves did not show a high pollution. Possibly, the material and the pollutants emitted in those cities were transported to the floodplains at Floßdorf. Similar impacts on the river system were caused by weirs (as in Schophoven) or reservoirs (such as the Rurtalsperre or Obermaubach reservoir). They can function as a sink for sediments and sediment-bound pollutants, which are likely released during floods with high discharge. The latter illustrates the importance of structural anthropogenic measures in rivers for pollutant distribution and deposition.

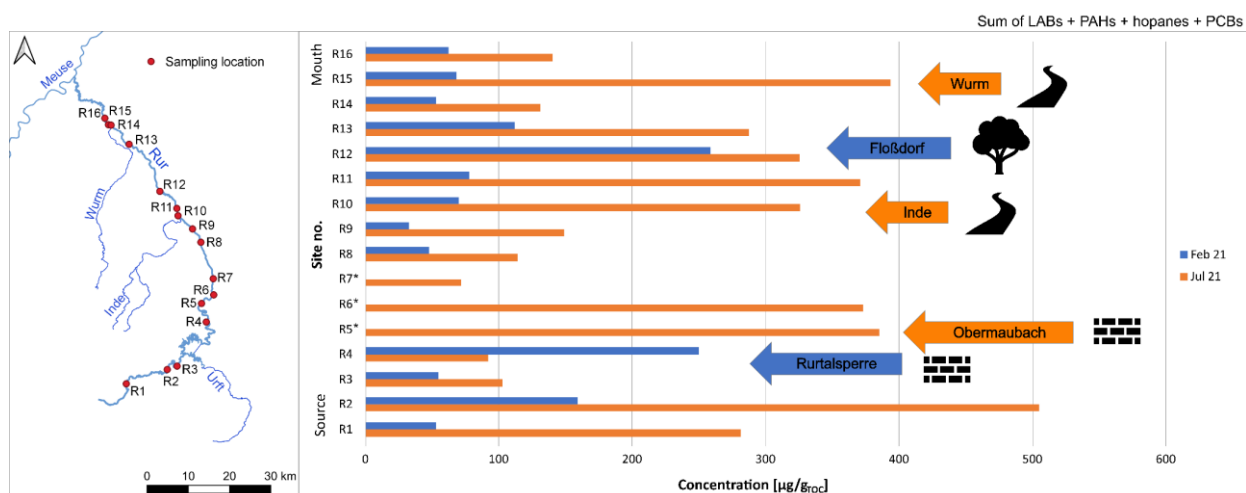


Figure 5.6 Total contamination as a sum of LABs, PAHs, hopanes and PCBs in the Rur catchment. Samples have been taken after two flood events in January/February and July 2021. Important structural measures, (re)naturalized areas and tributaries are highlighted. (*) R5 to R7 were not sampled in February.

Another clearly recognizable difference in the pollution situation occurred regarding the tributaries Inde and Wurm. In February, there were only very slight increases in concentrations, while in July there were large peaks for most of the identified substances. For instance, there was more than a doubling of the previous PAH concentrations. In July, both tributaries experienced severe flood damage, resulting in many pollutants being introduced into the rivers or remobilized and then transported. A considerable part was then also carried into the receiving river of the Rur and deposited there. Thus, both tributaries were major sources of contaminants in July 2021. The affected floodplains are located in the more

agricultural part of the catchment system. This is of special relevance as it poses another (in)direct risk to humans.

However, flood protection also plays a decisive role in the mentioned influence of the tributaries. On the Inde and Wurm, flood protection measures are far less developed than on the Rur with its dam and reservoir system. For better understanding: the extreme inflows to the dam system from the catchment area of the Rur amounted to a total of approximately 760 m³/s in July, but were retained in the Rur reservoirs and reduced to less than 100 m³/s (WVER, 2021a). Consequently, the flood was less destructive in the lower course of the river. Nevertheless, such water retaining capacity was not present in the tributaries.

For most substances, the Wurm had a stronger impact on the pollution situation of the Rur river than the other tributaries. However, the flood caused worse destruction and damage on the Inde and its tributaries such as the Vichtbach (Hermanns, 2021; Szönyi et al., 2022). Thereby, a big part of the released and remobilized pollutants was probably deposited before they reached the course of the Rur. There are two explanations for this. In 2005, the last section of the Inde before its confluence with the Rur has been relocated and renaturalized due to the open-pit lignite mining in this region. Thus, the previously 5 km long old section was transformed into a 12.5 km long new course, whereby regular flooding of the adjacent floodplains was also taken into account (Maaß et al., 2018). Furthermore, during the summer flood in July 2021, the Inde river flooded and destroyed a dike near the open pit at the beginning of its relocation due to the high discharge, and a large part of the river water flowed into the lignite pit (RWE AG, 2021). Accordingly, sedimentation of particulate matter as well as bound pollutants probably occurred in these areas, reducing the influence of the Inde river on the Rur river. Nevertheless, Inde and further tributaries were major emission sources, which underlines the need to investigate those areas for risk assessments where the pollutants are actually deposited. Hence, the relationship between micro- and meso-scale rivers should always be addressed during flood events.

Interestingly, regarding most of the pollutants the influences of the tributaries were only noticeable in July but caused peaks in LAB concentrations in both campaigns. There are many wastewater treatment plants located on the tributaries constantly discharging their effluents into the river system. Already the smaller, more regular winter flood caused the input of LABs in similar and, in the case of the Wurm tributary, even slightly higher concentrations than in July 2021. In general, the LAB input over the entire river course was almost the same for both events and thus dimensions. Since LABs are an indicator of wastewater pollution, special attention should be given to these substances during flood events. Their introduction probably depends less on the dimension of the flood than on the occurrence of a flood itself. Even in the case of small events, a relevant input of substances from wastewater must be

assumed. Possible reasons for the emission include the flooding of wastewater treatment basins, pumping stations or stormwater overflow basins, which are usually located a short distance from the rivers.

5.5 Conclusions

Accumulation of contaminated particulate matter in floodplains is of remarkable interest as it often results in a long-term storage. Thus, these sediment deposits can act as ecological archives, but also as secondary emission sources due to remobilization processes during large flood events. Therefore, it is of particular importance to consider the pollution at those rivers and its floodplains where the contaminants are actually deposited. In the catchment area of the Rur, especially in July 2021, major damage occurred to infrastructure, industry, agricultural and urban areas, particularly on the tributaries Wurm and Inde. However, many of the released pollutants were then deposited in the floodplains of the superior Rur river. This shows the large impact of smaller rivers on meso-scaled catchment systems and the relevance of remobilization for risk assessments. On the Rur itself, there are already several flood protection measures in place, and the dams and reservoirs have reduced discharges of the summer flood to a manageable level. However, such measures did not exist at the tributaries of the Rur. This statement is also true for many other micro-scale rivers in Germany and Europe. Therefore, meso-scaled river systems are particularly important for short- and long-term risk assessments since many of the pollutants accumulate and remain in their floodplains. Nevertheless, the accumulation and distribution processes are also highly influenced by structural measures, which must be carefully considered (e.g., an enrichment of pollutants in dam sediments that may be released during floods). In this context, different pollutants and pollutant groups may also exhibit different behavioral patterns (as identified here for LABs). Overall, organic indicators are very useful to gain information about indirect flood effects and the relevance of morphological settings. Especially regarding climate change and the increasing tendency of heavy rainfall and flood events, these factors need to be addressed as it was done in this study using the example of the meso-scaled Rur catchment.

6 Dynamic Transport and Distribution of Organic Pollutants in Water and Sediments of the Rur River

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Abstract

The distribution and fate of organic pollutants within different compartments of a river system are determined by several key effects and drivers. Within the scope of this study, the aqueous and sedimentary compartments have been analyzed complementary to understand transport and accumulation pathways and to determine temporospatial effects. The bi-annual campaigns allow general statements to be made about relevant processes and effects on pollutant distribution. GC/MS non-target screenings revealed that there is only a minor group of contaminants that occur both in the water and in the riverbed. Nevertheless, for both phases, the main contamination with organic compounds occurred in the anthropogenic, middle to lower course of the river with loads up to 18.3 kg/d (2,4,7,9-tetramethyl-5-decyne-4,7-diol, TMDD) in the water and amounts up to 3.3 mg/g_{TOC} (ΣEPA16 polycyclic aromatic hydrocarbons, PAHs) in the riverbed. Main emission sources were comparable, resulting in a high, almost constant contamination level which also contributes to the pollution of the superior, receiving river. Indeed, the pollution transport of the aqueous and sedimentary phases was closely connected, but with slight temporal and spatial heterogeneities. For the aqueous compartment, seasonal effects were identified while a remarkable change in riverbed contamination occurred due to an extreme flood event. However, dams within the catchment system cause a disconnection of the transport of lipophilic and hydrophilic substances. Overall, the combined investigation of different phases is an important aspect for a comprehensive view of river and environmental contamination.

Keywords: Organic pollution, River compartments, Fluvial transport, Emission patterns

6.1 Introduction

Despite the increase in environmental awareness, rivers remain important for various anthropogenic activities and are intensively used, e.g., for shipping, water withdrawal, and discharge of treated wastewater. Accordingly, river systems worldwide have been and continue to be strongly affected by the introduction of a heterogeneous mixture of anthropogenic contaminants (Lin et al., 2017). Overall, rivers can therefore be defined as transitional systems for pollutants between their source and deposition areas (Esser et al., 2020).

In particular, low-molecular-weight organic contaminants such as pesticides or pharmaceuticals are of high environmental relevance as they are often toxic and bioaccumulative and can persist for long periods in environmental compartments (Bernhardt et al., 2017; Morin-Crini et al., 2021; Wilkinson et al., 2017). These substances are very diverse and show a large structural variety as they are also used in a wide range of applications (Petrovic et al., 2016; Schwarzenbach et al., 2010). In combination with specific environmental conditions, this diversity results in numerous dispersal mechanisms, pathways, different distribution ranges, and accumulation sites.

For instance, hydrophilic components accumulate primarily in the aqueous phase and can therefore be rapidly transported within river systems (Heim et al., 2004). Due to their different chemical and physical behavior, these compounds show a high environmental mobility. In combination with the high dynamics of the watery river compartment, transport and distribution processes are usually very short-term, but still complex and challenging to analyze. In contrast, hydrophobic respectively lipophilic contaminants tend to be enriched in sedimentary material. In a river system, this includes suspended particulate matter as well as river sediment, but also material on floodplains or in reservoirs. Due to the more anaerobic conditions, sediments often act as a sink for lipophilic organic pollutants (Dsikowitzky et al., 2020; Heim et al., 2004). However, this is not limited to floodplains, as pollutants also accumulate in the hyporheic zone at the riverbed (Gandy et al., 2007; Lawrence et al., 2013; Weatherill et al., 2018). Although the particulate compartment is clearly less dynamic than the aqueous phase, different transport and (re)mobilization pathways of pollutants need to be considered for holistic risk and hazard assessments. Especially riverbed sediments can be easily mobilized due to changes in flow dynamics and annual discharge patterns (Cofalla et al., 2012; Westrich & Förstner, 2007).

Therefore, for a comprehensive assessment of the dynamic and long-term impact potential of organic substances in a complex river system, it is crucial to consider both the particulate and the aqueous phases in a complementary manner (e.g., Da Silva et al., 2011). However, most studies focus on a single compartment or on a single sampling campaign. Nevertheless, only regular sampling and monitoring

of several compartments can provide reliable, general statements on relevant processes and effects on the pollutant distribution and accumulation. In addition, the consideration of different substances is also crucial and should cover the high diversity in terms of molecular structures as well as physicochemical properties (e.g., lipophilic vs. hydrophilic; polar vs. non-polar).

This is the first study to consider regular sampling of different compartments with a high spatial coverage on the Rur river. The Rur itself is a typical meso-scaled river in Central Europe, which originates in the High Fens in Belgium, covers most of its flow distance in Germany, and finally discharges into the Meuse at Roermond (Netherlands). It has a total length of 163 km and a catchment area of about 2340 km² (MKULNV NRW, 2005). Generally, it is divided into two physiographic parts: a typical low mountain range landscape of the Eifel in the South and the northern lowland part belonging to the Lower Rhine Embayment. Along its river course, it shows a complex picture of anthropogenic impacts such as river regulation, water withdrawal, and discharge of treated wastewater. However, most of the world's river systems are anthropogenically influenced (Best, 2019; Ekka et al., 2020; Notebaert et al., 2018; Tockner et al., 2009). Therefore, the Rur river system is well suited for the analysis of input, transport, and deposition of various pollutants due to the diverse but clearly definable influences and emission sources. Processes and effects can be correlated with specific conditions and thus enable transferability to other river systems.

The main objectives were to determine the contaminant inventories in the different compartments and to understand distinct transport and accumulation pathways and processes. Differences in the contamination situation of the specific compartments and the general distribution of pollutants were identified. In particular, spatial, seasonal, and temporal variations in the state of pollution were investigated. Therefore, pollutant loads, amounts, and mass fluxes were determined, and emission profiles were established for a distinct emission characteristic and for a holistic assessment of environmental fate and behavior.

6.2 Methods

6.2.1 Study Area and Sampling

As mentioned above and shown in Figure 6.1, the Rur catchment consists of two different physiographic zones, which are relevant for different pollutant emissions and distributions. In the southern upper course, the flow dynamics are mostly close to a natural state. However, various dams and reservoirs determine the flow pattern, which are among others of great importance for drinking water supply and flood protection (WVER, 2017a). They also play an important role in sediment and

suspended matter retention (Wolf et al., 2022). The middle and lower courses of the Rur are more anthropogenically influenced by various industries (e.g., paper, metal, and textile processing), lignite mining, and agriculture (MKULNV NRW, 2005). In addition, several wastewater treatment plants (WWTPs) discharge their effluents into the Rur and its tributaries (especially Inde and Wurm). Overall, more than 40 WWTPs are located in the catchment area, with the WWTP Aachen-Soers (on the tributary Wurm) and the WWTP Düren-Merken being the largest and most relevant dischargers (WVER, 2017c).

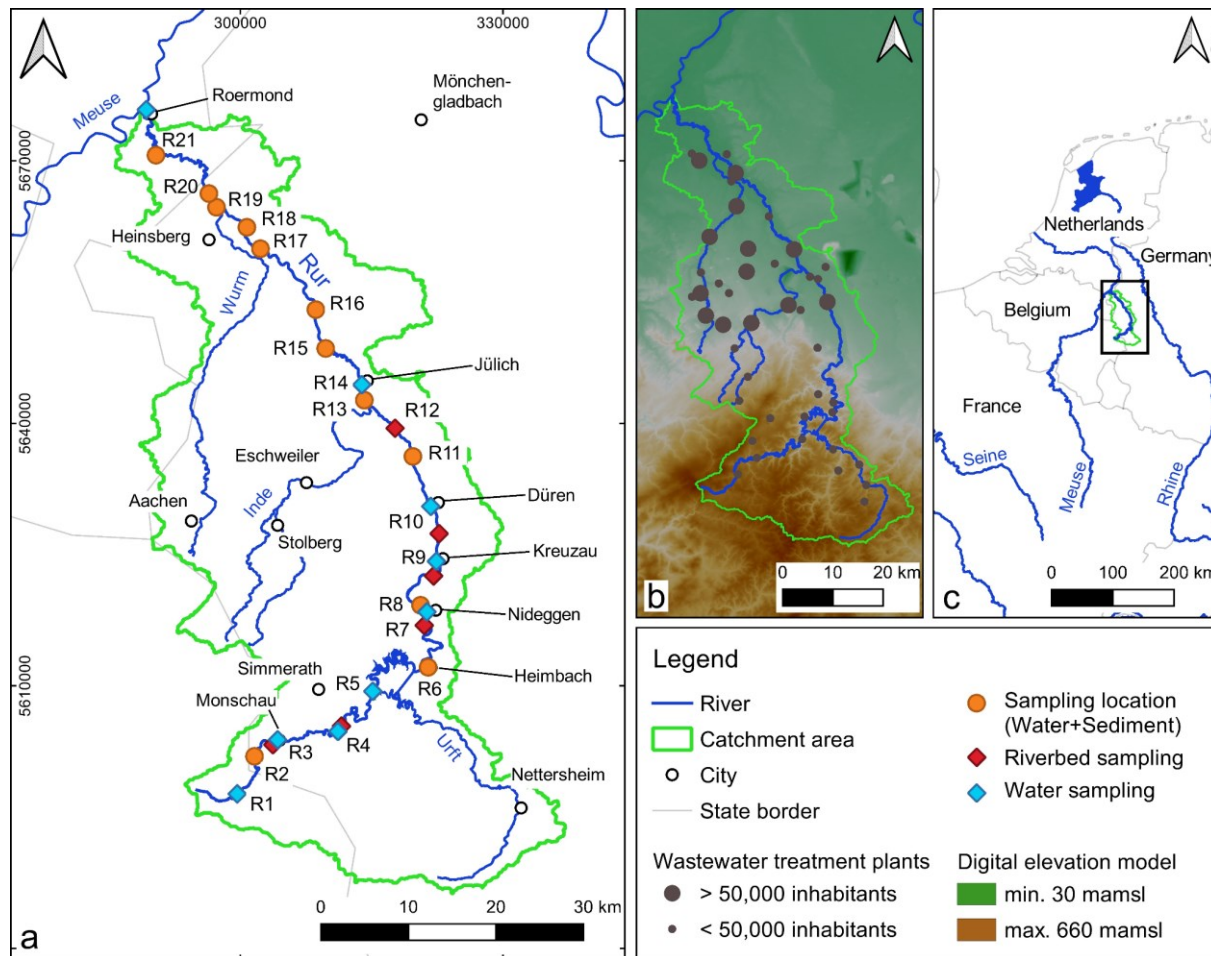


Figure 6.1 a) Overview of the Rur catchment (North Rhine-Westphalia, Germany) including sampling locations and tributaries; b) shows wastewater treatment plants and elevation; c) shows the catchment in a European context; Coordinate system: ETRS89 / UTM zone 32N.

The samples were taken at two different seasons according to the annual flow pattern of the Rur river. Sampling was carried out along the entire course of the river to account for differences in the landscape, hydrological conditions and anthropogenic influences. A total of four sampling campaigns was performed between November 2020 and May 2022 (cf. Table 6.1). Grab water samples (1 L) were scooped from midstream of the river close to the water surface. Sediment samples (200 to 300 g) were

collected from the same river sections in stillwater zones near to the riverbanks. At some sites (e.g., in Monschau (R3) and Roermond (R22)), collection of sediment samples was not possible in the immediate vicinity of the water sample location and needed to be moved. Thus, water and sediment sampling locations differ slightly from each other in some cases (cf. Table 6.2 and Table 6.3).

All samples (sediment and water) were stored in solvent-cleaned glass flasks in the dark at 4 °C prior to extraction. The sampling, extraction, and measurement procedures were the same for all sampling campaigns.

Table 6.1 Overview of the sampling campaigns and the number of samples taken from different compartments (river water & riverbed).

Sampling campaign	Date	Number of samples	
		Water	Sediment
1	November 23-24, 2020	21	17
2	June 15-16, 2021	20	17
3	November 23-24, 2021	21	18
4	May 11-12, 2022	21	18

6.2.2 Total Organic Carbon Analysis

For sediment samples, the content of total organic carbon (TOC), total carbon (TC), and total inorganic carbon (TIC) was determined. 100 mg dried sample aliquots were heated and ashed in a furnace (liquiTOC II; Elementar Analysensysteme GmbH, Langenselbold, Germany) at 550 °C (TOC) and 1000 °C (TIC). Subsequently, TOC concentrations were used for normalization of the sediment samples to ensure comparability between samples and different campaigns.

6.2.3 Organic Geochemical Analysis

6.2.3.1 Water Sample Extraction and Fractionation

Sample treatment and analysis followed well-established and previously described methods (Dsikowitzky et al., 2002; Schwanen & Schwarzbauer, 2022). First, water samples were filtered through pre-cleaned GF/F filters (Macherey-Nagel, Düren, Germany) to remove suspended particulate matter. Then, a sequential liquid-liquid extraction was performed by adding 50 mL each of *n*-pentane (fraction 1) and dichloromethane (fraction 2) to the 1-L-aliquots.

Both fractions were spiked with 50 μL of an internal standard solution consisting of the reference compounds benzophenone- d_{10} (6.3 $\text{ng}/\mu\text{L}$), hexadecane- d_{34} (6.0 $\text{ng}/\mu\text{L}$), and fluoroacetophenone (5.8 $\text{ng}/\mu\text{L}$). In the following, the extracts were concentrated to volumes of approximately 2 mL and dried with anhydrous granulated sodium sulfate (Na_2SO_4). Prior to injection, fractions 1 and 2 were concentrated to final volumes of 10 to 100 μL .

6.2.3.2 Sediment Sample Extraction and Fractionation

According to Schwanen et al. (2023), aliquots of 15 to 20 g of untreated sediment were extracted using accelerated solvent extraction (ASE). Approximately 30 mL of acetone, acetone/*n*-hexane (1:1; v:v) and *n*-hexane were used for sequential extraction. The extraction cell was kept at a pressure of 10 MPa and a temperature of 100 °C for 5 min each. In the following, the extracts were combined and dried with anhydrous granulated sodium sulfate (Na_2SO_4). Finally, they were desulfurized by the addition of activated copper in combination with ultrasonic treatment and concentrated to a volume of 0.5 mL.

For fractionation, mixtures of *n*-pentane, dichloromethane, and methanol were used according to the polarity of the organic contaminants. In the end, 6 fractions were obtained (B1: 5 mL *n*-pentane; B2: 8.5 mL *n*-pentane/DCM 95/5; B3: 5 mL *n*-pentane/DCM 90/10; B4: 5 mL *n*-pentane/DCM 40/60; B5: 5 mL DCM, B6: 5 mL methanol). The acidic compounds in fraction B6 required further methylation by addition of BF_3 -methanol (B6K1: 3 mL *n*-pentane/DCM 40/60 plus 6 mL DCM; B6K2: 5 mL methanol). 50 μL of the above-mentioned internal standard was added to fractions B1 to B5 and 200 μL to fraction B6K1. Prior to GC/MS analyses, all fractions were reduced to final volumes of 20 to 400 μL (B1 to B5) respectively 100 to 800 μL (B6).

6.2.3.3 Gas Chromatography – Mass Spectrometry Analyses

Gas chromatographic/mass spectrometric (GC/MS) analyses were performed on a quadrupole ThermoQuest Trace MS mass spectrometer coupled with a ThermoQuest Trace GC which was equipped with a ZB-5 fused silica capillary column (Phenomenex, Aschaffenburg, Germany; 30 m $\times$ 0.25 mm ID $\times$ 0.25 μm film thickness). The flow of the carrier gas helium was set to 1.5 mL/min. For all fractions (water and sediment), the temperature program and gas chromatographic conditions were a 1 μL injection (injector temperature of 270 °C) at 60 °C with a splitless time of 60 s, 3 min at the initial temperature, and then programmed to 310 °C at a rate of 3 °C/min followed by 20 min isothermal time. The mass spectrometric operation took place in full-scan mode (EI^+ , 70 eV) with a source temperature of 200 °C, scanning from 35 to 700 amu at a rate of 1.5 scans/s.

6.2.3.4 Compound Identification and Quantification

Identification of organic compounds was based on a comparison with mass spectral databases (e.g., NIST) and previously published information. Further on, they were verified by comparing specific gas chromatographic and mass spectral parameters (e.g., retention times and elution orders) with those of purchased reference materials. Quantitative data were obtained by peak integration of characteristic ion chromatograms and determined using external four-point calibrations. Compound concentrations were within the range of expected values in the samples and within the linear detection range. To correct injection and sample volume inaccuracies, a surrogate standard was used. The quantification limits were in the range of 5 ng/g_{TOC} in sediment samples and 5 ng/L in water samples (calculation based on signal-to-noise ratios in real sample matrices). Furthermore, blank analyses were performed to determine possible background contamination (n=4 for both water and sediment samples). They revealed negligible concentrations of several plasticizers such as phthalates and triacetin and tocopheryl acetate, some PAHs, DIPNs, and BHT. Detailed information on recovery rates can be found in previous studies (Schwanen et al., 2023; Schwanen & Schwarzbauer, 2022).

6.3 Results and Discussion

Emission profiles were established for substances in both the aqueous and the sedimentary phase over the entire course of the river. As different river runoffs (cf. Table 6.2) can strongly affect the compound concentrations in river water, loads, L (g/d), were calculated using the specific concentration in water, C (ng/L), and the median river runoff, MQ (m³/s): $L = C \times MQ \times (3600 \times 24 / 10^6)$ (Dsikowitzky et al., 2004b).

Table 6.2 Overview of the water samples and the corresponding river runoff data from several gauges along the Rur river in November 2020, June 2021, November 2021, and May 2022.

Site no.	River km	Gauge	River runoff MQ [m ³ /s]			
			Nov. 2020	Jun. 2021	Nov. 2021	May 2022
R1	159.5	Monschau	1.7	0.5	0.8	1.1
R2	152.8	Monschau	1.7	0.5	0.8	1.1
R3-W	148.1	Monschau	1.7	0.5	0.8	1.1
R4-W	137.9	Dedenborn	2.2	1.1	1.9	1.1
R5	124.5	Dedenborn/Heimbach	3.0	5.0	4.0	2.7
R6	109.3	Heimbach	5.0	9.1	7.4	4.4
R7-W	96.6	Zerkall	6.2	9.1	7.6	4.7
R8	94.2	Zerkall	6.2	9.1	7.6	4.7
R9-W	84.2	Obermaubach	5.0	9.9	7.9	5.0
R10-W	77.3	Obermaubach	5.0	9.9	7.9	5.0
R11	71.0	Obermaubach/Jülich	7.0	11.5	7.7	5.3
R13	61.4	Jülich	9.4	12.8	7.5	5.6
R14	59.6	Jülich	9.4	12.8	7.5	5.6
R15	51.2	Jülich/Linnich	9.0	12.0	9.0	7.0
R16	46.2	Jülich/Linnich	9.0	12.0	9.0	7.0
R17	34.7	Jülich/Linnich	9.0	12.0	9.0	7.0
R18	30.8	Jülich/Linnich	9.0	12.0	9.0	7.0
R19	26.2	Stah	8.8	11.2	11.4	8.5
R20	24.2	Stah	8.8	11.2	11.4	8.5
R21	10.4	Stah	8.8	11.2	11.4	8.5
R22	0.3	Stah	8.8	11.2	11.4	8.5

The amounts of the sediment samples were also normalized to allow better comparability between different locations as well as campaigns. In particular, the TOC content has a major influence on the pollutant distribution and accumulation; hence, a TOC normalization was performed. As shown in Table 6.3, the TOC content was between 0.2 and 5.7%. The TOC concentrations and the variability along the river course were very low in the winter sampling campaigns (Nov. 2020: 0.2 to 1.6%; Nov. 2021: 0.2 to 1.8%). Both were higher and more pronounced in June 2021 and May 2022 (Jun. 2021: 0.3 to 5.7%; May 2022: 0.3 to 4.3%). Similar seasonal distributions were observed in the Odra river (Poland). They are probably related to increased biological activities and subsequently higher primary production in summer (Kubo & Kanda, 2017; Niemirycz et al., 2006).

Table 6.3 Overview of the sediment samples and the corresponding TOC content in November 2020, June 2021, November 2021, and May 2022.

Site no.	River km	TOC [%]			
		Nov. 2020	Jun. 2021	Nov. 2021	May 2022
R2	152.8	n.s.	1.27	0.64	0.91
R3-S	148.9	0.49	0.74	0.70	1.00
R4-S	136.1	0.67	0.68	0.45	0.83
R6	109.3	0.92	0.63	1.08	0.73
R7-S	98.6	1.22	1.15	0.46	0.44
R8	94.2	0.17	5.69	0.50	4.31
R9-S	86.3	0.67	0.55	0.52	0.60
R10-S	80.7	0.34	0.28	0.66	0.35
R11	71.0	0.17	0.28	0.53	0.31
R12	66.9	1.18	3.73	0.89	2.67
R13	61.4	0.24	1.85	0.22	0.31
R14	59.6	0.58	0.52	0.68	0.49
R15	51.2	1.57	5.31	1.72	1.27
R16	46.2	1.00	1.29	0.34	0.78
R17	34.7	0.35	0.73	0.71	2.36
R18	30.8	0.23	0.90	0.55	1.34
R19	26.2	0.27	n.s.	0.52	2.11
R20	24.2	1.13	4.50	1.84	3.89

n.s. (not sampled)

The loads, amounts, and emission profiles were used to identify triggers and drivers of environmental behavior. Additional information on the toxicity of various substances identified in the Rur catchment area can be found in the Supplementary Material (Appendix to Chapter 6). Based on the data measured for the Rur river, some basic implications can be deduced about pollutant behavior and associated processes in the environment. However, there is only a small group of contaminants in this river system that occur in both the aqueous and particulate phases. Therefore, it is reasonable to consider these phases separately to derive environmental fate and transport.

6.3.1 River Water

The aqueous phase is a highly dynamic compartment with a generally fast and continuous pollutant transport, so that any sampling campaign is only a snapshot of the respective contamination. Nevertheless, emission profiles can be used to identify general trends and to determine specific fates

and behaviors, as the framework conditions have not changed over the period considered (e.g., WWTP features, population development, and water demand).

Previous non-target screening from sampling campaign 1 (Nov. 2020) revealed a high structural diversity of various lipophilic to semi-polar substances within the aqueous phase of the Rur river (Schwanen & Schwarzbauer, 2022). Indeed, a high level of structural diversity (~ 60 compounds) was found in all sampling campaigns during the observation period. In general, these substances can be assigned to different categories based on their (technical) application or chemical structures. Among others, pharmaceuticals, biocides, and constituents of personal care products and several industrial compounds have been identified. Contamination levels were generally similar across all sampling campaigns. An overview of the determined loads is given in Table 6.4. The main contamination occurred in the middle to lower reaches of the Rur river. This roughly reflects the anthropogenic influence on the catchment system, as this region is heavily populated and used for industrial and agricultural purposes. For comparison with other studies, it is usually necessary to use concentrations, as many authors do not specify any loads. However, it should be noted that for river systems, loads are clearly more informative, as they are independent of the specific runoff and thus allow comparability of different discharge situations and hence different river systems.

Overall, the highest loads were detected for the industrial substance 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD), which is probably related to its use in the paper industry in the Rur catchment (up to 18.3 kg/d). In general, considerable pollution occurred downstream of the WWTP Düren (R11), which also treats wastewater from paper production. Only slightly higher concentrations were found in the effluents of German and Swedish WWTPs (maxima: ~ 18.3 µg/L (Rur river, this study), 37 µg/L (Swedish WWTP effluent), 28 µg/L (German WWTP effluent)) indicating the high contamination of the Rur river itself (Dsikowitzky et al., 2015; Sternbeck et al., 2012).

Further on, methyl dehydroabietate and triacetin were found with loads in the range of kilograms per day. Methyl dehydroabietate (up to 11.9 kg/d) is widely used in cosmetic formulations as an emollient and skin care agent. It is therefore likely to be introduced via wastewater effluents (Bährle-Rapp, 2007). However, it is also known to be a toxic anti-estrogenic organic agent used in the paper industry, and the maximum value found was similar to the effluent concentration from a Canadian paper mill (Terasaki et al., 2009; Wartman et al., 2009). The plasticizer triacetin (up to 6.6 kg/d) also has several industrial applications (e.g., in the paper industry). In general, the occurrence of both substances was rather diffuse and could not be clearly assigned to any emission source. Another substance probably originating from paper production is the industrial substance 1,2-diphenoxyethane (DPE). Between November 2020 and November 2021, the respective maximum loads (between 6 and 20 g/d) occurred

behind the inflow of the tributary Kall (R8). This is possibly caused by a paper factory located in Zerkall near the confluence of Kall and Rur. Yet, the paper factory was severely damaged by an extreme summer flood in July 2021, which led to a temporary closure (Aachener Zeitung, 2021). In addition, load increases in the industrial centers of Düren and Jülich (R10 and R14) were observed in the emission profile of November 2021. Paper factories are again a possible source of emissions at these locations. In May 2022, the highest loads (94 g/d) also occurred in the industrially characterized lower course of the Rur river. The distribution was similar in Indonesian surface waters, where DPE was mainly found in industrial and urban areas (Dsikowitzky et al., 2017). However, concentrations of up to 3.3 µg/L were clearly higher than the maximum concentration at the Rur (128 ng/L).

Overall, the paper industry has a major influence on the contamination of the Rur river. In particular, online trade and the associated delivery services have increased the demand for packaging. As a result, paper producers along the Rur have also greatly expanded their production capacities (Kaleß et al., 2020). This may have led to higher levels of contamination with specific compounds.

Besides the high impact of the paper industry, compounds emitted from other applications have also been detected. Due to its antioxidant properties and use in anti-aging cosmetics, tocopheryl acetate is likely to be introduced by municipal wastewater effluents (Silva et al., 2019). Its occurrence in the Rur river was in the load range of kg/d (maximum of 1.4 kg/d in May 2022), but rather diffuse in all sampling campaigns. Eganhouse & Kaplan (1985) investigated tocopheryl acetate as a possible marker for municipal waste in the environment and detected concentrations of 6 to 25 µg/L in the effluents of various WWTPs in California (USA). The maximum concentration found in the Rur river was 3.1 µg/L, while the average concentrations of the four sampling campaigns were in the range from 31 to 475 ng/L.

The antiepileptic drug carbamazepine was regularly identified throughout the Rur, with loads of up to 124 g/d. It showed a downstream increasing contamination correlating well with the adjacent land use, the population density and, thus, the contributions from WWTPs. In fact, besides the WWTP in Düren (discharging directly into the Rur river; R11), the ones in Jülich (discharging directly into the Rur river; between R14 and R15) and in Aachen (discharging into the Wurm tributary; R19) were the main emitters within this river system (Schwanen & Schwarzbauer, 2022). The increasing trend is related to carbamazepine's high stability in the environment, but also during wastewater treatment (Andreozzi et al., 2003; Löffler et al., 2005). Accordingly, its occurrence in aquatic systems is well studied, and the highest loads in the Rur river downstream of the WWTP Düren (population served: ~94,000) were similar to those in the river Taff in Wales (up to 157 g/d) downstream of a WWTP of similar size (population served: 111,000) (Kasprzyk-Hordern et al., 2008).

Table 6.4 Span of minimum and maximum loads [g/d] of organic compounds detected in Rur river water samples (taken in November 2020, June 2021, November 2021, and May 2022).

No.	Compounds	Detected loads [g/d]			
		Nov. 2020	Jun. 2021	Nov. 2021	May 2022
	<i>Pharmaceuticals</i>				
1	Carbamazepine	n.d. - 124	n.d. - 55	n.d. - 107	n.d. - 115
2	Oxcarbazepine	n.d. - 17	n.d. - < 6	n.d. - < 5	n.d.
3	Caffeine	n.d. - 110	n.d. - 133	n.d. - 142	n.d. - 133
4	Lidocaine	n.d. - 125	n.d. - 96	n.d. - 233	n.d. - 74
	<i>Personal care products</i>				
5	Tocopheryl acetate	n.d. - 48	n.d. - 523	n.d. - 1019	n.d. - 1355
6	N,N,N',N'-Tetraacetylenediamine, TAED	n.d. - 59	n.d. - 39	n.d. - 37	n.d. - 8
7	4-Methoxycinnamic acid 2-ethylhexylester	n.d. - < 4	1 - 22	n.d. - 7	n.d.
8	Drometrizole	n.d. - < 4	n.d. - < 0.2	n.d. - 6	n.d.
9	Galaxolide	n.d. - 56	< 0.2 - 78	< 0.4 - 223	< 0.5 - 63
10	Tonalide	n.d. - 5	< 0.2 - 6	n.d. - 9	n.d. - 9
11	4-Oxoisophorone	1 - 12	1 - 15	< 0.4 - 9	1 - 9
12	Lilial	n.d. - < 4	n.d. - 19	n.d. - < 5	n.d.
13	Dihydromethyljasmonate	3 - 29	1 - 72	1 - 64	4 - 153
14	Coumarin	n.d. - 19	n.d. - < 6	n.d. - 7	n.d. - 6
15	4-tert-Butylcyclohexanone	n.d. - 9	n.d. - < 6	n.d. - < 5	n.d.
16	Benzophenone	< 1 - 18	0.2 - 7	< 0.4 - 20	< 0.5 - 30
17	Isopropylaurate	22 - 271	7 - 498	3 - 346	2 - 1337
18	Isopropylpalmitate	3 - 48	18 - 978	n.d. - 157	n.d. - 16
19	Methyl dehydroabietate	122 - 3078	8 - 5543	19 - 11907	47 - 3860
	<i>Pesticides and biocides</i>				
20	N,N-Diethyl- <i>m</i> -toluamide, DEET	n.d. - 27	1 - 45	n.d. - 17	n.d. - 55
	<i>Technical additives, plasticizers and other industrial compounds</i>				
21	Di- <i>iso</i> -propylnaphthalenes, DIPNs	n.d. - < 4	n.d. - < 6	n.d. - < 5	n.d. - < 2
22	N-Butylbenzenesulfonamide, NBBS	n.d. - 67	< 0.3 - 32	< 0.4 - 40	n.d. - 79
23	2,4,4-Trimethylpentane-1,3-dioldi- <i>iso</i> -butyrate, TXIB	3 - 42	< 0.2 - 102	< 0.4 - 26	1 - 101
24	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	4 - 14294	4 - 15408	< 1 - 18287	1 - 12194
25	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	n.d. - 16	n.d. - 41	2 - 292	4 - 126
26	Triethylcitrate	1 - 70	n.d. - 44	0.5 - 31	16 - 730
27	Acetyl tributylcitrate	n.d. - 48	n.d. - 28	n.d. - 19	n.d. - 235
28	Triacetin	234 - 6579	n.d. - 6383	n.d. - 934	n.d. - 6133
29	Triethylphosphate	n.d. - 158	1 - 174	n.d. - 196	n.d. - 135

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No.	Compounds	Detected loads [g/d]			
		Nov. 2020	Jun. 2021	Nov. 2021	May 2022
30	Tributylphosphate	n.d. - 13	n.d. - 9	n.d.	n.d. - 259
31	Tris(2-chloroethyl)phosphate, TCEP	n.d. - 8	n.d. - 8	n.d. - 81	n.d. - 18
32	Tris(chloropropyl)phosphate, TCPP	< 1 - 68	0.3 - 61	n.d. - 130	< 0.5 - 72
33	Triphenylphosphate	n.d.	n.d. - < 6	< 0.4 - < 5	n.d.
34	Triphenylphosphine oxide	n.d. - 206	n.d. - 79	n.d. - 140	n.d. - 130
35	Dimethyl phthalate	2 - 52	2 - 57	< 0.4 - 35	1 - 17
36	Diethyl phthalate	12 - 117	8 - 168	2 - 189	6 - 112
37	Di- <i>iso</i> -butyl phthalate	19 - 370	9 - 451	10 - 106	20 - 599
38	Di- <i>n</i> -butyl phthalate	33 - 970	24 - 703	23 - 298	49 - 473
39	Benzyl butyl phthalate	n.d. - 12	n.d. - 56	n.d. - 14	< 0.5 - 86
40	Bis(2-ethylhexyl) phthalate, DEHP	105 - 1060	n.d. - 1580	n.d. - 675	n.d. - 1134
41	2,2-Dimethoxy-1,2-diphenylethane, DMPA	n.d. - 24	n.d. - < 6	n.d. - 16	n.d. - 23
42	Diphenoxyethane, DPE	n.d. - 6	< 0.2 - 7	n.d. - 20	2 - 48
	<i>Miscellaneous contaminants</i>				
	<i>Halogenated compounds</i>				
43	Dichloroaniline	n.d. - 6	n.d. - 15	n.d. - 6	n.d. - < 2
44	1,1,2,2-Tetrachloroethane	n.d. - 253	n.d. - 28	n.d. - 167	n.d. - 108
	<i>S-containing compounds</i>				
45	Diphenylsulfone	n.d. - 14	n.d. - < 6	n.d. - 9	n.d. - 2613
46	Methylphenylsulfone	n.d. - 25	n.d. - 7	n.d. - 20	n.d. - 22
47	Benzothiazole	n.d. - 6	< 0.2 - 7	n.d. - 6	n.d. - < 2
48	2-Methylthiobenzothiazole	n.d. - 42	< 0.2 - 32	n.d. - 48	n.d. - 76
49	N-Phenylbenzenesulfonamide	n.d. - 25	n.d. - 251	n.d. - 15	n.d. - 114
50	N-Ethyl- <i>o</i> -toluenesulfonamide	n.d. - 111	n.d. - 32	n.d. - 66	n.d. - 49
51	N-Ethyl- <i>p</i> -toluenesulfonamide	n.d. - 149	n.d. - 25	n.d. - 57	n.d. - 69
	<i>N-containing compounds</i>				
52	2-Methylbenzotriazole	n.d. - 217	n.d. - 70	n.d. - 84	n.d. - 27
53	Quinoline	n.d. - 15	n.d. - 6	n.d. - < 5	n.d. - < 2
54	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d. - < 4	n.d.	n.d.	n.d.
55	Phenylisocyanate	n.d. - 129	n.d. - 14	n.d. - 664	n.d. - 275
56	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	n.d. - 756	n.d. - 173	n.d. - 526	n.d. - 216
57	N,N-Dibutylformamide	26 - 432	6 - 375	1 - 72	2 - 540
	<i>O-containing compounds</i>				
58	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone, BHT quinone	n.d. - 10	< 0.2 - 17	1 - 91	1 - 119
59	Butylated hydroxytoluene, BHT	1 - 13	1 - 43	1 - 30	1 - 124
60	1,3,3-Trimethyloxindole	n.d. - 16	n.d. - < 6	n.d. - 8	n.d. - 7

n.d. (not detected)

6.3.2 Riverbed

Although the sedimentary compartment, characterized by a discontinuous pollutant transport, is not as dynamic as the aqueous phase, riverbed sediments are easily mobilized and resuspended compared to areas of longer-term accumulation such as floodplains or reservoirs (Cofalla et al., 2012; Westrich & Förstner, 2007). Generally, the distribution of (suspended) particulate matter in fluvial systems is quite complex, determined by permanent ongoing processes such as accumulation, but also resuspension of particles, depending mainly on flow velocities and particle sizes (Morehead et al., 2003; Rhoads, 2020; Vercruysse et al., 2017). As the riverbed samples were collected at a single spot close to the riverbanks, the pollution in the middle of the riverbed may be different due to higher flow velocities.

The analysis of subaquatic riverbed sediments revealed the presence of several organic pollutant groups that have already been identified in the Rur floodplains after the 2021 flood events (Schwanen et al., 2023). These include polycyclic aromatic hydrocarbons (PAHs) as indicators of petrogenic contamination, linear alkylbenzenes (LABs) as anthropogenic markers of wastewater pollution, and polychlorinated biphenyls (PCBs) as man-made substances that were commonly used in industrial and mining applications in the past. Further on, various industrial compounds (e.g., chlorinated benzenes (Cl_2 to Cl_6), diphenoxyethane (DPE), and di-*iso*-propylnaphthalenes (DIPNs)), but also methyltriclosan and pesticide residues such as DDE and DDD were identified. The TOC normalized amounts are summarized in Table 6.5. For comparison with other studies, dry weight concentrations have also been used. However, for the environmental behavior and distribution of organic contaminants, the TOC normalized amounts are more interesting as they reflect the actual environmental behavior of the substances. In addition, they show the direct risk of contaminant accumulation in organic material.

Maximum LAB amounts were similar for all sampling campaigns and ranged from $5.1 \mu\text{g/g}_{\text{TOC}}$ (Jun. 2021) to $7.6 \mu\text{g/g}_{\text{TOC}}$ (Nov. 2021). In general, the main contamination was found downstream of Düren (R11) correlating with the distribution of WWTPs (cf. Figure 6.1). In particular, in November 2021, the concentration peaks could be easily assigned to different WWTPs. The maxima were located at R12 ($7.6 \mu\text{g/g}_{\text{TOC}}$), R16 ($6.3 \mu\text{g/g}_{\text{TOC}}$), and R20 ($7.4 \mu\text{g/g}_{\text{TOC}}$) and, thus, slightly offset to the inputs of the WWTPs in Düren (R11), in Jülich/Linnich (R14 and R15) and in Aachen via the Wurm tributary (R19). This offset is probably due to the high flow velocities and dynamics during the extreme flood event in July 2021, which prevented immediate adsorption to suspended particulate matter or rather immediate sedimentation of these particles (cf. Temporal Effects). A possible consequence is also a remobilization of already deposited material. Overall, the concentrations were mostly lower than those found in several Asian rivers on a dry weight basis (Isobe et al., 2004; Wang et al., 2014). In

particular, the average LAB contamination (between 9 and 24 ng/g_{dw}) was very low in the Rur river, as almost no LAB contamination was found upstream of Düren (R1 to R10). The maximum of 184 ng/g_{dw} was also clearly lower than the maxima found by Isobe et al. (2004). They detected particularly high concentrations in Indonesia, Thailand, and the Philippines, with maximum values of 42.6 µg/g_{dw}, 14.1 µg/g_{dw} and 13.0 µg/g_{dw}. These values are at least 70 times higher than the maximum value at the Rur.

The highest cumulative sum of six representative PCB congeners (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) was between 8.1 µg/g_{TOC} and 51.8 µg/g_{TOC}. In general, the individual amounts were highest for the Cl₆-and Cl₇-congeners, and the middle course of the Rur showed the highest PCB contamination with the maximum amounts. Specifically, the river section near Winden (R9/R10) showed a particularly high level of contamination. At R9, high summarized PCB amounts occurred in June 2021 (29.2 µg/g_{TOC}) and May 2022 (28.1 µg/g_{TOC}). Sampling campaign 3 (Nov. 2021) showed an even larger maximum at the next location R10 (51.8 µg/g_{TOC}). Again, this spatial shift is probably due to the high discharges and dynamics during the summer flood event in 2021. As the respective maxima at R9 and R10 have a similar composition, they probably originated from the same emission source. In Winden and Kreuzau, there are two paper factories as well as some metal and plastic processing companies. Partly, they discharge their wastewater effluents and precipitation water directly into the Rur river, which could be the cause of the PCB introduction. In addition, there is a reported PCB-contaminated site from a former industrial facility, which also affects the Rur river (MKULNV NRW, 2015). Considering the values based on dry weight, the ΣPCB6 maxima were between 94 and 333 ng/g_{dw}. Accordingly, they were slightly lower than those of the heavily anthropogenically influenced and industrialized Huveaune river in France (up to 435 ng/g_{dw}), but higher than those of several Chinese rivers (Kanzari et al., 2014; Lv et al., 2015; Zhang et al., 2010).

ΣEPA16 PAHs were detected in the mg/g_{TOC} – range with up to 3.3 mg/g_{TOC} (Nov. 2021). Phenanthrene, fluoranthene, pyrene, chrysene, and benzo[b]fluoranthene accounted for the largest share of contamination. PAH maxima were distributed similarly to the maxima of PCBs, mainly in the middle course and especially in November 2021. The amounts decreased downstream of the most contaminated river section at Winden (R9/R10), but the substances were still ubiquitously present. They were also found to be ubiquitous along the Huveaune river in France (Kanzari et al., 2014). Nevertheless, the concentrations in the Rur sediments are higher with an average of 3.6 µg/g_{dw} (mean value across all campaigns) compared to about 2 µg/g_{dw} in the French river (Kanzari et al., 2014). The Rur mean value was also higher than that of several Chinese rivers (e.g., Licun river, Yang river, and Dagou river), but similar to that of the Moshui (Ø 4 µg/g_{dw}) and the Daliao river (Ø 3.7 µg/g_{dw}) in China, and the Prai river (Ø 4.4 µg/g_{dw}) in Malaysia (Han et al., 2021; Keshavarzifard et al., 2014; Zheng et al.,

2016). According to Net et al. (2015), there are also several French rivers that show an even higher contamination, with average values of 6.4 $\mu\text{g/g}_{\text{dw}}$ (Senseé river), 9.9 $\mu\text{g/g}_{\text{dw}}$ (Deûle river) and 20.7 $\mu\text{g/g}_{\text{dw}}$ (Scarpe river).

Furthermore, DIPNs were the most frequently detected industrial compounds with the highest amounts ranging from 6.2 $\mu\text{g/g}_{\text{TOC}}$ (Nov. 2020) to 33.0 $\mu\text{g/g}_{\text{TOC}}$ (Nov. 2021). As many other organic pollutants, they occurred in high amounts downstream of Düren. However, these amounts on a dry weight basis (max. 310 ng/g_{dw}) were much lower than in various Indonesian river sediments (max. 16,000 ng/g_{dw}), but still higher than in the meso-scaled Lippe river (max. 83 ng/g_{dw}) and the macro-scaled Rhine river (max. 61 ng/g_{dw}) in Germany (Dsikowitzky et al., 2020; Franke et al., 2007).

Table 6.5 Span of minimum and maximum amounts [ng/g_{TOC}] of organic compounds detected in Rur riverbed samples (taken in November 2020, June 2021, November 2021, and May 2022).

No.	Compounds	Detected amounts [ng/g_{TOC}]			
		Nov. 2020	Jun. 2021	Nov. 2021	May 2022
	<i>Linear alkylbenzenes, LABs</i>				
1	Phenyldecane (C_{10})	n.d. - 400	n.d. - 220	n.d. - 120	n.d. - 280
2	Phenylundecane (C_{11})	43 - 2400	17 - 1200	5 - 2400	< 5 - 1800
3	Phenyldodecane (C_{12})	99 - 2900	27 - 2000	14 - 2600	6 - 2400
4	Phenyltridecane (C_{13})	120 - 1800	27 - 1900	20 - 3400	n.d. - 2800
	Σ LABs	285 - 7500	72 - 5100	39 - 7620	6 - 6510
	<i>Polychlorinated biphenyls, PCBs</i>				
5	Cl_3 -PCB (PCB 28)	n.d. - 2300	n.d. - 1300	n.d. - 1300	n.d. - 780
6	Cl_4 -PCB (PCB 52)	n.d. - 690	n.d. - 310	n.d. - 670	n.d. - 540
7	Cl_5 -PCB (PCB 101)	n.d. - 660	n.d. - 2400	n.d. - 4100	n.d. - 2600
8	Cl_6 -PCB (PCB 138)	13 - 1900	n.d. - 10000	n.d. - 15800	n.d. - 8600
9	Cl_6 -PCB (PCB 153)	9 - 2000	n.d. - 9500	n.d. - 17200	n.d. - 9900
10	Cl_7 -PCB (PCB 180)	9 - 1200	n.d. - 7000	n.d. - 13100	n.d. - 6500
	Σ PCBs (6 representative congeners)	31 - 8050	93 - 29175	n.d. - 51770	n.d. - 28110
	<i>Polycyclic aromatic hydrocarbons, PAHs</i>				
11	Acenaphthylene	84 - 2100	36 - 9900	8 - 47900	37 - 8700
12	Acenaphthene	44 - 3400	210 - 5900	17 - 34800	65 - 10100
13	Fluorene	86 - 5300	360 - 16400	5 - 90400	67 - 6600
14	Phenanthrene	2500 - 45400	4800 - 168000	7400 - 269000	4700 - 172000
15	Anthracene	370 - 5100	1200 - 43200	1100 - 296000	900 - 32300

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No.	Compounds	Detected amounts [ng/g _{TOC}]			
		Nov. 2020	Jun. 2021	Nov. 2021	May 2022
16	Fluoranthene	6300 - 73300	2900 - 228000	12000 - 248000	8400 - 143000
17	Pyrene	4800 - 57400	5200 - 196000	13500 - 230000	8700 - 177000
18	Benz[<i>a</i>]anthracene	2700 - 22600	4900 - 165000	9800 - 314000	6400 - 141000
19	Triphenylene / Chrysene	4300 - 29100	5900 - 196000	15300 - 328000	8900 - 182000
20	Benzo[<i>b</i>]fluoranthene	3700 - 27200	10300 - 303000	22000 - 623000	13600 - 282000
21	Benzo[<i>k</i>]fluoranthene	220 - 1800	1100 - 24700	1400 - 74900	1100 - 35000
22	Benzo[<i>a</i>]pyrene	1300 - 10200	4400 - 128000	9200 - 233000	5900 - 147000
23	Naphthalene	600 - 20900	280 - 11700	n.d. - 8700	n.d. - 550
24	Indeno[1,2,3- <i>cd</i>]pyrene	740 - 10400	5000 - 113000	8600 - 295000	10100 - 175000
25	Benzo[<i>g,h,i</i>]perylene	580 - 6800	3800 - 79800	6500 - 189000	6400 - 130000
26	Dibenz[<i>a,h</i>]anthracene	110 - 2200	1200 - 19100	1400 - 62600	1700 - 31300
	Σ EPA16 PAHs	37359 - 255980	56750 - 1538580	140680 - 3288000	89610 - 1577950
	<i>Industrial compounds</i>				
27	Di-iso-propylnaphthalenes, DIPNs	16 - 6200	n.d. - 8300	< 5 - 33000	n.d. - 11800
28	Diphenoxyethane, DPE	n.d. - 120	n.d. - 260	n.d. - 2200	n.d. - 140
29	Mesamoll®	n.d. - 310	n.d. - 7900	n.d. - 1900	n.d. - 3500
30	Butylated hydroxytoluene, BHT	n.d. - 78	n.d. - 130	n.d. - 120	n.d. - 320
31	Dichlorobenzenes (Cl ₂)	n.d. - 498	n.d. - 64	n.d. - 329	n.d. - 161
32	Trichlorobenzenes (Cl ₃)	n.d. - 247	n.d. - 24	n.d. - 117	n.d. - 62
33	Tetrachlorobenzenes (Cl ₄)	n.d. - 11	n.d.	n.d.	n.d. - < 5
34	Pentachlorobenzene (Cl ₅)	n.d. - < 5	n.d. - < 5	n.d.	n.d. - < 5
35	Hexachlorobenzene (Cl ₆)	n.d. - 10	n.d. - < 5	n.d.	n.d. - < 5
	Σ Chlorinated benzenes (Cl ₂ to Cl ₆)	n.d. - 756	n.d. - 81	n.d. - 446	n.d. - 210
	<i>Pesticide residues</i>				
36	Dichlorodiphenyldichloroethylene, DDE	n.d. - 180	n.d. - 180	n.d. - 29	n.d. - 120
37	Dichlorodiphenyldichloroethane, DDD	n.d. - 10930	n.d. - 630	n.d. - 990	n.d. - 940
	Σ DDX	n.d. - 10944	n.d. - 681	n.d. - 990	n.d. - 1060
	<i>Personal care products</i>				
38	Methyltriclosan	n.d. - 160	n.d. - 64	n.d. - 46	n.d. - 36
39	Octocrylene	n.d.	n.d. - 27	n.d.	n.d. - 32

n.d. (not detected)

6.3.3 Temporal Effects

Time is a crucial factor in the fate and behavior of organic pollutants in our environment. Some substances are rapidly degraded, while others remain stable in different compartments for long periods of time. Partly, they are very persistent or form transformation products. However, time is also critical for transport and accumulation, as some phases are more dynamic than others, river systems undergo annual changes, and extreme events such as heavy rainfall, storms, or floods can lead to increased remobilization (e.g., Crawford et al., 2022; Förstner, 2004; La Farré et al., 2008).

Temporal variations of the highly dynamic aqueous phase over a longer period of time (2004 to 2020) have already been investigated in a previous study (Schwanen & Schwarzbauer, 2022). Nevertheless, even in the shorter period of this study when more regular, monitoring-like sampling was conducted, general trends in the emission profiles were recognizable for some substances (cf. Figure 6.2).

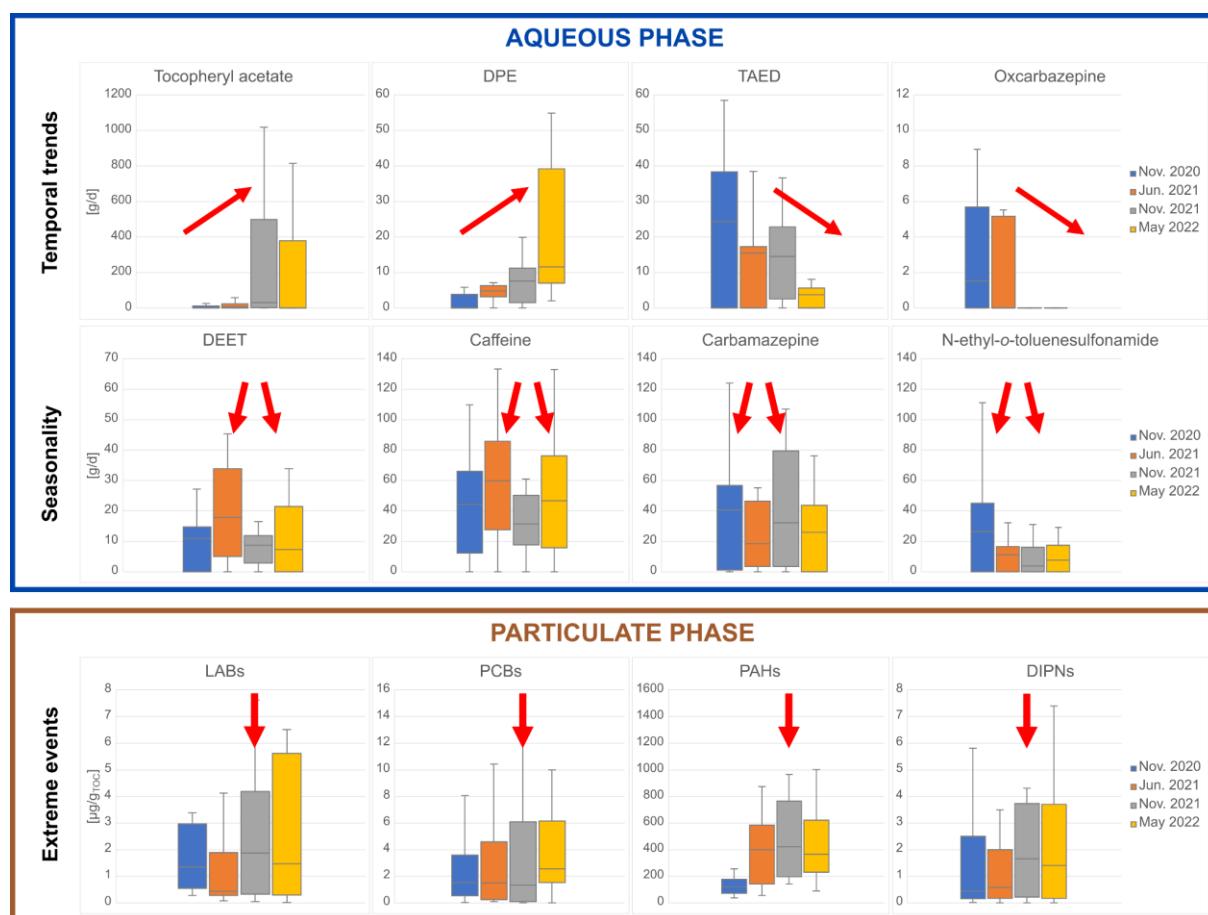


Figure 6.2 Box and Whisker plot of the loads and amounts of selected xenobiotic organic pollutants in the aqueous and particulate (riverbed) phase of the Rur river in November 2020 (blue), June 2021 (orange), November 2021 (gray), and May 2022 (yellow).

For instance, a steady increase in tocopheryl acetate loads was observed (up to 48 g/d in November 2020 and up to 1,355 g/d in May 2022), which is likely to be associated with higher consumption. Additionally, the contamination with DPE and other industrial substances such as triethylcitrate and acetyl tributylcitrate increased from 2020 to 2022, especially in the urbanized lowland part (cf. Figure 6.2). In contrast, slight decreases were recognizable for some substances such as the pharmaceutical oxcarbazepine or tetraacetylenediamine (TAED), a bleaching activator in laundry detergents. This could be due to a reduced use or an improved wastewater treatment, as for the latter this trend was already clearly visible in an earlier, longer period from 2004 to 2020 (Schwanen & Schwarzbauer, 2022).

Such longer-term developments or trends are essentially determined by external factors (e.g., changes in consumer behavior or improved treatment processes in WWTPs). These factors may also lead to seasonal differences in the contamination situation. However, there may also be other reasons for seasonality, such as (natural) degradation and transformation processes in the river. The emission profiles and the comparison of the annual patterns can give some indication in this context. Important questions are whether the amounts or loads introduced into the river system were comparable in summer and winter, whether consumption quantities varied and whether the substance degraded rapidly immediately after its introduction or not. Due to the higher dynamics of the aqueous phase compared to the sedimentary phase, seasonal phenomena are particularly expected in this compartment.

In the Rur river, many substances in the watery phase showed a seasonal behavior. These were mainly physiologically active substances (e.g., the pharmaceuticals carbamazepine and lidocaine), but industrial compounds (e.g., triphenylphosphine oxide) and naturally occurring substances (e.g., coumarin) were also identified with specific distribution patterns.

The seasonal behavior of carbamazepine has already been addressed in several studies (Fernández et al., 2014; Golovko et al., 2014; Lindholm-Lehto et al., 2016). Although its removal efficiency and biodegradation potential are very low throughout the entire year (Andreozzi et al., 2003; Fernández et al., 2014; Löffler et al., 2005; Matamoros et al., 2009), seasonal differences have been observed, showing a higher level of pollution during the winter months (see Figure 6.2). As carbamazepine is also used in the treatment of depression and mania or in alcohol withdrawal, Lindholm-Lehto et al. (2016) and Matamoros & Salvadó (2012) suspect a higher consumption during the winter months due to an increased use of psychotropic drugs.

Consumption patterns are also likely to explain the observed seasonal variations of caffeine and N,N-diethyl-*m*-toluamide (DEET). In contrast to carbamazepine, these two substances had higher loads in

summer. As DEET is mainly used as an insect repellent, extended application during the summer insect season is likely (Quednow & Püttmann, 2009). Recreational use may be a reason for the seasonal differences of the psychoactive substance and stimulant caffeine, as higher summer loads were also reported in Greek and Polish rivers, due to higher human consumption as a result of longer periods of daylight and increased human activity (Jagoda et al., 2015; Kosma et al., 2010). Removal efficiencies in WWTPs are generally high (> 99%) and not seasonal dependent (Buerge et al., 2003; Fernández et al., 2014). Yet, there were larger fluctuations in the summer emission profiles. In winter, the loads remained quite high after caffeine introduction, i.e., there was only a minor degradation. In summer, there was typically a rapid decline and much lower loads at the subsequent sites. This could be due to increased bioactivity or other degradation processes (Buerge et al., 2003; Lam et al., 2004). For instance, Buerge et al. (2003) demonstrated that biodegradation and especially photodegradation of caffeine was more effective in midsummer under clear skies.

N-Ethyl-toluenesulfonamides (NETSA) are used as plasticizers in resins, coatings, adhesives, and printing inks (e.g., Štěpek & Daoust, 1983). In the Rur catchment, food packaging factories are a likely emission source, probably requiring the same quantities for production throughout the year (Alexander et al., 2008; Skjevrak et al., 2005). However, the maximum loads of N-ethyl-*o*-toluenesulfonamide were noticeably higher in winter (Nov. 2020: 111 g/d, Nov. 2021: 66 g/d) than in summer (Jun. 2021: 32 g/d, May 2022: 49 g/d). This is likely due to a lower treatment performance of the WWTPs in winter, although precise data on removal efficiencies are lacking. Sui et al. (2011) have shown that the removal of pharmaceuticals and personal care products by conventional activated sludge as biological treatment process (as it is the case for most of the WWTPs in the catchment) varies throughout the year. Possibly, this difference in efficiency is similar for industrial compounds.

When looking at the minimum and maximum amounts in Table 6.5 and the corresponding emission profiles, it is immediately apparent that seasonality does not play a major role for the contaminants detected in the sedimentary phase. This result was to be expected due to the lower dynamics of this compartment and the typically higher persistence of lipophilic substances. Occasionally, octocrylene was found in summer sampling campaigns. The associated emission profiles thus showed a certain degree of seasonality, probably due to consumption behavior, as octocrylene is still used commercially in sunscreen products (Schneider & Lim, 2019). However, the amounts were very low (up to 27 ng/g_{TOC} in June 2021 and 32 ng/g_{TOC} in May 2022).

Nevertheless, a remarkable change in the sediment contamination due to an extreme flood event in July 2021 was evident (Schwanen et al., 2023). Amounts before this flood were, for the most part, considerably lower than afterwards. In particular, the November 2021 sampling campaign showed

several extreme maxima and more severe contamination along the entire river course. This was particularly evident for LABs, PCBs, and PAHs, but also for industrial substances such as DIPNs (cf. Figure 6.2).

On average, the sum of LABs ($C_{10} - C_{13}$) was $1.9 \mu\text{g/g}_{\text{TOC}}$ in November 2020, $1.3 \mu\text{g/g}_{\text{TOC}}$ in June 2021, $2.6 \mu\text{g/g}_{\text{TOC}}$ in November 2021, and $2.5 \mu\text{g/g}_{\text{TOC}}$ in May 2022. Thus, a clear difference in contamination before and after the extreme flood in July 2021 was observed. The amounts in November 2021 and May 2022 were comparable and mostly even higher than those detected at the Rur floodplains in July 2021. Thus, the majority of the flood-induced LAB contamination remained in the immediate riverbed, which is important for further risk assessment as there is only a minor washing out but a clear enrichment in the river itself.

For the pollutant groups of PCBs, PAHs, and DIPNs, the difference between riverbed and floodplain amounts is even more pronounced (see Table 6.6). In November 2021 (sampling campaign 3), the highest sum of six representative PCB congeners was $51.8 \mu\text{g/g}_{\text{TOC}}$. This value is almost 4 times higher than the flood-maximum of $13.7 \mu\text{g/g}_{\text{TOC}}$ at the corresponding floodplain in July 2021. Generally, the PCB contamination was highest in November 2021 with an average of $5.7 \mu\text{g/g}_{\text{TOC}}$ compared to the values of November 2020 ($2.2 \mu\text{g/g}_{\text{TOC}}$), June 2021 ($4.1 \mu\text{g/g}_{\text{TOC}}$), and May 2022 ($4.9 \mu\text{g/g}_{\text{TOC}}$). The modest increase from November 2020 to June 2021 could be due to a smaller winter flood in late January/early February 2021, while the large increase from June to November 2021 is most likely due to the extreme flood in July 2021 (Schwanen et al., 2023). The trend is also very similar for the pollutant groups of PAHs and DIPNs showing a clear difference in contamination before and after the summer flood. Again, for both groups, the amounts in November 2021 were much higher than in the adjacent floodplains in July 2021.

Table 6.6 Comparison of maximum amounts [$\mu\text{g/g}_{\text{TOC}}$] of organic compounds detected in Rur riverbed samples (taken in November 2021) and floodplain samples (taken immediately after the flood event in July 2021, cf. Schwanen et al. (2023)).

Pollutant (group)	Maximum amounts [$\mu\text{g/g}_{\text{TOC}}$]	
	Riverbed	Floodplain
Σ LABs	7.6	4.4
Σ EPA16 PAHs	3300	500
Σ PCB6	51.8	13.7
DIPNs	33	14.2
DPE	2.2	0.8

6.3.4 Spatial Effects

Besides the temporal aspect, the spatial distribution and, particularly, the range of contaminants within different compartments of a river system are of crucial importance for risk assessment and pollutant mitigation. Distribution ranges can be identified based on the emission profiles of various marker substances and the location of the corresponding emission sources. Along the Rur, the latter are mainly located in the northern, lowland part and can be traced back to urban and industrial applications. Depending on the different dynamics of the river compartments as well as the persistence and stability of the substances, longer transport distances and thus a greater range can be assumed.

For both, the aqueous and sedimentary phases, the main contamination with organic compounds occurred in the middle to lower reaches of the Rur. The input of substances due to WWTPs, particularly those in Düren, Jülich, Linnich, and Aachen (the latter discharging into the Wurm tributary), plays a decisive role. Most of the WWTPs in the Rur catchment treat both municipal and industrial influents, showing a diverse xenobiotic contamination. However, the WWTP Düren (R11) is the main emitter of most of the identified compounds. It is the largest WWTP in the catchment area discharging directly into the Rur river, with an annual treated wastewater volume of 21 million m³ (WVER, 2017c). Accordingly, the contamination is generally higher downstream of Düren, in the urban part of the catchment system, than in the more natural Eifel region.

For example, this influence is very clear in the case of the already mentioned hydrophilic, industrial substances N-ethyl-*o*-toluenesulfonamide and azobisisobutyronitrile (AIBN) respectively its degradation product tetramethylsuccinonitrile (TMSN). They were detected almost exclusively in the urban and industrial part of the Rur catchment, starting downstream of the discharge location of the WWTP Düren. This is also where the maximum loads were found. Although the loads decrease immediately after the sampling location R11, they remain at a quite constant level from this point onwards, indicating a specific stability of these compounds (cf. Schwanen & Schwarzbauer, 2022).

In general, the emission patterns are similar for most of the identified contaminants in the aqueous phase. Looking at the total water contamination as shown in Figure 6.3, sampling location R11 immediately downstream of the WWTP Düren is of outstanding relevance. Afterward, the overall load remains at a high, almost constant level. In fact, most of the substances identified in the river water show relative persistence and stability and are even transported to the superior river system throughout the year. Similar emission patterns for several organic pollutants have also been identified in the Lippe river, which is a meso-scaled tributary of the Rhine river (Dsikowitzky et al., 2004b). In contrast, the Rhine river itself shows a more variable and dynamic contamination due to multiple emission sources and inflowing meso-scaled tributaries (Schwarzbauer & Heim, 2005). Range and

transport of different contaminants therefore varies depending on the size and dimension of the river system and the corresponding flow patterns and discharges. Further information on specific environmental behaviors and emission characteristics in this compartment can be found in Schwanen & Schwarzbauer (2022).

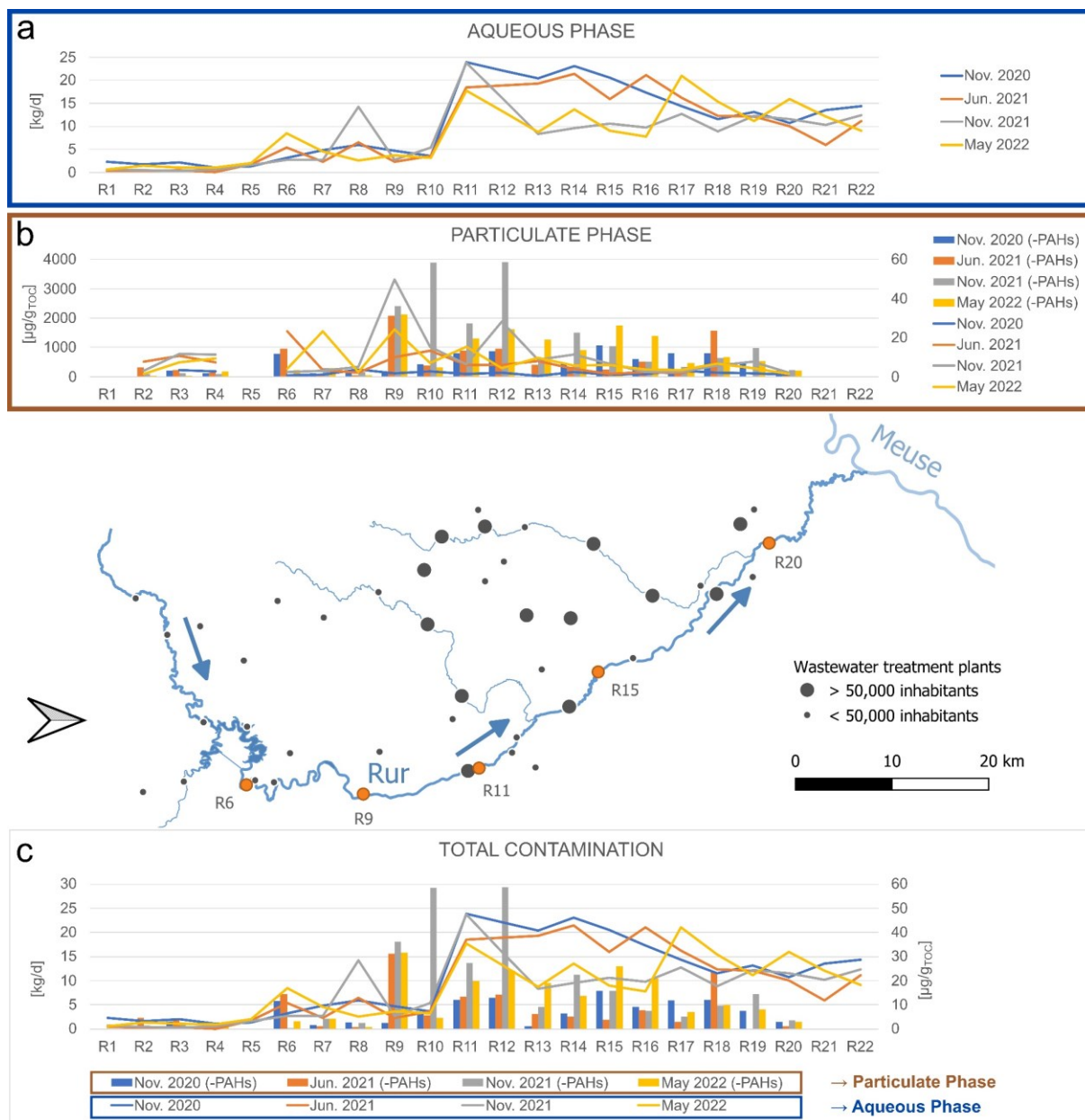


Figure 6.3 Spatial and temporal distribution of xenobiotic organic contaminants in different phases of the Rur river in November 2020 (blue), June 2021 (orange), November 2021 (gray), and May 2022 (yellow). a) shows the total aqueous contamination as a sum of the compounds in Table 6.4. b) shows the total sedimentary contamination as a sum of the compounds in Table 6.5 with (lines, primary axis) and without (bars, secondary axis) the amounts of Σ EPA16 PAHs. No sediment samples could be taken at locations R1, R5, R21 and R22. c) combines the total contamination of both phases (lines: aqueous contamination; bars: particulate contamination (without PAHs)).

As for the river water, the main contamination of the riverbed compartment occurred in the middle to lower reaches of the Rur, with the point source WWTP Düren (R11) having a major impact. Especially in November 2021, high amounts were detected at this river section. However, the maxima were shifted slightly downstream, probably due to high flood discharges in the summer of 2021 (cf. Temporal Effects). Instead of having amount maxima at sampling location R11, i.e., immediately downstream of the WWTP, high amounts were detected 4 km further downstream at R12 (Schophoven). A weir located at this sampling location dams up the river reduces the flow velocity and presumably leads to an increased sedimentation of suspended particles. In particular, LABs as wastewater indicator were detected at this site.

In general, the sampling campaign of November 2021 shows a higher contamination with peak values not only downstream of the WWTP Düren at Schophoven (R12) but also at Üdingen/Winden (R9/10). The emission profiles for the other sampling campaigns are similar. The total contamination (lines in Figure 6.3b) is generally dominated by high PAH amounts, so that it looks almost identical to the corresponding PAH emission profile. PAHs are ubiquitously present and often originate from diffuse sources. Therefore, the total contamination without PAHs is also visible as bars, showing a slight shift of the first maximum from R9 to R10 as well as a greater contamination difference between the upper and lower course of the river. Thus, the results indicate a specific dynamic transport of the riverbed sediment and the associated pollution, probably even reaching the superordinate river system.

Finally, although the contaminants are not the same in the different compartments, the pollution situation and emission patterns are comparable. Main emission sources are located in the industrial and urban centers, and the pollutant inputs are mainly from the corresponding WWTP effluents. The overall contamination profiles of the riverbed and the river water are very similar, especially when the ubiquitous group of PAHs is subtracted (see Figure 6.3c). Both compartments contribute to a dynamic contaminant input into the superior river system of the Meuse. Therefore, the transport and range of hydrophilic and lipophilic pollutants within this catchment system appears to be closely connected. Nevertheless, the input of the respective contaminants is slightly different. In the case of the sedimentary phase, the maximum contamination results not only from the inputs from municipal WWTPs but also from industrial direct dischargers. Downstream of the main emissions in the middle reaches, the pollution decreases clearly but remains at a much higher level than in the near-natural Eifel region. The difference between these two regions is even more pronounced in the highly dynamic aqueous phase. Thus, the distribution ranges of contaminants for both phases clearly exceed the dimension of a meso-scaled river system and need to be considered in risk and hazard assessments of superior, macro-scaled river systems.

6.3.5 Limiting Factors

In particular, the transport of lipophilic pollutants is closely linked to the transport of suspended particulate matter. However, most river systems are strongly influenced by anthropogenic measures and regulations. Meso-scaled rivers such as the Rur are often regulated by a single or even a chain of larger dams. Furthermore, channelization and the construction of, e.g., weirs are typical anthropogenic measures (Petts, 1999). These can therefore provide restrictions on the transport and range of pollutants. As shown above, the main pollutant transport of the two investigated phases seems to be closely connected in the middle and lower reaches of the Rur, despite the presence of weirs and channelization within this part of the river.

Yet, the largest anthropogenic regulation in the Rur catchment is the system of dams in the mountainous landscape of the Eifel. The corresponding reservoirs are used for flood protection, energy generation, drinking water supply, and also for recreational purposes, among other things (WVER, 2017d). Therefore, this river section was focused on to determine the anthropogenic influence on the transport of pollutants and on the close connection of the aqueous and particulate phases (cf. Spatial Effects). Reservoirs are located between R4 and R6 ("Rurtalsperre") and between R8 and R9 ("Obermaubach basin"). Sampling site R5 is located within the dam system of the Rurtalsperre and only water sampling could be performed at this location.

In general, the Rurtalsperre is one of the largest reservoirs in Germany with a storage volume of 202.6 million m³ of water (WVER, 2017a). In contrast, the Obermaubach basin is much smaller with a storage capacity of only 1.65 million m³ (WVER, 2017b). As shown by Wolf et al. (2022), both of them function as sinks for suspended particulate matter and accumulated inorganic pollutants (Cu and Pb). Thus, they are also expected to be a major sink for lipophilic organic pollutants and to have a strong influence on the sedimentary pollutant transport.

In November 2020, the total riverbed contamination as the sum of all substances in Table 6.5 was generally low in the Eifel region. Nevertheless, the influence of the reservoirs was recognizable in the overall emission profile (see Figure 6.4). The total amounts were higher before than after the reservoir (R4: 177.7 µg/g_{TOC} vs. R6: 49.9 µg/g_{TOC} and R8: 258.6 µg/g_{TOC} vs. R9: 125.4 µg/g_{TOC}). This is attributed to the sediment retention in the reservoirs, which greatly reduces the amount of suspended and fine particulate matter, resulting in a sediment deficit downstream of the dams (Dai & Liu, 2013; Schmidt & Wilcock, 2008; Wolf et al., 2022). However, the situation is different for the following sampling campaigns. In June 2021, the amounts downstream of the reservoirs were higher than at the previous sampling locations. In fact, the maximum of the entire sampling campaign was detected at R6 downstream of the Rurtalsperre (1.6 mg/g_{TOC}). At the end of January/beginning of February 2021,

there was a smaller flood event in this river system, which may have led to a remobilization of fine sediments and associated pollutants deposited in the reservoirs (cf. Schwanen et al., 2023). Similarly, the extreme flood in July 2021 is likely to have caused remobilization of reservoir sediments. In November 2021, the highest overall maximum was detected at R9 downstream of the Obermaubach basin (3.3 mg/g_{TOC}). This maximum was still recognizable in May 2022, but due to further transport and remobilization, the contamination level had already decreased again (1.6 mg/g_{TOC}).

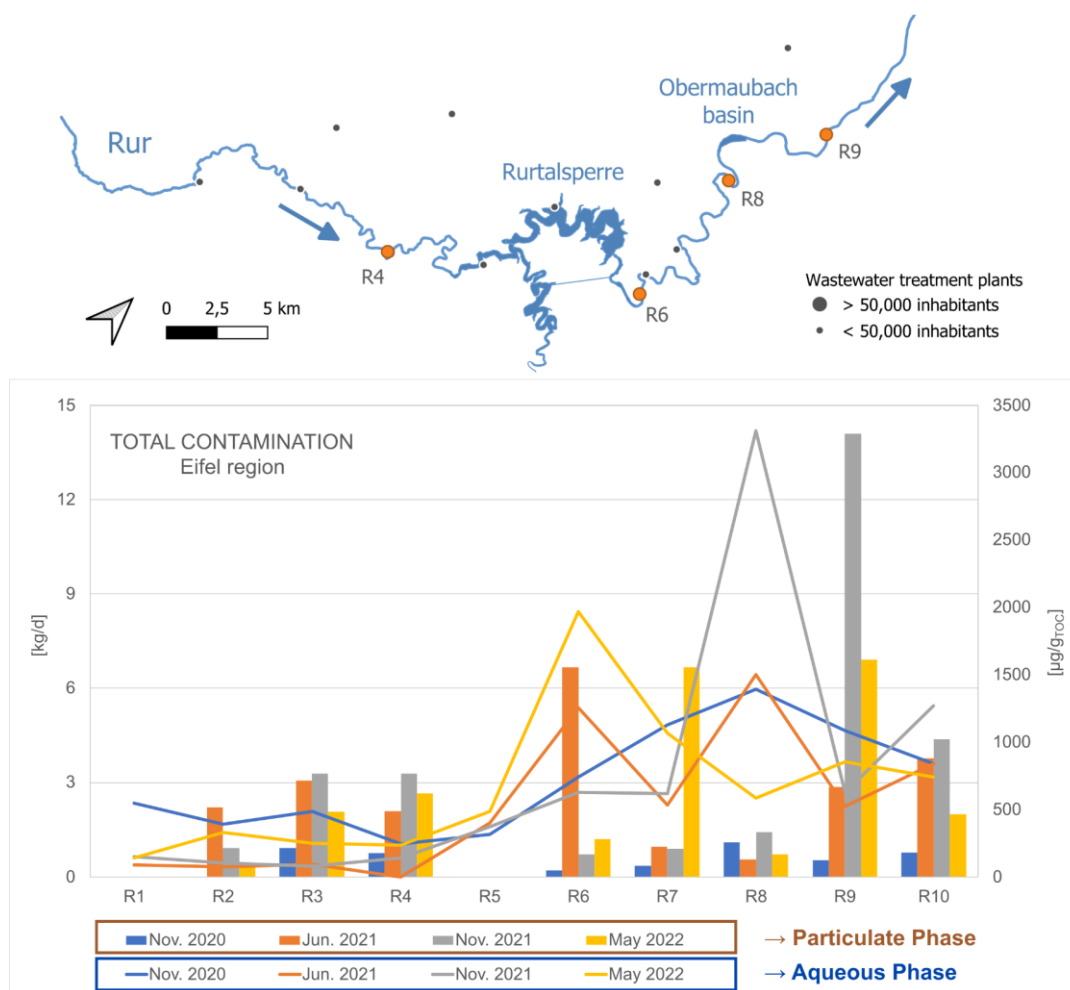


Figure 6.4 Spatial and temporal distribution of xenobiotic organic contaminants in the aqueous and particulate (riverbed) phase of the Rur river in the near-natural Eifel region in November 2020 (blue), June 2021 (orange), November 2021 (gray), and May 2022 (yellow). The respective total contamination is the sum of the compounds in Table 6.4 and Table 6.5 (without the amounts of ΣEPA16 PAHs). Reservoirs are located between R4 and R6 (“Rurtalsperre”) as well as between R8 and R9 (“Obermaubach basin”).

In contrast, no contaminant retention by the reservoirs could be identified for the aqueous phase. Instead, the Rurtalsperre was an additional emission source in the catchment system due to its recreational usage (such as camping, passenger shipping, sailing, swimming, and other water sport

activities). In summer months (sampling campaigns 2 and 4), the stimulant caffeine was detected with increased loads downstream of the reservoir (cf. Temporal Effects). Additionally, load peaks of the fragrance dihydromethyljasmonate were detected at the corresponding sampling location.

Overall, the dam system results in a disconnection of the dynamic contaminant transport in the aqueous and particulate phases, highlighting the anthropogenic influence not only on the emission but also on the transport and thus the range of different pollutants. Nevertheless, there are also several other anthropogenic measures that affect the sediment budget and possibly lead to a sediment excess or deficit. These include changes in land use (e.g., due to deforestation or sealing), but also renaturation measures (Maaß et al., 2018; Vercruysse et al., 2017; Vörösmarty et al., 2003). The latter could also contribute to the creation of sediment and pollutant sinks. However, small renaturalized areas in the middle and lower reaches of the Rur river (e.g., at Körrenzig near R16) had no influence on sediment transport and did not lead to a disconnection of particulate and aqueous phases. The situation was similar for weirs and straightened sections. Thus, a decoupling of the dynamic pollution transport from different compartments is likely to occur only in the case of large-scale anthropogenic measures with at least regional influence.

6.4 Conclusion

This study investigated the accumulation, transport, and fate of organic pollutants in different dynamic compartments of the Rur river over a period of four bi-annual sampling campaigns. Using the example of the Rur river, some generally valid statements regarding the contamination of the river water as well as the riverbed could be proven:

- **Temporal Effects:** Temporal effects occur in different dimensions for both the aqueous and particulate phases within a river system. For the more dynamic water phase, mainly regular, seasonal effects can be identified, while the transport of riverbed sediment and the accumulated pollutants is mainly determined by exceptional events, such as heavy rainfall and floods. Interestingly, after an extreme flood event, the amounts found in the riverbed were mostly higher than on the adjacent floodplains.
- **Spatial Effects:** The main emission sources are comparable for the aqueous and sedimentary phases. WWTPs, and thus associated industrial and urban effluents (especially from the paper industry), are mainly responsible for the peak loads and amounts. In addition to direct discharges, indirect discharges resulting from surface runoff and flooding are also of great relevance for sedimentary pollution. Both compartments show a high, almost constant contamination level after the main input in the more urban part of the catchment system and

consequently a similar range of pollutant transport. Thus, both lipophilic and hydrophilic substances contribute to the contamination of the superior river.

- **Limiting Factors:** Anthropogenic regulations such as weirs, dams, and channelization have a major impact on the transport of pollutants associated with the particulate but not the aqueous compartment. Reservoirs in particular act as temporary sinks for lipophilic pollutants but sediments can be remobilized during flood events and increased discharges.

Overall, this study provides a good overview of the different triggers and factors that influence the distribution, fate, and accumulation of hydrophilic and lipophilic contaminants in a river system. Although there is some slight temporal and spatial heterogeneity, pollutant transport in the aqueous and particulate phases is closely connected. The complementary investigation of the different phases in a river system has only been done in a few studies. However, this combined approach is an important aspect for a comprehensive view of environmental contamination. Therefore, the general approach and implications investigated in this study can be transferred and applied to other anthropogenically influenced river systems. The consideration of multiple phases and different triggers or key drivers is the first crucial step for risk assessment and, more importantly, for subsequent pollutant mitigation and reduction.

7 Reconstruction of the Pollution History of the Urft Reservoir – An Organic-Geochemical Investigation

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Abstract

Background: The reconstruction of the pollution history using aquatic sedimentary archives is of major relevance not only for the present and past, but also for future actions. The extent and influence of past anthropogenic emissions can be correlated with site-specific (e.g., industrial) developments as well as political actions, regulations, and initiatives. Finally, the need for further restrictions, specific monitoring or other countermeasures can be defined. Accordingly, within the scope of this study, a drilling core of subaquatic sediment was comprehensively analyzed to reconstruct the pollution history of the Urft reservoir and to understand the linkage between introduction, fate, and behavior of different organic pollutants.

Results: The Urft reservoir is well suitable for pollution reconstruction as the investigated interval covered a period of nearly 60 years of undisturbed sedimentation of fine-grained material. Additionally, specific input factors and their development (e.g., in industrial production) could be easily correlated to the emission profile detected for the reservoir. Overall, quantitative data of more than 60 lipophilic organic compounds were obtained and traced back to urban and industrial emissions. Concentrations were mainly in the range of ng/g_{TOC} to µg/g_{TOC} showing a decreasing tendency towards the surface and thus, the effectiveness of political regulations. In addition, a clear maximum was detected for almost all substances at the end of the 1970s/beginning of the 1980s, probably related to an exceptional event such as a flood or a malfunction affecting wastewater-related compounds of both urban and industrial origin.

Conclusions: Based on the organic-geochemical investigation and the associated dating, it was possible to reconstruct the pollution history of the Urft catchment in the northern Eifel mountains. Overall, organic indicators have proven to be very useful to obtain information on distribution patterns and the

influence of industrial as well as governmental actions. For instance, catchment-specific developments such as the closure of ironworks were recognizable in the identified emission patterns. Generally, in the last 50 years, the pollution of the reservoir sediment has decreased clearly showing the efficiency of increasing environmental awareness and corresponding regulations.

Keywords: Pollution reconstruction, Sedimentary archives, Emission profiles, Organic pollution sink

7.1 Background

Humans and the fluvial environment are directly linked, as rivers and lakes have always been a preferred settlement area and are still used for various anthropogenic activities and demands (e.g., shipping, drinking water supply, discharge of process and treated wastewater). Accordingly, several pollutants have entered and enter the surface waters causing a complex pollution. However, environmental studies of the sedimentary compartment in river systems focus mainly on near-surface, contemporary pollution (Heim & Schwarzbauer, 2013). In addition to this recent pollution, it is particularly important to understand the history of the pollution as well. Indeed, the corresponding reconstruction using aquatic sedimentary archives is relevant not only for the present and past, but also for future actions. Firstly, the extent and influence of past anthropogenic emissions can be determined and correlated with site-specific developments, e.g., in industry or urban settlement (Bigus et al., 2014). Such studies have already been carried out worldwide, mainly in coastal environments and lacustrine systems (e.g., Liu et al., 2005; Smith & Levy, 1990; Valette-Silver, 1993; Vane et al., 2011). The results obtained can be used to assess the effectiveness of previous or current regulations and initiatives (e.g., Brandenberger et al., 2008; Hartmann et al., 2005). Subsequently, these information can be used to evaluate the need for further action as restrictions, specific monitoring or other countermeasures (e.g., Bigus et al., 2014; Heim & Schwarzbauer, 2013). Indeed, pollution reconstruction can even be useful for predicting the future development of aquatic contamination.

Particularly, the sedimentary compartment is suitable for a long-term reconstruction of pollution (Heim & Schwarzbauer, 2013). Both lipophilic organic and inorganic pollutants (e.g., heavy metals) have a high affinity to associate with particulate matter (Hilberg, 2022). However, organic compounds generally show a broader diversity, but nevertheless also clearer specificity. They can usually be assigned to distinct emission sources and are often man-made, so that their introduction into the environment can also be related to their market introduction date (Buchty-Lemke et al., 2019). Besides their lipophilicity and known emission sources, a certain persistence of the organic compounds is necessary to identify them or their metabolites even after a time interval of several decades (Korosi et al., 2015). Therefore, the compounds need a specific resistance to different processes including chemical or biological

degradation. Such persistent organic pollutants (POPs) are predominantly of anthropogenic origin and have been used especially since the Second World War (Lorgeoux et al., 2016; Morin-Crini et al., 2021; Vasanthi et al., 2022). In fact, different xenobiotics (e.g., polychlorinated biphenyls (PCBs) or dichlorodiphenyltrichloroethane (DDT)) are especially suitable for assessing the historical pollution. They originate from various anthropogenic activities associated with urban, agricultural, or mostly industrial processes (Donner et al., 2010). For instance, the main emission sources in Western Europe in the 1960s were the chemical, coal and steel industries leading to a contamination of the aquatic compartments of surface and groundwater (Piwowarska & Kiedrzyńska, 2022). Due to their extensive usage, some of the organic contaminants are already ubiquitously distributed in our environment (e.g., Hashmi et al., 2017; Kallenborn et al., 2012; Vasanthi et al., 2022). At this point, it is also important to note that persistence and further properties such as bioaccumulation and toxicity lead to adverse effects on human health and the environment, thus highlighting the relevance of these marker substances not only for pollution reconstruction, but also for risk assessment and mitigation (Petrovic et al., 2016). For instance, PCBs have been produced on a large scale for industrial use since about 1930 (Cairns & Siegmund, 1981). However, due to toxic responses in humans and animals, they were banned in Germany in 1989 (Bundesgesetzblatt, 1989; Safe, 1994).

The deposition of particulate matter and associated contaminants is the first precondition for potential accumulation areas to act as a sink for pollutants. Areas with low turbulence and low flow velocities are particularly suitable. In a fluvial environment, these areas can be natural such as floodplains, oxbows, or (palaeo)channels, but also constructed, such as dammed reservoirs (Dhivert et al., 2015; Hudson-Edwards, 2003; Vauclin et al., 2021). However, to be suitable for reconstruction, a sedimentary archive must fulfill further requirements. For ideal archives, sedimentation should be undisturbed and continuous for a sufficiently long time, resulting in long-term storage of sediments and contaminants (Heim & Schwarzbauer, 2013). Emission sources and the history of the river basin should be known in order to evaluate and understand the pathways and fate of different organic compounds (Ayrault et al., 2021). Accordingly, knowledge of site-specific developments and land use is highly relevant, which is available for the Urft reservoir in western Germany (cf. Figure 7.1a-c).

The Urft reservoir is located in the northern part of the low-mountain range of the Eifel. It has been constructed between 1900 to 1905 with a total length of 12 km and covers a catchment area of 372.6 km² (WVER, 2018). The reservoir is used for flood protection, energy generation and low-flow raising to maintain water levels and supply downstream industries on the superior Rur river (Stauch et al., 2023a). The main inflow is the Urft river with a length of 46.4 km (MKULNV NRW, 2005). Mean sediment accumulation in the reservoir basin was around 1.54 m. However, in the upstream area of the reservoir values of more than 6 m were reached (Stauch et al., 2023a).

As can be seen in Figure 7.1a and b, the catchment area is characterized by different land uses, including urban settlements and villages, which are mainly located in the valleys of the Urft river and its tributary Olef. 3 of the 4 wastewater treatment plants (WWTPs) in the catchment area are also located near these cities as shown in Figure 7.1a (WVER, 2017c). The municipality of Schleiden includes the cities of Schleiden (2252 inhabitants in 2023) and Gemünd (3710 inhabitants in 2023), where an improvement and expansion of wastewater treatment plants took place in the early 1990s (Stadt Schleiden, 2023; WVER, 1994). The city of Kall is also located directly on the Urft river (11112 inhabitants in 2022), while the city of Hellenthal is located at its tributary Olef (7925 inhabitants in 2022) (IT.NRW, 2023b, 2023c).

Although the Urft reservoir is now located in the Eifel National Park (established in 2004, see Figure 7.1a-b), there were and still are several further emission sources in its catchment area. As in the superior catchment of the Rur river, the paper industry is an important branch of industry. At the end of the 19th and the beginning of the 20th century, there were several factories mainly specialized on pulp and paper board production (Lang, 2023; Pappenfabrik Nierfeld, 2023). Several paper production facilities are still in operation today. In addition, the chemical industry in the field of charcoal and glass production played an important economic role in the Urft catchment area until 2008 (Heinen, 2019). Moreover, the village of Gemünd was important for iron production for centuries, until the last company ceased production in 1966 (LVR, 2015). In general, the region is an old mining area (mainly lead, zinc, and iron) and the pollution with heavy metals and other inorganic trace elements has been dealt with in a complementary study by Stauch et al. (2023b). Agriculture is of minor importance in the catchment area and agricultural land has been increasingly afforested or converted to pasture and grassland since the end of the 19th century (Corine Landcover, 2018; Nilson, 2006; Stauch et al., 2023a).

The main objectives of this study were to reconstruct the pollution history of the Urft reservoir and to understand the linkage between introduction, fate, and behavior of different organic pollutants. In general, research on reservoir sediments and thus sedimentary archives within the river body is still limited (Heim & Schwarzbauer, 2013). However, due to the permanent damming and high accumulation rates, reservoirs can reflect the entire sedimentation and thus pollution interval with a high temporal resolution (Vauclin et al., 2021). In addition, reservoirs typically show an undisturbed, continuous and homogeneous sedimentation, with conditions that are less variable than in floodplains (Ciszewski & Grygar, 2016). Therefore, time-resolved contamination profiles of several organic contaminants or contaminant groups were evaluated in detail and related to the historical, anthropogenically induced development of the catchment system and general environmental policy issues. The sediments of the Urft reservoir were previously studied regarding their sedimentological

and inorganic composition (e.g., heavy metals) as well as their microplastic content, which can be used for comparison with the results of this study (Stauch et al., 2023b).

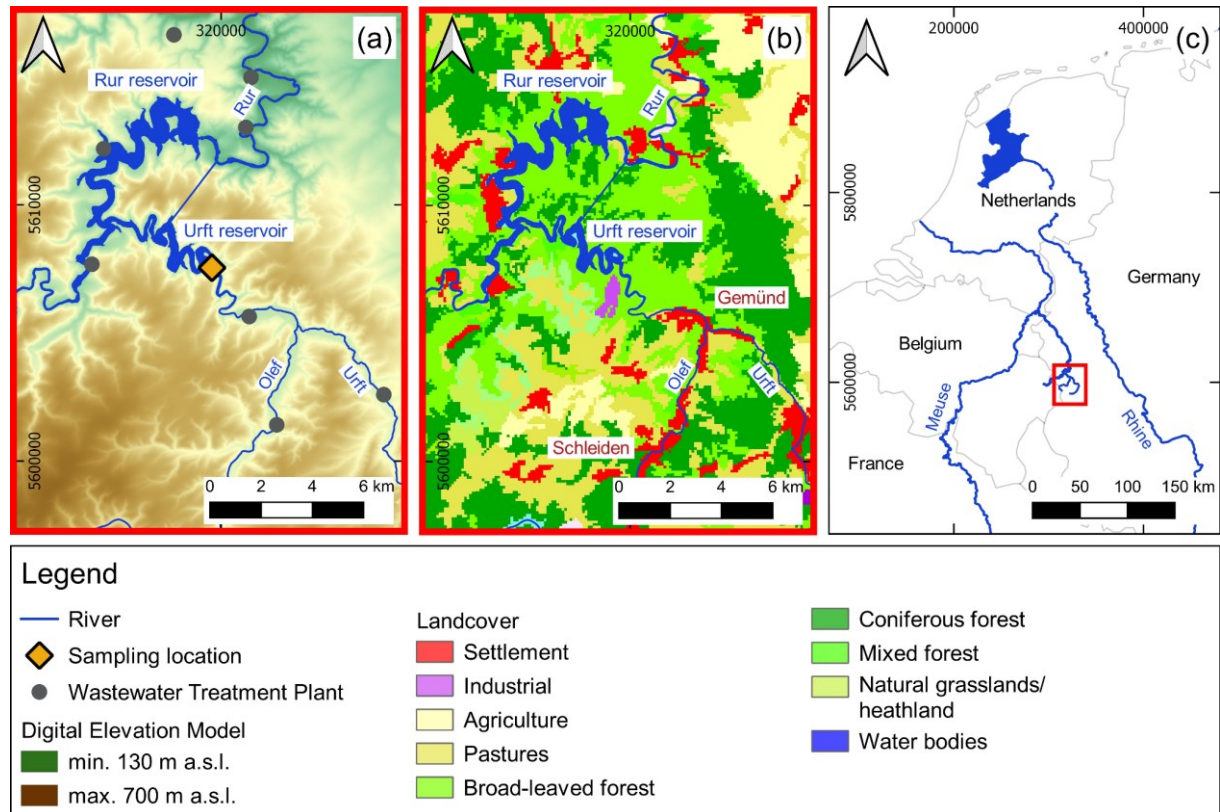


Figure 7.1 a) Overview of the Urft reservoir including the sampling location and the elevation (meters above sea level, m a.s.l.) (Geobasis NRW, 2023); b) shows the landcover according to Corine Landcover (2018) data; c) shows the sampling area in a European context; Coordinate system: ETRS89 / UTM zone 32N.

7.2 Methods

7.2.1 Sampling

The investigated core (U3) was taken as part of the study from Stauch et al. (2023a), which is focusing on the sediment deposition in the Urft reservoir (Figure 7.1). In November 2020, the reservoir was partially drained allowing direct sampling from the surface of the reservoir sediments. The core was collected using a peat auger with a coring chamber of 50 cm. A continuous sediment sequence was obtained by repeated extension. The total length of the core was 369 cm, which was divided into 38 subsamples (intervals of 6 to 13 cm). Of these, 13 homogenized and dried samples were analyzed for organic contamination down to a depth of 250 cm to cover the more recent period of anthropogenic

contamination with different organic compounds. Prior to their extraction and analysis, the dried samples were stored in solvent-cleaned aluminum cups at a temperature of 4 °C in the dark.

7.2.2 Standard Sedimentological Parameters

Besides the analysis of organic contaminants, samples were also analyzed for grain size and total organic carbon (TOC) content. Grain sizes (< 2 mm) were determined using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer (Beckman Coulter GmbH, Krefeld, Germany). For further information on the method see Stauch et al. (2023b). Total organic carbon (TOC), total carbon (TC) and total inorganic carbon (TIC) were determined using a liquiTOC II (Elementar Analysensysteme, Langenselbold, Germany). Therefore, aliquots of 100 mg of the dried samples were heated and finally ashed at 550 °C for TOC and 1000 °C for TIC. As the organic content plays a crucial role in the accumulation, behavior and fate of pollutants in river systems, a TOC normalization was performed for the quantitative data (Hilberg, 2022; Winkels et al., 1998).

7.2.3 Dating

Stauch et al. (2023b) applied Cs-137 dating for a detailed chronology of a core, which was taken 4.5 m away from the core analyzed in this study, so that the data obtained could be transferred to this study. The artificial radionuclide Cs-137 is mainly caused and produced by anthropogenic activities such as thermonuclear weapon tests and nuclear accidents (Heim & Schwarzbauer, 2013). Samples covering intervals of 2.5 to 5 cm were analyzed up to a depth of 240 cm using high-purity germanium detectors (HPGe, from ORTEC and Canberra) in a low-level shielding with relative efficiencies of 30-70% at the Forschungszentrum Jülich (FZJ) and a counting time of 15 h. A certified geometry reference source containing the nuclides Ba-133, Co-57, Ce-139, Sr-85, Cs-137, Mn-54, Zn-65 and Y-88 was used for the calibration of the detector efficiencies (Stauch et al., 2023b).

7.2.4 Organic Geochemical Analysis

7.2.4.1 Sample Extraction and Fractionation

Aliquots of 10 to 15 g of homogenized, dried sediment were extracted using accelerated solvent extraction (Dionex ASE 150, Thermo Fisher Scientific, Waltham, MA, USA). According to Schwanen et al. (2023), approximately 30 mL each of acetone, acetone/*n*-hexane 1:1 (v:v) and *n*-hexane were used to extract the samples sequentially. During each extraction sequence, the extraction cell was kept at a temperature of 100 °C and a pressure of 10 MPa for 5 min. Following this, the individual extracts were

combined, and the aqueous phase was separated and disposed. Afterwards, the concentrated extract of about 5 mL was then dried with anhydrous granulated sodium sulfate (Na_2SO_4). Finally, the extract was desulfurized using activated copper powder combined with an ultrasonic treatment for 15 min.

Fractionation was performed by column chromatography according to Schwarzbauer et al. (2000) using mixtures of *n*-pentane, dichloromethane (DCM), and methanol as eluents of increasing polarity. Columns with 2 g of activated silica gel were conditioned overnight at 200 °C and finally used for the separation of the extract into the following 6 fractions:

- Fraction 1: 5 mL *n*-pentane
- Fraction 2: 8.5 mL *n*-pentane/DCM 95/5
- Fraction 3: 5 mL *n*-pentane/DCM 90/10
- Fraction 4: 5 mL *n*-pentane/DCM 40/60
- Fraction 5: 5 mL DCM
- Fraction 6: 5 mL methanol.

Individual fractions were spiked with 50 µL of a surrogate standard solution (6.3 ng/µL benzophenone- d_{10} , 5.8 ng/µL fluoroacetophenone, 6.0 ng/µL hexadecane- d_{34}). Prior to injection, the fractions were concentrated to volumes of 20 to 400 µL.

7.2.4.2 Gas Chromatography/Mass Spectrometry (GC/MS) Analyses

GC/MS analyses were carried out on a quadrupole ThermoQuest Trace MS mass spectrometer coupled to a ThermoQuest Trace GC equipped with a ZB-5 fused silica capillary column (30 m x 0.25 mm ID x 0.25 µm film thickness; Phenomenex, Aschaffenburg, Germany). The carrier gas flow was adjusted to 1.5 mL/min. A 1 µL injection (injector temperature of 270 °C) at 60 °C with a splitless time of 60 s was followed by 3 min at the initial temperature, then programmed at a rate of 3 °C/min to 310 °C with an isothermal time of 20 min. MS analysis was performed in full-scan mode (EI^+ , 70 eV) having a source temperature of 200 °C, scanning from 35 to 700 amu at a rate of 1.5 scans/s.

7.2.4.3 Identification and Quantification

To identify the organic contaminants, mass spectra of the individual compounds were compared with mass spectral databases (e.g., NIST, Wiley) and other published information. In addition, verification was achieved by the comparison of specific gas chromatographic retention times and elution orders. Quantification was obtained by peak integration of characteristic ion chromatograms and determined using external four-point calibrations. The respective concentrations of the compounds ranged within the expected values in the samples and within the linear detection range. Inaccuracies of injection and

sample volume were corrected with a surrogate standard. The limit of detection (LOD) was in the range of 1 ng/g_{TOC} (calculation based on signal-to-noise ratios in real sample matrix) and the limit of quantification (LOQ) was in the range of 5 ng/g_{TOC}. Recovery rates of the analytes were between 70 and 100% (except for naphthalene and DIPNs with rates of around 50%). Further information on recovery rates can be found in previous studies (Schwanen et al., 2023; Schwanen et al., 2024). Blank analysis revealed neglectable background and laboratory contamination with LABs and phthalates.

7.3 Results

7.3.1 Standard Sedimentological Parameters

The grain size distribution and organic content of the samples have been analyzed as basic sedimentological parameters (see Table 7.1). Predominantly fine-grained material was deposited in the Urft reservoir. The grain size distributions of the samples from different depths varied only slightly. The clay content of all samples was less than 20% and the sand content was between 5 and 16%. The silt content was consistently more than two thirds, particularly medium and coarse silt (69 to 76%). In general, the TOC content varied between 1.8 and 6.0%. The highest values were detected for depths of 160 to 230 cm (average of 5.3%). In depths of 70 to 150 cm the average was lower (2.5%), while in lower depths of 30 to 60 cm it was again higher (3.9%).

Table 7.1 Overview of the samples and corresponding depths and the basic sedimentological parameters including grain size distribution, mean and median values as well as the TOC content of a sediment core taken in the Urft reservoir in November 2020.

Sample number	Sample depth [cm]	Grain size distribution [%]			Grain size parameters [µm]		TOC [%]
		2000 – 63 µm	63 – 2 µm	< 2 µm	Mean value	Median value	
1	30 - 40	17	72	11	26	14	4.4
2	50 - 60	16	71	14	30	16	3.5
3	70 - 80	17	76	7	22	12	2.2
4	80 - 90	16	74	10	25	14	1.8
5	90 - 100	17	75	8	24	13	2.0
6	107 - 114	15	69	16	32	17	2.8
7	121 - 130	20	75	6	19	9	3.5
8	140 - 150	17	69	14	28	12	2.6
9	160 - 170	17	70	13	28	13	4.8
10	180 - 190	17	71	12	26	12	5.7
11	200 - 210	19	72	10	24	11	5.7
12	220 - 230	19	75	6	19	10	6.0
13	240 - 250	18	69	13	28	13	4.1

7.3.2 Indicators of Organic Contamination

Based on gas chromatographic/mass spectrometric analyses and an associated non-target screening, several pollutant groups have been identified. However, as the main focus was laid on the reconstruction of the anthropogenic pollution history, selected xenobiotic compounds and compound groups were quantified according to their emission source specificity (see Table 7.2). For instance, polychlorinated biphenyls (PCBs) have been largely produced since about 1930 and were finally banned in Germany in 1989 (Bundesgesetzblatt, 1989; Cairns & Siegmund, 1981). Six indicator congeners (PCBs 28, 52, 101, 138, 153 and 180) were identified throughout the depth profile showing a cumulative contamination with an average of $2.5 \mu\text{g/g}_{\text{TOC}}$. However, a clear contamination peak occurred at a depth of 121 to 130 cm with a PCB6 sum of $11.6 \mu\text{g/g}_{\text{TOC}}$. This value is more than 4 times higher than the above average of the other samples.

Further marker compounds of industrial emissions (e.g., chlorinated benzenes, alkylsulfonic acid phenyl esters (ASEs), di-*iso*-propylnaphthalenes (DIPNs)), but also indicators of wastewater pollution (e.g., linear alkylbenzenes (LABs)) were found in the drilling core. DIPNs and LABs were clearly identified in the $\mu\text{g/g}$ -range. Similar to the group of PCBs, both the DIPN and LAB (C_{10} to C_{13}) profiles showed their highest amounts at a depth of 121 to 130 cm (DIPNs: $299 \mu\text{g/g}_{\text{TOC}}$; LABs: $18.9 \mu\text{g/g}_{\text{TOC}}$). In general, the highest contamination was found in the middle of the analyzed depth profile. Concentrations closer to the surface (30 – 40 cm) were the lowest for both contaminant groups (DIPNs: $8.0 \mu\text{g/g}_{\text{TOC}}$; LABs: $0.8 \mu\text{g/g}_{\text{TOC}}$). However, the average DIPN concentration ($68.6 \mu\text{g/g}_{\text{TOC}}$) was much higher than the average LAB concentration ($7.6 \mu\text{g/g}_{\text{TOC}}$). Other industrial compounds showed maxima in the range of $15 \text{ ng/g}_{\text{TOC}}$ (N-benzylformamide) to $2.6 \mu\text{g/g}_{\text{TOC}}$ (di-*n*-octylphthalate) (see Table 7.2).

Moreover, substances with an origin in municipal applications, such as in personal care and consumer products, were detected. Methyltriclosan originates from the bactericide triclosan, which was first introduced in the early 1970s and is used in shampoo, toilet soap, deodorants, toothpaste, footwear, and plastic articles (Balmer et al., 2004; Lindström et al., 2002). Octocrylene is commercially used in sunscreens and further personal care products such as shampoos, hair sprays and conditioners (Downs et al., 2021; Schneider & Lim, 2019). Both substances were detected at depths greater than 107 cm with maxima of $1.6 \mu\text{g/g}_{\text{TOC}}$ (methyltriclosan) and $62 \text{ ng/g}_{\text{TOC}}$ (octocrylene).

Insecticide residues of dichlorodiphenyltrichloroethane (DDT), which has been widely used since the early 1940s, have also been found regularly (Jarman & Ballschmiter, 2012). However, it was banned in most western industrialized countries in the 1970s due to its bioaccumulative and persistent properties, leading to adverse effects on humans and wildlife (e.g., endocrine disrupting potential)

(Harada et al., 2016; Turusov et al., 2002). The average sum of DDT residues (including dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD)) was $2.1 \mu\text{g/g}_{\text{TOC}}$ with a minimum of $0.2 \mu\text{g/g}_{\text{TOC}}$ (30 – 40 cm) and a maximum of $6.7 \mu\text{g/g}_{\text{TOC}}$ (140 – 150 cm).

In addition, substances without an exclusively anthropogenic origin, such as polycyclic aromatic hydrocarbons (PAHs) or (geo)hopanes, are useful for the reconstruction of the (petrogenic) pollution history. PAHs can originate from fossil fuels that enter the environment, e.g., due to oil spills or in incomplete combustion processes (e.g., Abdel-Shafy & Mansour, 2016; Baek et al., 1991; Patel et al., 2020). Partly, these processes result from natural mechanisms, such as wild fires, but most are caused by anthropogenic emissions (Ravindra et al., 2008). The diffuse origin can be further clarified by PAH diagnostic ratios (Tobiszewski & Namieśnik, 2012; Yunker et al., 2002). The cumulative sum of EPA16 PAHs shows decreasing concentrations with decreasing depth. The maximum of $1.3 \text{ mg/g}_{\text{TOC}}$ (180 – 190 cm) is more than 27 times higher than the minimum of $48.3 \mu\text{g/g}_{\text{TOC}}$ (30 – 40 cm). Several hetero-PAHs (dibenzofuran, dibenzothiophene, carbazole) containing oxygen, sulfur or nitrogen in their structure show similar profiles with maxima ranging from $2.1 \mu\text{g/g}_{\text{TOC}}$ to $10.9 \mu\text{g/g}_{\text{TOC}}$ and minima ranging from $0.08 \mu\text{g/g}_{\text{TOC}}$ to $0.8 \mu\text{g/g}_{\text{TOC}}$. Overall, PAHs are the most abundant and dominate the total contamination with the highest individual concentrations (see Table 7.2). Correspondingly, the concentrations of geohopanes (C_{29} to C_{35} stereoisomers) were much lower, showing a peak at a depth of 107 to 114 cm ($3.6 \mu\text{g/g}_{\text{TOC}}$). In contrast to the PAHs, there was an increasing tendency with decreasing depth.

Table 7.2 Concentrations [ng/g_{TOC}] of different pollutants/pollutant groups in different depths of a sediment core taken in the Urft reservoir in November 2020.

Com- pound		Detected amounts [ng/g_{TOC}]												
	Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13
	Sample depth [cm]	30 - 40	50 - 60	70 - 80	80 - 90	90 - 100	107 - 114	121 - 130	140 - 150	160 - 170	180 - 190	200 - 210	220 - 230	240 - 250
<i>Linear alkylbenzenes, LABs</i>														
Phenyldecane (C_{10})		40	180	310	440	410	490	800	500	190	260	330	120	230
Phenylundecane (C_{11})		220	960	2100	3200	2900	3500	4900	3100	1200	1600	2100	600	1300
Phenyldodecane (C_{12})		290	1200	2700	5300	3900	4900	6400	3300	1500	1700	1800	1200	1800
Phenyltridecane (C_{13})		240	990	1900	4000	2600	3300	6800	3300	1600	1800	2000	1200	1700
Σ LABs		790	3330	7010	12940	9810	12190	18900	10200	4490	5360	6230	3120	5030
<i>Polychlorinated biphenyls, PCBs</i>														
Cl_3 -PCB (PCB 28)		n.d.	14	n.d.	35	34	9	23	220	n.d.	110	230	n.d.	n.d.
Cl_4 -PCB (PCB 52)		7	10	27	16	34	33	74	130	12	66	85	5	2
Cl_5 -PCB (PCB 101)		27	54	120	140	180	170	760	400	180	210	340	78	58

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Com- pound		Detected amounts [ng/g _{TOC}]												
	Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13
	Sample depth [cm]	30 - 40	50 - 60	70 - 80	80 - 90	90 - 100	107 - 114	121 - 130	140 - 150	160 - 170	180 - 190	200 - 210	220 - 230	240 - 250
Cl ₅ -PCB (PCB 138)		100	240	590	790	870	670	3800	570	920	300	1000	230	250
Cl ₆ -PCB (PCB 153)		100	230	600	830	870	830	4200	790	1000	400	1100	260	240
Cl ₇ -PCB (PCB 180)		67	170	420	630	610	570	2700	110	650	59	570	130	130
Σ PCBs (6 representative congeners)		301	718	1757	2441	2598	2282	11557	2220	2762	1145	3325	703	680
<i>Polycyclic aromatic hydrocarbons, PAHs</i>														
Acenaphthylene		76	220	360	620	770	340	450	2100	1200	690	1000	780	3500
Acenaphthene		120	330	420	810	640	590	440	1900	1600	1200	950	660	2300
Fluorene		120	390	540	1000	1000	940	830	4100	3500	2700	2000	1700	6600
Phenanthrene, Ph		3400	12000	19200	18900	17100	35300	22200	30000	35400	572000	28600	16600	79100
Anthracene, An		820	2400	3100	5100	4400	7100	4500	18200	12500	10100	6900	7400	25300
Fluoranthene, Fl		5500	9300	24900	13300	19700	91500	14400	24900	27500	71300	15200	153000	47000
Pyrene, Py		4500	11300	31700	13100	26300	69200	19600	17800	28800	90700	18100	63000	46700
Benzo[a]anthracene, BaA		3700	12700	28600	23900	29300	53700	24200	20500	37900	73300	37200	118000	69100
Chrysene, Ch		5600	16500	38500	16600	23300	72300	23600	17800	29700	109000	31100	167000	57100
Benzo[b]fluoranthene		9300	27200	65800	52900	62600	102000	51800	68900	97600	168000	76200	284000	168000
Benzo[k]fluoranthene		680	3700	6900	9800	10600	9000	7600	14600	15400	13300	10900	23500	39600
Benzo[a]pyrene		3700	12300	28900	25300	29800	42100	23100	33700	41800	65600	33400	125000	89000
Naphthalene		490	560	1100	1700	1100	1800	2000	3500	2800	2400	4400	1100	12100
Indeno[1,2,3-cd]pyrene, IP		5100	16900	37800	33300	39000	17800	32300	40600	52100	73200	32900	116000	124000
Benzo[g,h,i]perylene, Bghi		4300	13000	28400	23700	28200	8300	24300	25000	36700	53200	25400	85000	82400
Dibenz[a,h]anthracene		850	4800	8900	11300	12100	4100	9600	9800	12300	13100	7000	22200	39800
Σ EPA16 PAHs		48256	143600	325120	251330	305910	516070	260920	333400	436800	1319790	331250	1184940	891600
C ₁ phenanthrenes and anthracenes		1800	4700	8600	11400	16800	12300	9400	42500	34300	30600	13400	13500	46900
C ₁ fluoranthenes and pyrenes		2700	12200	26000	33800	40800	38700	23100	90800	83200	63300	46300	63600	171000
Biphenyl		290	140	200	330	480	69	130	490	600	220	230	330	700
Retene		49	120	170	220	190	420	380	1600	2200	1200	990	550	1500
Benzo[e]pyrene		4100	12300	29700	25300	30400	44100	25300	38800	46700	71600	38200	127000	82400
Perylene		1200	6700	10800	12000	13400	12600	11300	14900	18600	19200	15600	35100	50500
<i>NSO-PAHs</i>														
Carbazole		83	310	340	720	730	810	510	2300	1500	1600	1000	1200	3500
Dibenzothiophene		120	240	310	480	430	390	390	1300	1100	1000	990	540	2100
Dibenzofuran		850	1200	1700	2700	2400	1200	1600	4900	5200	3800	3000	3000	10900
<i>Hopanes</i>														
Trisnorneohopane, Ts		43	110	89	130	180	250	86	77	< 5	n.d.	n.d.	22	7
Trisnorhopane, Tm		88	120	75	130	190	300	92	130	< 5	< 5	< 5	38	< 5
C ₂₉ -hopanes		390	350	52	200	610	1000	120	140	10	9	12	39	10
C ₃₀ -hopanes		410	180	21	66	380	950	63	100	13	10	14	22	14
C ₃₁ -hopanes		450	140	13	31	300	760	31	48	14	10	10	42	15
C ₃₂ -hopanes		230	48	< 5	9	150	390	13	24	< 5	< 5	< 5	< 5	8

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Com- pound		Detected amounts [ng/g _{TOC}]												
	Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13
	Sample depth [cm]	30 - 40	50 - 60	70 - 80	80 - 90	90 - 100	107 - 114	121 - 130	140 - 150	160 - 170	180 - 190	200 - 210	220 - 230	240 - 250
C ₃₃ -hopanes		180	15	< 5	< 5	87	270	5	18	n.d.	< 5	n.d.	< 5	5
C ₃₄ -hopanes		120	8	n.d.	n.d.	40	140	n.d.	8	n.d.	n.d.	n.d.	n.d.	< 5
C ₃₅ -hopanes		120	< 5	n.d.	n.d.	35	120	n.d.	6	n.d.	n.d.	n.d.	n.d.	n.d.
Σ C ₂₉ - C ₃₅ hopanes		1900	741	86	306	1602	3630	232	344	37	29	36	103	52
<i>Industrial compounds</i>														
Di-iso-propylnaphthalenes, DIPNs		8000	12000	40500	74900	33100	75500	299000	74500	72200	39500	69300	31700	61400
Diphenoxyethane, DPE		1000	1800	1800	1800	1300	840	1400	1400	870	1100	590	680	1900
Alkylsulfonic acid phenyl esters, ASEs		170	440	400	950	2200	980	3800	1400	750	1700	860	270	470
Butylated hydroxytoluene, BHT		29	5	< 5	n.d.	17	52	7	9	5	7	18	< 5	11
Bis(2-ethylhexyl) adipate, DEHA		8	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Di-iso-butyl phthalate, DIBP		n.d.	n.d.	< 5	n.d.	n.d.	930	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.
Di-n-butyl phthalate, DBP		n.d.	n.d.	100	40	5	500	11	9	130	n.d.	n.d.	< 5	< 5
Bis(2-ethylhexyl) phthalate, DEHP		< 5	18	7	8	15	2600	10	9	23	< 5	7	n.d.	9
N-Benzylformamide		< 5	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	15	< 5	< 5	n.d.	7
Dichlorobenzenes (Cl ₂)		< 5	< 5	< 5	10	25	25	18	7	< 5	< 5	11	5	6
Trichlorobenzenes (Cl ₃)		< 5	n.d.	< 5	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tetrachlorobenzenes (Cl ₄)		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pentachlorobenzene (Cl ₅)		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexachlorobenzene (Cl ₆)		n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Σ Chlorinated benzenes (Cl ₂ to Cl ₆)		< 5	< 5	< 5	10	25	25	18	7	< 5	< 5	11	5	6
<i>Pesticide residues</i>														
Dichlorodiphenyldichloro-ethylene, DDE		49	120	200	200	210	140	790	340	150	210	310	81	37
Dichlorodiphenyldichloro-ethane, DDD		200	3100	1800	2100	850	680	1400	6400	1900	1600	1100	2600	850
Σ DDX		249	3220	2000	2300	1060	820	2190	6740	2050	1810	1410	2681	887
<i>Personal care products</i>														
Methyltriclosan		n.d.	n.d.	n.d.	n.d.	n.d.	1600	190	640	510	42	36	210	160
Octocrylene		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5	23	30	42	23	12	62

n.d. (not detected)

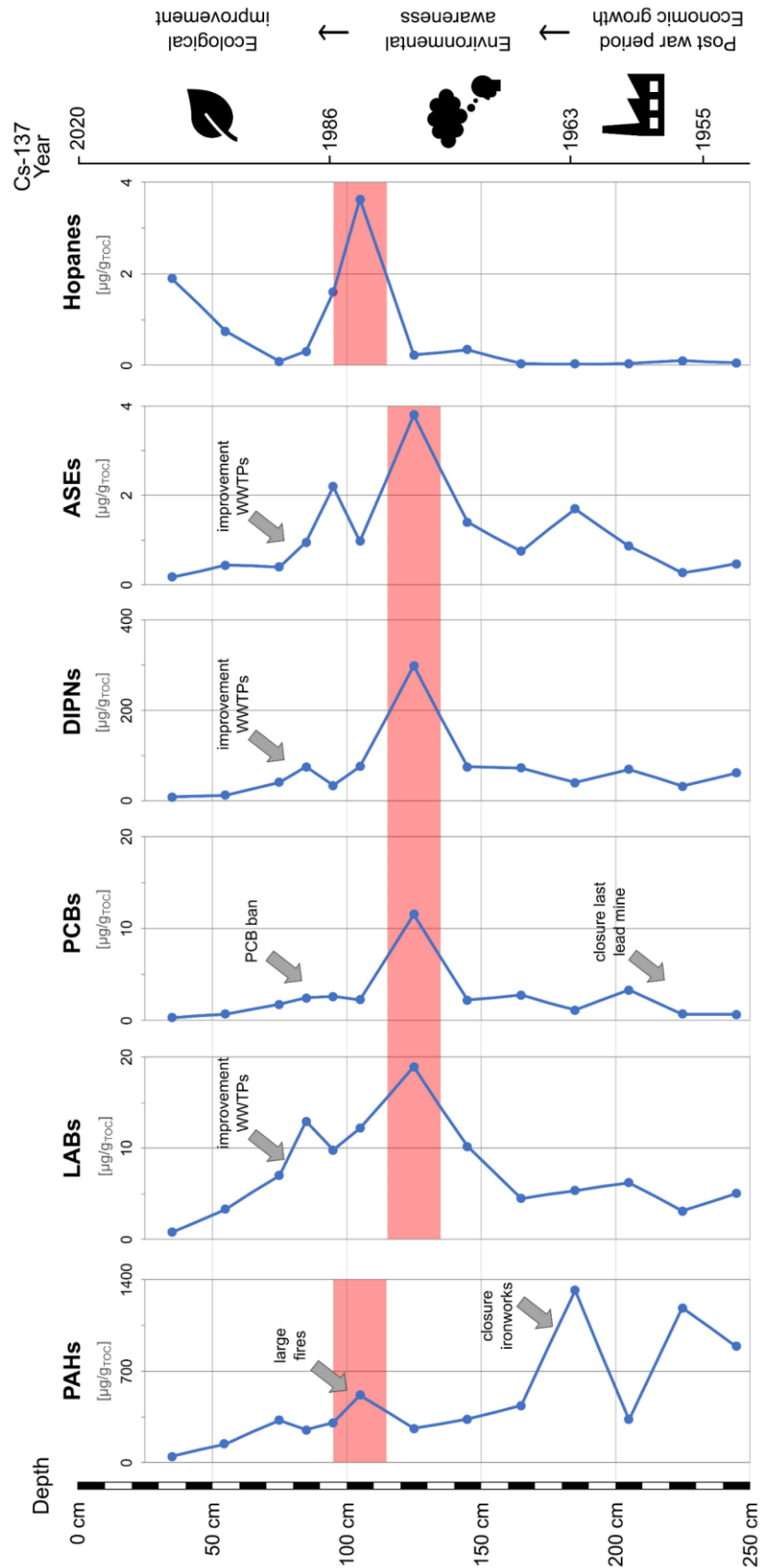


Figure 7.2 Overview of different contamination profiles correlated with depth and general as well as catchment-specific time markers. The layer marked in red shows particularly high concentrations and thus indicates a possible extraordinary event.

7.4 Discussion

7.4.1 Reconstruction of the pollution history and contamination trends

Looking at the depth profiles of different organic pollutants, general statements about emission and accumulation trends can be made. For this purpose, market introduction dates and legal regulations such as bans and restrictions were taken into account. However, radioisotopic dating enables a much more detailed chronological assignment than using only organic components and their time markers. Stauch et al. (2023b) studied the sediment deposition in the Urft reservoir combined with Cs-137 dating of a core, adjacent to the core analyzed in this study. The first appearance of Cs-137 occurred in a depth of 232.5 cm and corresponds to the beginning of nuclear weapon tests in 1955. The maximum fallout in 1963 was identifiable as a Cs-137 peak at a depth of 183.75 cm and the Chernobyl nuclear accident in 1986 as a peak at a depth of 93.75 cm. Based on the assumption of constant sedimentation between the dated points and the top of the core, a simple age-depth model and mean sedimentation rates were determined. Accordingly, these information can be used for the core of this study to reconstruct the pollution history of the reservoir. In this study, the age-depth model is combined with the results of the organic geochemical analysis to understand emission trends within the Urft catchment and to estimate the influence of human activities and inputs on reservoirs and subsequently on the fate and accumulation of pollutants of different origin. Temporal markers and intervals as well as relevant contamination profiles are summarized in Figure 7.2.

Based on the Cs-137 dating, the samples examined in this study roughly cover the period from 1950 to 2010 and thus, a time of more modern pollution. The basis of the depth profile can be assigned to the post-war period in Germany. Due to the increase in industrial emissions, the environmental situation initially deteriorated markedly during these decades (Chaney, 2008; Uekötter, 2007; Wey, 1982).

Corresponding problems were first addressed in the late 1960s and then in the 1970s recognized by the general public (Böcher & Töller, 2012; Rink, 2020). At that time, the first pioneering studies on organic water pollution were carried out (e.g., Jungclaus et al., 1978; Lopez-Avila & Hites, 1980). These focused on the discharge of industrial wastewater from chemical production sites and the transport of associated pollutants into sediments. Since then, there has been an increase in research activities, political interest, and the establishment of several nature conservation organizations (Böcher & Töller, 2012; Uekötter, 2007). However, in the 1990s, environmental policy stagnated during the German reunification, until a new government enacted comprehensive environmental policy reforms and new laws starting in 1998 (Rink, 2020).

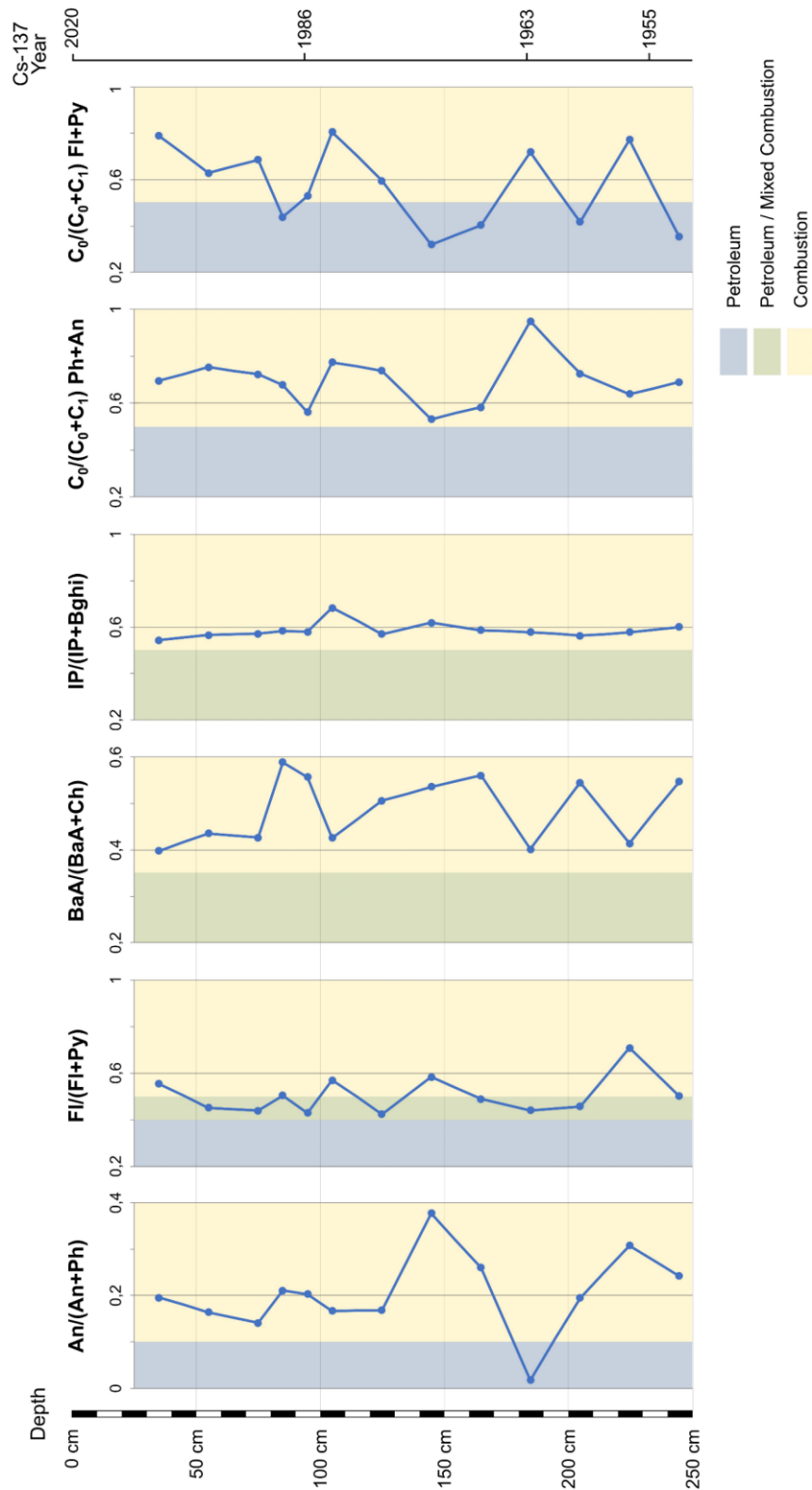


Figure 7.3 Overview of different PAH diagnostic ratios based on the detected concentrations of anthracene (An), phenanthrene (Ph), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Ch), indeno[1,2,3-cd]pyrene (IP), benzo[g,h,i]perylene (Bghi), C_1 phenanthrenes and anthracenes and C_1 fluoranthenes and pyrenes correlated with depth and general time markers to differentiate and classify emission sources (petrogenic vs. pyrogenic) according to Yunker et al. (2002).

In the sediments of the Urft reservoir, PAHs show a general decreasing trend with decreasing depth, with the contamination being the lowest closest to the surface (Figure 7.2). According to this trend, even lower concentrations can be estimated at the surface of the reservoir sediment. Samples from a depth of 180 to 250 cm show the strongest pollution, which corresponds to the period from 1950 to ~1970. During this period, particularly in the 1950s, Germany experienced a phase of economic growth as a result of the government support and encouragement of the industry (Görtemaker, 1999). For example, the ironworks in Gemünd, which had been destroyed in 1944, was rebuilt and restarted as part of this process (LVR, 2015). The corresponding production may have caused higher PAH emissions, as several PAH diagnostic ratios indicate a primarily pyrogenic origin (cf. Figure 7.3). Most of the samples correlate to petroleum combustion as well as grass, wood or coal combustion (cf. Tobiszewski & Namieśnik, 2012; Yunker et al., 2002). However, the economic recession of 1966/67 and the so-called mining crisis also led to the closure of the last ironworks in the catchment area correlating with a clear decrease in PAH contamination (Hinz-Wessels, 2003; LVR, 2015). Subsequently, German environmental policy developed rapidly from the 1970s onwards, so that considerable improvements in pollutant emissions were achieved through legislation and subsequent technical installations (such as filter and desulfurization systems) (Uekötter, 2007). In line with this, PAH concentrations were considerably decreasing with lower depths.

A slightly different depth profile was detected for the industrially used group of PCBs. The greatest amounts were found at medium depths in the drill core, with by far the highest summarized concentrations being found at a depth of 121 to 130 cm. This corresponds to the late 1970s. However, no flooding was recorded at the river gauge in Gemünd during this period. Increased discharges were measured at the end of 1974 and from 1980 onwards (ELWAS-WEB, 2023). Thus, an extraordinary emission and introduction of pollutants from a specific contaminated site or a (malfunctioning) WWTP is more conceivable here. However, the PCB composition of sample 7 (121 – 130 cm), i.e., the distribution of the individual indicator congeners, was very similar to that of the sediment layers deposited above (samples 1 to 6; < 114 cm). Contrary, in the preceding period and thus depths of 140 to 210 cm, the proportions of low-chlorinated compounds were higher. Especially these low-chlorinated PCBs were used in mining equipment (Friege et al., 1989; Schettgen et al., 2018), and the higher proportions may be attributed to the neglect and abandonment of the last mining sites. Most of the mines were already closed in the 19th century or early 20th century (Kley & Brunemann, 1995; LVR, 2018). However, lead ore mining in the Eifel region came to a final end with the closure of the last mine in 1957 (Bergbaumuseum Mechernich, 2023). Remobilization of corresponding sediments is therefore a likely emission pathway for PCBs to the Urft and its tributaries. Except to the clear peak at 121 to 130 cm, PCB6 concentrations were at an almost similar level at depths of 80 to 210 cm and thus

in the time period from the late 1950s to early 1990s. A clear increase in concentration at a depth of 210 cm (~1958) can probably be attributed to the German economic growth and industrial expansion in the post-war period. At smaller depths (< 80 cm, early 1990s), a distinct decrease in concentrations towards the surface can be seen. Accordingly, this development coincides quite well with the German ban of PCBs by the PCB-, PCT-, VC-Prohibition Ordinance in 1989 (Bundesgesetzblatt, 1989). Until then, especially the higher chlorinated PCBs were widely used in industrial applications, e.g., in electrical insulation or hydraulic equipment (Waid, 1986; Walker et al., 2019). However, because they are generally more stable and resistant to degradation, they have been detected more regularly in several river systems and reservoirs worldwide (e.g., Hagemann et al., 2019; Micić et al., 2013).

The depth profile of LABs shows a similar trend, with the greatest concentrations at medium depths. Unlike PCBs, LABs are not an indicator of industrial production, but of domestic wastewater pollution. Specifically, they are raw materials and byproducts in the industrial production of linear alkylbenzene sulfonates (LASs), the most widely used anionic surfactants (Fernández Cirelli et al., 2008; Heim et al., 2004). At depths between 160 and 250 cm and thus from the late 1940s to the late 1960s, the concentrations in the Urft reservoir were almost constant. Since the early 1960s, LAS-type detergents have been increasingly used as substitute for the poorly degradable tetrapropylene-based alkylbenzene sulfonates (Reiser et al., 1997; Zeng & Yu, 1996). Nevertheless, LABs have already been identified in older sediments (~1950), indicating the beginning substitution process of these surfactants. This was also the case in riparian wetland sediments of the Lippe river, also in western Germany (Heim et al., 2004). The highest LAB contamination at a depth of 80 to 150 cm corresponds to the time period of the early 1970s to early 1990s and likely reflects the increased use and large-scale production of LASs and thus LABs. Subsequently decreasing concentrations are probably related to improvements in wastewater treatment techniques and technologies. In 1991, the WWTPs in Gemünd and Schleiden have been expanded and renovated, with special requirements being placed on the treatment performance of the plant in Gemünd, as it is located directly at the Urft river (WVER, 1997). In general, particularly in the last forty years, great efforts have been made in Germany to improve the efficiency of wastewater treatment (UBA, 2023a). Further on, the decline in agricultural land use in the catchment area and the council directive of 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC), have probably also contributed to the decrease in near-surface LAB contamination (The Council of the European Communities, 1986). Concentrations in the modern, near-surface layers are therefore even lower than around 1950, when the use of LASs began.

The contamination profiles of the industrial representatives DIPNs and alkylsulfonic acid phenyl esters (ASEs) show similar emission trends as the domestic wastewater markers LABs. In the Urft catchment,

they are mainly introduced by the discharge of treated wastewater from WWTPs that process both urban and industrial influents. Concentrations are lowest at the top and the end of the profile, while the main contamination covers a depth of 80 to 210 cm (late 1950s – early 1990s). Again, respective maximum concentrations were detected for sample 7 (121 to 130 cm; late 1970s). As this peak was detected for several wastewater-related substances, it can be assumed that there was an exceptional event during this period which led to the introduction of several pollutants. However, as mentioned above, no increased runoffs were detected in the river system and the event was probably the result of a malfunction in wastewater treatment (ELWAS-WEB, 2023). In addition, a new patent for the production of ASEs was registered by a German company in 1975, which may have led to increased production in the following years (Lange & Welz, 1975). The general decrease of ASEs and DIPNs with decreasing depth is likely based on the improvements of the wastewater treatment plants in Gemünd and Schleiden (starting in 1991). The latter contamination trend also applies to the profile detected for chlorinated benzenes, which, depending on the isomer, enter the aquatic environment via domestic as well as industrial wastewater (Hagemann et al., 2019; Koch, 2008).

Overall, most of the organic compounds show their main contamination at depths between 80 and 150 cm and thus in the period from early 1970s to the early 1990s. At greater depths (> 150 cm), there is an increasing trend with decreasing depth, while there is a decreasing trend towards the surface. The increase can be roughly attributed to Germany's industrial development from the post-war period onwards and the near-surface decline to increasing environmental awareness and environmental policies (including bans and restrictions, e.g., on PCBs). Similarly, the content of heavy metals in the Urft Reservoir declined until the mid-1980s and has been relatively constant since this time (Stauch et al., 2023b).

However, some organic pollutants show different contamination profiles. 1,2-Diphenoxyethane (DPE) shows a rather diffuse occurrence over the entire depth profile, which is possibly related to the still very strong influence of the paper industry. DPE has already been regularly detected in the superior Rur river, which is also characterized by the paper industry (Schwanen et al., 2023). Certain substances were mostly found at great depths (> 107 cm) and thus in sediment layers older than approximately 1980 (e.g., methyltriclosan, octocrylene, N-benzylformamide). Yet, particularly for octocrylene and methyltriclosan, this does not match their market introduction dates. Accordingly, both substances should not be detected in older sediment deposits. Triclosan as parental compound of methyltriclosan was firstly produced in the early 1970s. However, the original bactericide is comparatively polar and more mobile than methyltriclosan (Butler et al., 2012; Lindström et al., 2002). Probably, a leaching of triclosan into saturated deeper sediment layers of the reservoir has taken place before it has been (bio)degraded into methyltriclosan. Similarly, N- benzylformamide was already suspected to be a

degradation product of other contaminants, so that the leaching and subsequent transformation are also a possible environmental pathway (Bellanova et al., 2022). However, it is a member of formamides, which are typically used as solvents and could therefore also migrate related to the higher polarity as and, thus within the aqueous compartment. In general, the presence of N-benzylformamide in sediments has rarely been studied so far. Contrary, leaching does not provide a clear explanation for the occurrence of octocrylene. Its commercial usage in sunscreens and anti-aging creams started about 15 years ago (Medici et al., 2022). However, octocrylene is strongly lipophilic and shows only a low water solubility (Blum et al., 2018).

Other organic substances were detected with high amounts closer to the surface (e.g., bis(2-ethylhexyl) adipate (DEHA), butylated hydroxytoluene (BHT) and (geo-)hopanes). Geohopanes, in particular, showed the highest contamination between 30 and 150 cm (1971 – 2009). Therefore, the underlying emission sources and trends of hopanes must be different from those of most of the other identified pollutants. This may be related to pollutant emissions from a former military base. The base was located right next to the reservoir and was first used by the British military from 1946 to 1950 and then by the Belgian military until 2005 (Vogelsang IP, 2023). Throughout Germany, contaminations with mineral oil products have been regularly detected at former military sites (Miller & Foran, 2012; Mulisch, 2006; Szelinski, 1999). It is therefore possible that a respective contamination of the Urft reservoir has also occurred, leading to a more recent introduction of pollutants into the catchment.

Another common feature of most of the contamination profiles is the presence of a peak or maximum concentration at a depth of 107 to 114 cm (early 1980s) or 121 to 130 cm (late 1970s). This peak is particularly pronounced for LABs, PCBs, methyltriclosan, ASEs, DIPNs and other industrial substances such as BHT and different phthalates. Most of these substances originate from urban and industrial sources and are introduced via the discharge of (treated) wastewater from the respective facilities or WWTPs. An event may have occurred that affected one or more WWTPs in the catchment area. This could have been, for example, a flood. However, no extreme discharge values were measured at the Gemünd gauge (Urft) or at Schleiden (tributary Olef) between 1976 and 1979, whereas from 1980 onwards there was a period of regularly increased discharges. In some cases these values were even higher than the average flood discharge (ELWAS-WEB, 2023). However, no historical records and documents prove such an exceptional event. Thus, it is more likely that there was a local malfunction or problem with the purification process at one of the WWTPs, resulting in the discharge of untreated or only poorly treated wastewater. Emissions from another point source than a WWTP are rather unlikely due to the variety of wastewater-related substances showing high concentrations. The contamination profile of the predominantly pyrogenic PAHs also shows a very slight increase at 107 to 114 cm (1981 – 1982), but this could rather be attributed to two large fires in paper and plastic

warehouses in Olef in 1980 and a movie theater in Schleiden in 1982 (Gutmann & Lang, 2023; Heinen, 2016). Similar effects of a fire on the pollution situation were also recorded for the microplastic content in the Urft Reservoir. A large fire in a glass and plastic factory in 1991 resulted in a major input of particles which could be traced across several drilling cores in the upper part of the reservoir (Stauch et al., 2023b).

Trends correlating with the environmental legislation and the beginning of environmental awareness since the 1970s were also identified in other studies. For instance, Hagemann et al. (2019) showed generally decreasing trends of several organic compounds in Djerdap lake sediments in Serbia since 1972. A very similar PCB emission profile to the one detected for the Urft reservoir was found in a Swiss lake (Zennegg et al., 2007). PCB contaminations were increased after 1940 reflecting the beginning of their industrial production showing the maxima in the early 1960s. This matches the development in the Urft reservoir having a period with an increased post-war production. Maximum levels of various organic pollutants were also detected in the Venice lagoon for this timespan (Frignani et al., 2005). In the following decades contamination was strongly decreasing in the Swiss lake and the Italian lagoon, which corresponds to the ban of PCBs, but also modernized wastewater treatment and environmental awareness. Franců et al. (2010) also detected decreasing contaminations of PCBs and PAHs towards the surface. In addition, they were able to determine flood events in the Brno reservoir in the Czech Republic. Micić et al. (2013) examined various organic pollutants in a reservoir of the Danube river and determined a similar emission profile for PAHs as obtained in this study. For LABs, they did not detect a specific emission trend, probably related to the low population density and developments in regional wastewater treatment. However, as they did not provide a dating of the sediments, no specific developments in the study area or on a political scale could be correlated.

Contrary to the PCB decline in the surface Urft sediments and other subaquatic sedimentary archives in Europe, no clear trend could be identified for drilling cores of the floodplains of the Wurm, which is a tributary of the Rur river. Buchty-Lemke et al. (2019) investigated three cores in a transect with a spacing of 20 m, but only the one adjacent to the river itself showed a pattern of decreasing contaminations with sampling depth. However, no clear correlation to specific emission periods could be obtained. Similarly, Heim et al. (2004) detected high concentrations of PCBs in the top layers of wetlands of the Lippe river in western Germany. In contrast to Buchty-Lemke et al. (2019), they also applied radiological dating approaches and were therefore able to date the uppermost layers to around 1990. Consequently, the high concentrations in these layers are not in complete contrast to the period of increased environmental awareness and protection, as ecological improvements and decreasing contamination trends in the Urft catchment were also particularly noticeable from the beginning of the 1990s. This highlights the need for detailed dating approaches combined with the reconstruction of

the organic as well as inorganic contamination within aquatic archives. Organic indicators in particular have proven to be successful, because they correlate with both catchment-specific as well as general developments (such as technological improvements in specific WWTPs, but also national bans and regulations). Generally, as the historical development of every catchment is quite specific, there is also always a need for individual studies such as from the Urft reservoir.

7.5 Conclusion

Based on the organic-geochemical investigation and the associated dating, it was possible to reconstruct the pollution history of the Urft catchment in the northern Eifel mountains. Emission sources could be identified and assigned, and the effectiveness of political regulations or catchment-specific closures and technological improvements (e.g., of different WWTPs) were recognizable in the contamination profiles. Generally, the substances showed decreasing concentrations towards the surface, which correlates with the period of increased environmental awareness and corresponding political regulations and measures in Germany since the 1970s. This decrease started even earlier for PAHs representing pyrogenically introduced substances, than for those that are mainly introduced by wastewater treatment plants. Another common feature for almost all substances was a maximum in contamination at the end of the 1970s/beginning of the 1980s, probably related to a malfunction or flood, which affected wastewater-related compounds of urban as well as industrial origin. Nevertheless, some organic compounds could not be correlated with specific emission sources and pathways and were accordingly not suitable for a distinct emission and pollution reconstruction.

8 Synthesis

This thesis provides a comprehensive assessment of the environmental behavior and fate of various organic pollutants in different compartments of the Rur river. The holistic investigation of the entire river course and corresponding emission profiles establish a framework with detailed conclusions on the structural diversity, relevant emission sources and pathways, (re)distribution processes, and the accumulation areas of a variety of compounds. A major focus was placed on flood events and the remobilization potential of accumulated pollutants, which is particularly relevant in the context of global warming and climate change. Altogether, the results illustrate the ubiquitous, but nevertheless varying pollution of our river systems. They form an essential basis for future monitoring measures and risk assessments regarding the endangerment of humans and nature (e.g., by determining accumulation points and long-term remobilization potentials). The holistic characterization of the emission situation of the Rur river can also be transferred to other river systems due to its morphological characteristics and historical contamination with diverse, but clearly definable and identifiable emission sources. Pollutant pathways could be clearly retraced, providing an important basis for studies of other aquatic systems.

The previously defined objectives and research questions (chapter 1.3) were pursued in all publications, and the main findings and results are summarized below to ultimately provide a conclusive, comprehensive assessment of the environmental fate of various organic pollutants:

1. *Qualitative determination of the structural diversity and quantification of organic pollutants as a basic organic-geochemical characterization of the catchment system*

Qualitative non-target screening and quantitative analysis were applied to all investigated samples and thus in all studies covering the different compartments of the Rur river (chapters 4 to 7). The main focus was on the anthropogenically induced pollution and therefore mainly on xenobiotics. Generally, the diversity of substances detected in the aqueous compartment was particularly high, covering pollutant groups such as pharmaceuticals, constituents of personal care products, pesticides and biocides, and various industrial compounds (e.g., plasticizers or other technical additives). A very detailed assessment of the structural diversity of mostly hydrophilic contaminants was performed in chapter 4. However, for the sedimentary compartments, the identified and quantified pollutants also originated from different types of emission sources. Several compounds were of urban or industrial origin and were mainly introduced into the river system via the effluents of WWTPs or discharges of industrial facilities. Furthermore, several petrogenic contaminants have been found. They can occur naturally, but may also originate from anthropogenic or urban emissions such as oil heating systems or

vehicles. In most cases, the concentrations, amounts, and loads were comparable to other German and European rivers. However, as some compounds have rarely been identified as environmental contaminants so far (e.g., AIBN/TMSN), data for other river systems are often lacking. This is similar regarding the knowledge on possible adverse effects. A detailed ecotoxicological assessment and evaluation is missing for most of the identified substances. This is in particular true for the very diverse contaminants in the aqueous compartment. In addition, the effects and interactions of substances within the “pollution cocktail” detected for the Rur river may lead to unknown and complex environmental consequences. Nonetheless, the qualitative and quantitative assessment of a broad spectrum of contaminants forms the basis for a detailed assessment of the distinct environmental behaviors and fates, which are evaluated in the upcoming research objectives.

2. Distribution and dispersion of organic pollutants in the different compartments of a dynamic river system

The distribution and dispersion of organic pollutants, and thus spatial effects, have also been assessed in each study from chapter 4 to 7. Even though the focus and main objectives of the investigations are different, the emission respectively depth profiles allow the identification of emission sources and pathways. Chapters 4, 5 and 7 dealt with the contamination and distribution processes of or in a specific compartment within the river system of the Rur. The aqueous compartment is generally very dynamic, and the determined pollutant loads were higher in the urbanized northern part of the catchment. This was particularly the case downstream of WWTPs, which mostly treat both municipal and industrial wastewater. Major emissions were attributed to the paper industry in the middle to northern part of the Rur catchment (mainly around Düren and Jülich). A direct comparison between the river water and the relatively easily mobilized riverbed sediments was done in chapter 6. WWTPs and their associated influent-origins were also mainly responsible for the contamination of this particulate compartment. In addition to WWTP discharges, (in)direct industrial discharges and the pollutant introduction via surface runoff and flooding were also highly relevant for the contamination of the riverbed. For both compartments, the highest contamination occurred downstream of Düren and the specific WWTP (Düren-Merken) and remained at an almost constant level till the confluence of the Rur and the superior Meuse river. This indicates a close connection of the pollutant transport in both river phases and thus within the immediate river corridor. The connection was only decoupled due to major anthropogenic measures or constructions, such as the dam system in the Eifel region. However, the contamination in this region is generally lower than in the northern, urban part, corresponding to the smaller urban and industrial agglomerations. An exception to the clear emission patterns was observed for petrogenic or pyrogenic contaminants (especially PAHs and geohopanes).

PAH diagnostic ratios mainly indicated a pyrogenic origin of hydrocarbons for all sedimentary matrices investigated. Accordingly, the distribution could not be correlated to specific emission sources but shows a ubiquitous appearance, probably of diffuse origin. Similarly, geohopanes were present almost evenly distributed along the entire river course.

3. Identification of potential accumulation points and sinks, including the effect of remobilization due to exceptional events such as floods

The identification of relevant accumulation points and sinks is also closely related to the general distribution processes and tendencies mentioned in the previous research objective. A few contaminants of the aqueous compartment showed clear degradation tendencies after their release into the aquatic environment. However, the overall contamination level remained high till the confluence with the Meuse, indicating a clear contribution to the pollution of the superior river. As mentioned before, the pollution transport of compounds in water and riverbed sediments is closely connected. Nevertheless, potential accumulation areas for sediment-associated contaminants could be identified. Consequently, this led to a disconnection of the dynamic contaminant transport within the two compartments (cf. chapter 6). Primarily, anthropogenic regulations and measures, in particular the dam system in the Eifel, caused a retention of sedimentary material and thus also of associated lipophilic pollutants. The suitability of the Urft reservoir as an environmental archive and accordingly the high relevance of its sediments as a subaquatic sink have also been proven and demonstrated in chapter 7. A continuous deposition of fine-grained sediments was ideal for the reconstruction of the pollution history of the catchment. Furthermore, floodplains areas have been identified as important accumulation areas and sinks for organic contaminants (cf. chapter 5). The determined pollutants originated mainly from the Rur tributaries, whereby the dimension of the flood was also reflected in the amounts detected. At this point, the effect of the dam system was also recognizable in the downstream floodplains, which partly showed a remobilization of pollutants due to the extreme flood event in the summer of 2021. In general, the regular monitoring-like analysis of the riverbed accumulations in chapter 6 has shown that after this extreme summer flood, the contamination in the riverbed was much higher than on the investigated floodplains. Instead of a washout effect, the pollutants accumulated in the river itself, which is highly relevant for flood-related risk assessment. Accordingly, the riverbed must also be defined as an important accumulation area, particularly in anthropogenically influenced or (re)naturalized areas (e.g., after weirs or in strongly meandering sections leading to a less dynamic flow behavior and the corresponding sedimentation of particulate matter).

4. Determination of temporal differences in the contamination situation, including the reconstruction of the pollution history

A long-term assessment of the aqueous compartment was possible due to two sampling campaigns of the Rur river water prior to the investigation period of this thesis (chapter 4). They were conducted in 2004 and 2015, covering the entire river course. Generally, decreased loads and concentrations of various compounds were detected in the timespan between 2004 and 2020, while only a few substances showed increasing tendencies. The composition of the water contamination has changed slightly, but the high diversity has remained. This indicates the continuous need for research on organic pollution in river systems, as new emerging contaminants are regularly detected in our environment. Long-term pollution trends could also be identified for the sedimentary compartment within the Urft reservoir as an environmental archive (chapter 7). The depth profile of a drilling core could be successfully correlated with historical site-specific and general political processes and developments. Thus, a reconstruction of the pollution history of the Eifel catchment area was possible, showing a period of increased environmental awareness, ecological and technical improvements since the 1970s. Besides the evaluation of long-term differences, short-term developments have been identified due to the regular bi-annual sampling campaigns for both the river water and the riverbed (described in chapter 6). Particularly for the aqueous phase, seasonal effects have been observed as a result of consumption behaviors and patterns, different removal efficiencies in WWTPs, and varying degradation pathways and rates in the riverine environment. In contrast, seasonality does not have a major effect on the pollution of the sedimentary phase. Instead, the transport and accumulation of sedimentary material and associated contaminants in the riverbed and on floodplains is determined by exceptional events such as the extreme flood of July 2021.

5. Comprehensive assessment of the dynamic and long-term impact potential of organic substances in a complex river system and its different compartments

A comprehensive assessment of the Rur river contamination is based on all previous research objectives. It combines the aforementioned results of chapters 4 to 7 to achieve a holistic understanding of the introduction, fate, and behavior of various organic pollutants in the aquatic environment. The combined results are also visualized in Figure 8.1. Generally, the fate of organic pollutants starts with their introduction into the riverine environment. The main emission sources in the Rur catchment are mostly WWTPs and the direct discharge of treated industrial and municipal wastewater effluents. Especially for lipophilic, sediment-bound pollutants, indirect introductions and inputs from surface run-off, e.g., from industrial facilities, streets, and other urban areas, have also been identified. The introduction of petrogenic contaminants, such as geohopanes or PAHs, is more

diffuse and occurs ubiquitously, so no specific emission sources could be identified. Once the pollutants have entered the riverine environment, they enrich and accumulate in their preferred aquatic compartment, depending mainly on their physicochemical properties. A particularly high diversity of contaminants was found in the river water, but various pollutant groups were also detected within the different sedimentary matrices and accumulation areas. Even though the aqueous compartment is more dynamic than the particulate phase of the riverbed, the transport of both hydrophilic and lipophilic pollutants within the river itself is closely connected. The connection is only disrupted by major anthropogenic measures such as dams and weirs, which create large artificial sedimentation areas and thus pollutant sinks. In general, the transport of lipophilic pollutants depends on the fluvial transport of sedimentary material (in suspension or as bed material load). Anthropogenic measures and partly (re)naturalized areas (e.g., close to Floßdorf), significantly reduce the flow dynamics and turbulence, so that fine-grained material can settle and accumulate in these areas. Due to the increased specific surface area and the higher adsorption capacity, fine sediments are especially contaminated with organic pollutants. Accordingly, these areas represent important pollutant sinks, as it was also demonstrated for the Urft reservoir. Apart from these regular sinks within the river corridor, a major part of the total contamination is transported to the superior river system. However, the situation is slightly different for extreme events such as the summer flood of 2021. This event and the associated pollutant distribution demonstrated the relevance of meso-scaled river systems, as the contaminants introduced in the tributary catchments were ultimately deposited on the Rur floodplains as well as within the Rur riverbed. At this point, the contribution of floods to riverbed contamination has been clearly underestimated so far and needs to be considered in risk assessments, especially as flood events are likely to become more frequent in the coming decades (e.g., Hirabayashi 2013, Kundzewicz 2013, Wilby 2012).

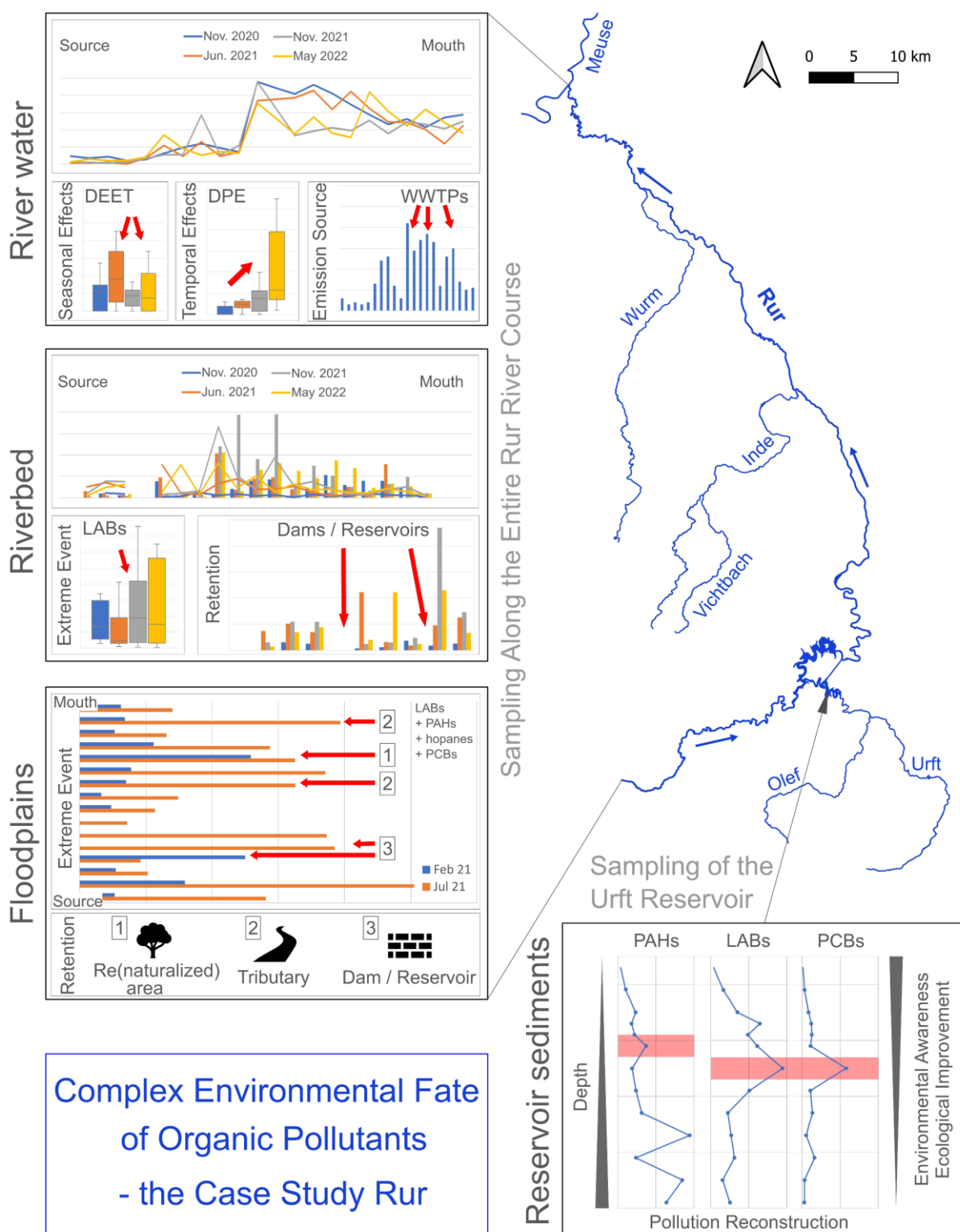


Figure 8.1 Comprehensive assessment of the complex environmental fate and behavior of organic pollutants in the Rur catchment by the combined analysis of different compartments (river water, riverbed, floodplains, reservoir sediments) to determine emission sources, environmental pathways, accumulation points, spatial and temporal effects as well as limiting factors on transport and distribution.

9 Outlook and Conclusion

Although a holistic assessment of the complex environmental fate of different organic pollutants was possible within the framework of this thesis, clear emission and introduction pathways and potential sinks could not be identified for each detected organic compound. Accordingly, further research should address specific compartments such as the porewater of the saturated riverbed and adjacent soils and sediments (e.g., on floodplains), the connection to groundwater bodies, or the hyporheic zone. Generally, in recent years, ecohydrological interfaces as dynamic transition zones at ecosystem boundaries have been identified as hotspots of ecological, biogeochemical, and hydrological processes and should therefore be the focus of future research (Krause et al., 2017). Furthermore, the suspended particulate matter has only been roughly investigated within this project, while the actual effects on the biota in the Rur catchment area have not been determined so far. For this reason, there is a need for further interdisciplinary analysis, including joint sampling campaigns and combined analysis of geochemical, geomorphological, hydrological, ecotoxicological, and other approaches. In general, past and future anthropogenic emissions and measures will continue to affect our river systems, highlighting the need for a thorough understanding of pollutant behaviors and fates. This also includes the consideration of non-extractable or bound residues, as they are also highly relevant for the assessment of temporary or permanent storage of different contaminants. Further on, continuous monitoring campaigns are necessary to determine changes within the contamination situation and to analyze significant temporal as well as spatial or limiting effects, as it has already been done in the framework of this study over a period of about 2 years with regular and event-related sampling. This is also important to evaluate the efficiency of political or technical interventions. For example, in this project such an evaluation was carried out for a period of about 50 years using the Urft reservoir as a sedimentary archive.

The aforementioned need for research also applies to the subordinate and superordinate river systems and the mill ditches associated with the Rur river. The latter were, and in some cases still are, of great importance for the water supply and wastewater discharge of the diverse industry in the catchment area. Accordingly, they also represent potential pollutant sinks. For this reason, the identification of indicator substances is of special importance in order to trace the contamination and the corresponding transport routes across river systems and dimensions. This project has shown the close connection between the transport of pollutants in the river water, but also in the riverbed into the superior Meuse river. In particular, the paper industry has created specific “fingerprint” contamination profiles within the Rur that should also be assessed for the Meuse river.

Besides the need for further research and monitoring to specify risks and hazards to humans and the environment, the immediate reduction and mitigation of pollutants in the aquatic environment should be an overall aim. Particularly, wastewater treatment plants are a good point of action to improve the pollution situation in the Rur catchment. They have been identified as the main emitters of contaminants for the aqueous as well as the particulate compartments. As in many other European countries, most of them rely on three treatment steps (mechanical, biological, and chemical stage of treatment) (Reineke & Schlömann, 2023). However, an additional step or process, such as the ozonation for the WWTP Aachen-Soers, could lead to a significant improvement and reduction of the pollutant concentrations or loads in the treated wastewater discharges. Indeed, this additional treatment step was clearly recognizable when looking at the aqueous pollution in the lower course of the Rur (after the confluence with the Wurm tributary, which receives the effluents of the WWTP Aachen-Soers). Thus, the impact on other compartments should also be investigated in more detail. In general, industrial substances such as those from paper production and processing have a major influence on the pollution situation of the Rur river. Therefore, direct (local) measures should also be considered for industrial facilities or the usage of industrial substances. Possible actions could be to minimize the corresponding consumption or to prevent the substances from leaking and being released by means of a closed water supply and/or wastewater cycle.

Overall, river systems will always be closely connected to anthropogenic life and thus affected by structural measures (e.g., dam construction), shipping and navigation, and various demands such as the supply of drinking and process water or the discharge of treated wastewaters. For this reason, it is of great importance to understand the anthropogenic contribution to the pollution of aquatic systems. This doctoral thesis enabled a comprehensive assessment of the organic, mostly anthropogenically induced contamination in the catchment of the Rur river. The fate and behavior of a variety of substances could be determined and important emission sources as well as accumulation sinks and their associated remobilization potential could be defined. Subsequently, the need for further detailed and “hot spot” research in the Rur catchment and aquatic systems in general was specified, as the results can also be easily transferred to other river systems. Accordingly, the main findings and results are also of major relevance to establish risk appraisals on aquatic pollution.

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Appendix

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Appendix to Chapter 1

Political decisions and regulations regarding the environmental law in Germany

Table A1 Detailed overview on the political decisions and regulations regarding the environmental law in Germany based on information of the corresponding, following reference list. The year determines the date when the decision/law came into force.

Year*	Political decision or act	Key content	Additional information (e.g., on reforms)
1957	Federal Water Act (Wasserhaushaltsgesetz – WHG)	- Regulates the management of water bodies - legal basis for transboundary, sustainable water management	2010 (large reform) - transposes the EU Water Framework Directive, EU Floods Directive, the Marine Strategy Framework Directive and the provisions of the Industrial Emissions Directive into German national law
1972	National Waste Disposal Act (Abfallbeseitigungsgesetz – ABfG)	- first uniform national waste disposal law - disposal fundamentally a public task	1996 (large reform) - Closed Substance Cycle and Waste Management Act (Kreislaufwirtschafts- und Abfallgesetz – KrW-/AbfG) - extends the policies enclosed in the Packaging Ordinance - Producer responsibility 2012 (large reform) - Waste Management Act (Kreislaufwirtschaftsgesetz – KrWG) - transposes EU Waste Directive into German law - aims on the combination and tightening of resource, climate and environmental protection regulations - five-step hierarchy (prevention; preparation for recycling; recycling; other types of recovery; disposal)
1972	Foundation of the Council of Environmental Experts (Sachverständigenrat für Umweltfragen – SRU)	- assesses the environmental conditions in Germany - supports the decision-making of all environmental policy stakeholders - independent and interdisciplinary	
1974	Federal Immission Control Act (Bundesimmissionsschutzgesetz – BImSchG)	- core of current immission control legislation - main purpose on air pollution control and noise abatement	2002 (large reform) - reinforcement in the form of numerous statutory instruments and two significant administrative provisions ○ Technical Instructions on Air Quality Control (TA Luft)

Year*	Political decision or act	Key content	Additional information (e.g., on reforms)
		- base for continuous emission monitoring	○ Technical Instructions on Noise Abatement (TA Lärm) - Implements important legal developments from European law (nowadays, e.g., EC directive on Industrial Emissions, EU air quality legislation and EU directives for noise pollution control)
1974	Foundation of the German Environment Agency (Umweltbundesamt – UBA)	- first national environmental agency - first tasks: ○ non-ministerial tasks in the field of environmental protection ○ establishment of central documentation ○ coordination of environmental research and related institutions	
1977	Federal Nature Conservation Act (Bundesnaturschutzgesetz – BNatSchG)	- legal basis for a comprehensive approach to nature conservation and landscape protection - mechanisms towards the integration in land planning - provisions on the classification and management of protected areas	2010 (large reform) - rules with a predominantly direct effect on federal states and their own nature conservation laws
1977	Fertilizer Act (Düngemittelgesetz – DüMG)	- requirements for the placing on the market and application of fertilisers, soil improvers, plant strengtheners and growing media - aims at ○ ensuring the nutrition of crops ○ preserving or sustainably improving soil fertility	2009 (replacement of the DüMG) - Düngegesetz (DüngG) - Definition of soil fertility as a key objective of fertilization - connected regulation: fertilizer regulation (Düngemittelverordnung – DüMV) ○ usage criteria in accordance with good agricultural practice for fertilizer use - connected regulation: manure transfer regulation (Wirtschaftsdüngerverbringungsverordnung – WDüngV)

Year*	Political decision or act	Key content	Additional information (e.g., on reforms)
		○ preventing or averting risks to human health, animal health and the ecosystem ○ ensuring a sustainable and resource-efficient handling of nutrients in agricultural production ○ transposing or implementing legal acts of the European Community or the European Union	
1990	Environmental Impact Assessment Act (Gesetz über die Umweltverträglichkeitsprüfung – UVPG)	- Environmental policy instrument of environmental precaution - Environmental impact assessment for projects that may have a significant impact on the environment due to their nature, size or location	- Implements important legal developments from European law into German law ○ Directive (85/337/EEC) on the assessment of the effects of certain public and private projects on the environment ○ Directive 2001/42/EC on the assessment of the effects of certain plans and programmes on the environment ○ Directive 2011/92/EU on the assessment of the effects of certain public and private projects on the environment
1992	Start of the development of a uniform environmental legislation		
1995	Environmental Audit Act (Umweltauditgesetz – UAG)	- implements key parts of the European Eco-Management and Audit Scheme (EMAS) ○ Independent, reliable and competent environmental	- Implements important legal developments from European law into German law ○ Regulation 1221/2009 on the voluntary participation by organisations in a Community eco-management and audit scheme (EMAS), repealing Regulation (EC) 761/2001 and Commission Decisions

Year*	Political decision or act	Key content	Additional information (e.g., on reforms)
		- verifiers and organisations ○ effective supervision of accredited environmental verifiers and organisations ○ Register of audited organisations	2001/681/EC and 2006/193/EC
1999	Ecological Tax Reform Act (Gesetz zum Einstieg in die ökologische Steuerreform)	- incremental increase in taxes on fuel and energy - tools for tackling ecological challenges	
2000	Renewable Energy Sources Act (Erneuerbare-Energien Gesetz – EEG)	- centerpiece of the legislative framework supporting renewable energies - preferential feed-in of electricity from renewable sources - originally feed-in tariff-based support system	2004, 2009, 2012, 2014, 2017, 2021 (several amendments and reforms – regular revision) 2023 (large reform) - foundations for Germany to become climate neutral - consistent and much faster expansion in order to increase the share of gross electricity consumption that is covered by renewables
2004	Greenhouse Gas Emissions Trading Act (Treibhausgas-Emissionshandels-gesetz – TEHG)	- Legal basis for trading greenhouse gas emission allowances in an EU-wide emissions trading system - Contributing to the cost-effective reduction of greenhouse gases for global climate protection - Implements Directive 2003/87/EC establishing a scheme for greenhouse gas emission allowance trading within the Community into German law	2011 (large reform) - Act on the adaptation of the legal basis for the further development of emissions trading - Inclusion of air transportation
2005	Electrical and Electronic Equipment Act	- manages the putting on the market, recovery, and recycling of	2015 (large reform) - Implements the new Directive 2011/65/EU on the restriction of the use of certain hazardous substances

Year*	Political decision or act	Key content	Additional information (e.g., on reforms)
	(Elektro- und Elektronikgerätegesetz – ElektroG)	electrical and electronic equipment - Major aims ○ protect health and the environment against harmful substances from electrical and electronic equipment ○ reduce the amount of waste through recovery or recycling - Implements Directives 2002/96/EC on waste electrical and electronic equipment (WEEE) and 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment into German law	in electrical and electronic equipment - Producers (also importers, exporters and distributors) with an increased responsibility for the entire life cycle - Further increase of the collection and recovery rates and easier registration procedures - Coverage of photovoltaic modules
2007	Environmental Damage Act (Umweltschadensgesetz – USchadG)	- Standardised requirements for the remediation of environmental damage caused by accidents - mainly serves the purpose of ensuring that no degradation of environmental goods and services takes place - Implements Directive 2004/35/CE on environmental liability with regard to the prevention and remedying of environmental damage in German law	

*Year of coming into force

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Appendix to Chapter 4

“Structural Diversity of Organic Contaminants in a Meso-Scaled River System”

Table A2 Characteristic ions used for quantification and recoveries from high-purity water (n=4).

No.	Compounds	Characteristic ions [m/z]	Reference compound used for quantification (if different)	Recovery rate [%]
	Pharmaceuticals			
1	Carbamazepine	193, 236		107 ± 7
2	Oxcarbazepine	180	Carbamazepine	107 ± 7
3	Caffeine	109, 194		23 ± 1
4	Chlorobutanol	59, 125		76 ± 20
5	Iminostilbene	165, 193		109 ± 13
6	Lidocaine	86		62 ± 12
7	Acetylsalicylic acid	120, 152	Lidocaine	22 ± 4
8	Diclofenac	214, 242		90 ± 36
9	Tocopheryl acetate	165, 430		75 ± 20
	Personal care products			
10	N,N,N',N'-Tetraacetylenethylenediamine, TAED	72, 127	Tocopheryl acetate	75 ± 20
11	4-Methoxycinnamic acid 2-ethylhexylester	178	Tocopheryl acetate	75 ± 20
12	Drometrizole	225		106 ± 10
13	Galaxolide	243, 258		94 ± 7
14	Tonalide	243, 258		109 ± 6
15	4-Oxoisophorone	96, 152		60 ± 7
16	Lilial	189	4-Oxoisophorone	60 ± 7
17	Viridine	75, 135		80 ± 15
18	Dihydromethyljasmonate	83, 153, 156		100 ± 4
19	Cineol	81, 108		96 ± 20
20	Coumarin	118, 146		64 ± 4
21	4-tert-Butylcyclohexanone	98, 154		86 ± 7
22	Benzophenone	105, 182		102 ± 4
23	Isopropylaurate	200	Isopropylmyristate	95 ± 12
24	Isopropylpalmitate	256	Isopropylmyristate	95 ± 12
25	Methyl dehydroabietate	239	Abietic acid	Not determined
	Pesticides and biocides			
26	N,N-Diethyltoluamide, DEET	119, 190		87 ± 17
27	4,4'-Dichlorobenzophenone, DBP	139, 141		47 ± 9

No.	Compounds	Characteristic ions [m/z]	Reference compound used for quantification (if different)	Recovery rate [%]
	Technical additives, plasticizers and other industrial compounds			
28	Di-iso-propylnaphthalenes, DIPN	197, 212		88 ± 2
29	N-Butylbenzenesulfonamide, NBBS	141, 170		102 ± 15
30	2,4,4-Trimethylpentane-1,3-dioldi-iso-butyrate, TXIB	111, 159		93 ± 7
31	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	109, 151		27 ± 4
32	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	99, 105		83 ± 24
33	Triethylcitrate	115, 203		92 ± 2
34	Acetyl tributylcitrate	185, 259		131 ± 2
35	Triacetin	43, 145		94 ± 9
36	Triethylphosphate	155		44 ± 7
37	Tributylphosphate	155		52 ± 6
38	Tris(2-chloroethyl)phosphate, TCEP	249, 251		92 ± 14
39	Tris(chloropropyl)phosphate, TCPP	201, 277		102 ± 4
40	Triphenylphosphate	170, 326		113 ± 12
41	Triphenylphosphine oxide	199, 277		62 ± 10
42	Dimethyl phthalate	163		113 ± 31
43	Diethyl phthalate	149		54 ± 4
44	Di-iso-butyl phthalate	149		125 ± 5
45	Di-n-butyl phthalate	149		125 ± 5
46	Benzyl butyl phthalate	149		49 ± 25
47	Bis(2-ethylhexyl) phthalate, DEHP	149		133 ± 25
48	2,2-Dimethoxy-1,2-diphenylacetophenone, DMPA	151		88 ± 23
49	Diphenoxyethane	121, 214		94 ± 11
	Miscellaneous contaminants			
	Halogenated compounds			
50	Dichloroaniline	161		103 ± 8
51	1,1,2,2-Tetrachloroethane	83, 85		56 ± 6
52	4-Bromoanisole	186, 188		66 ± 6
53	2,4-Dibromoanisole	223, 266		102 ± 5
54	2,4,6-Tribromoanisole	344, 346		96 ± 5
	S-containing compounds			
55	Diphenylsulfone	125, 218		52 ± 7
56	Methylphenylsulfone	141, 156		72 ± 4
57	Benzothiazole	108, 135		75 ± 19
58	2-Methylthiobenzothiazole	148, 181		76 ± 11
59	N-Phenylbenzenesulfonamide	92, 233	NBBS	102 ± 15
60	N-Ethyl-o-toluenesulfonamide	155	NBBS	102 ± 15

No.	Compounds	Characteristic ions [m/z]	Reference compound used for quantification (if different)	Recovery rate [%]
61	N-Ethyl-p-toluenesulfonamide	155	NBBS	102 ± 15
62	2-Aminodiphenylsulfone	168, 233	NBBS	102 ± 15
	N-containing compounds			
63	2-Methylbenzotriazole	133	Quinoline	67 ± 10
64	Quinoline	102, 129		67 ± 10
65	Quinoxaline	130		68 ± 3
66	2,3-Diethyl-2,3-dimethylsuccinonitrile	83, 153	Iminostilbene	109 ± 13
67	Phenylisocyanate	91, 119		66 ± 6
68	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile (TMSN)	41, 69		87 ± 7
69	N,N-Dibutylformamide	72, 114		41 ± 7
	O-containing compounds			
70	2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone	205, 220	Ionole	107 ± 11
71	Butylated hydroxytoluene, Ionole	205, 220		107 ± 11
72	1,3,3-Trimethyloxindole	117, 160	Indole	87 ± 7

Table A3 River runoff data from several gauges along the Rur river which correspond to the sampling sites.

Site no.	Gauge	River runoff [m ³ /s]		
		November 2020	March 2015	November 2004 December 2004
R1	Monschau	1.7	1.3	1.5
R2	Monschau	1.7	1.3	2.5
R3	Monschau	1.7	1.3	3.2
R4	Dedenborn	2.2	2.5	4.0
R5	Dedenborn/Heimbach	3.0	3.0	8.3
R6	Heimbach	5.0	5.0	12.6
R7	Zerkall	6.2	7.2	13.8
R8	Zerkall	6.2	7.2	13.8
R9	Obermaubach	5.0	7.5	14.5
R10	Obermaubach	5.0	7.5	15.1
R11	Obermaubach/Jülich	7.0	12.0	15.1
R12	Jülich	9.4	16.6	23.7
R13	Jülich	9.4	16.6	23.7
R14	Jülich/Linnich	9.0	15.2	22.8
R15	Jülich/Linnich	9.0	15.2	22.8
R16	Jülich/Linnich	9.0	15.2	22.8
R17	Jülich/Linnich	9.0	15.2	22.8
R18	Stah	8.8	13.6	27.3
R19	Stah	8.8	13.6	27.3
R20	Stah	8.8	13.6	27.3
R21	Stah	8.8	13.6	27.3

Table A4 Concentrations [ng/L] of organic compounds detected in Rur river water samples (taken in November 2020, March 2015, and November/December 2004).

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
	Pharmaceuticals																					
1	Carbamazepine	2020	n.d.	n.d.	n.d.	n.d.	< 5	5	10	< 5	6	80	50	70	70	80	70	50	80	160	80	70
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8	50	9	40	80	70	80	n.a.	80	50	120	130	190	170
		2004	n.d.	10	7	n.d.	50	100	60	70	40	10	n.a.	7	50	n.a.	50	50	n.a.	70	40	400
2	Oxcarbazepine	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	8	10	6	6	6	8	7	8	6	< 5
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.
3	Caffeine	2020	n.d.	n.d.	20	70	40	40	40	30	40	150	140	130	100	70	60	80	100	70	60	80
		2015	40	10	9	< 5	9	30	10	50	< 5	20	30	20	20	n.a.	30	30	30	70	50	50
		2004	n.d.	n.d.	< 5	n.d.	40	40	40	40	40	n.a.	n.a.	40	40	n.a.	40	90	n.a.	90	90	170
4	Chlorobutanol	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	< 5	< 5	n.d.	< 5	20	< 5	< 5	40	< 5	n.a.	n.a.	490	1600	n.a.	380	600	n.a.	40	620	160
5	Iminostilbene	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	n.a.	n.a.	20	< 5	n.a.	< 5	30	n.a.	30	10	20
5	Lidocaine	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	210	80	90	90	100	70	60	110	130	100	90
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	10	10	20	10	10	n.a.	n.a.	10	20	n.a.	40	40	n.a.	110	90	110
7	Acetylsalicylic acid	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	< 5	< 5	n.a.	< 5	< 5	n.a.	< 5	< 5	n.d.
8	Diclofenac	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	< 5	< 5	n.a.	< 5	< 5	n.d.

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
9	Tocopheryl acetate	2020	80	180	6	250	10	5	30	<5	<5	<5	<5	<5	20	8	<5	8	20	n.d.	n.d.	8	
		2015	n.d.	6	n.d.	n.d.	<5	n.d.	n.d.	20	<5	7	<5	6	6	n.a.	<5	n.d.	n.d.	<5	n.d.	<5	
		2004	20	70	n.d.	70	n.d.	160	n.d.	10	40	n.a.	n.a.	170	20	n.a.	80	n.d.	n.a.	40	10	20	
	Personal care products																						
10	N,N,N',N'- Tetraacetylenediamine, TAED	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	60	40	50	60	50	50	30	30	30	40	50	80	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	90	190	70	200	160	90	
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	80	20	n.a.	70	50	n.a.	50	60	n.d.	
11	4-Methoxydinamic acid 2- ethylhexylester	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	<5	<5	<5	n.d.	n.d.	<5	n.d.	
		2015	n.d.	6	n.d.	n.d.	<5	n.d.	8	n.d.	n.d.	<5	<5	10	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2004	130	80	40	80	160	110	30	40	40	20	n.a.	n.a.	220	170	n.a.	110	40	n.a.	50	20	40
12	Drometrizole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	50	
13	Galaxolide	2020	8	9	<5	10	<5	6	7	n.d.	6	<5	40	40	40	50	40	50	70	70	70	70	
		2015	7	10	<5	<5	6	10	20	20	40	20	30	40	30	80	n.a.	70	90	80	100	60	
		2004	50	20	10	30	10	40	50	40	20	20	n.a.	n.a.	90	90	n.a.	130	100	n.a.	170	120	110
14	Tonalide	2020	<5	<5	n.d.	<5	<5	<5	<5	n.d.	<5	<5	<5	<5	<5	<5	<5	5	5	6	<5	<5	
		2015	<5	5	<5	<5	<5	<5	<5	<5	5	<5	5	<5	9	n.a.	7	6	6	9	6	7	
		2004	<5	<5	<5	<5	<5	10	10	<5	<5	n.a.	n.a.	10	10	n.a.	20	10	n.a.	30	20	10	
15	4-Oxaisophorone	2020	10	10	6	9	<5	<5	5	5	<5	6	9	20	10	10	6	10	9	5	10	20	
		2015	20	7	5	7	10	5	<5	10	9	9	9	20	10	20	n.a.	10	40	50	40	30	30
		2004	70	90	120	20	90	30	90	30	30	70	n.a.	n.a.	50	50	n.a.	50	100	n.a.	70	50	50
16	Lilial	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	<5	n.d.	n.d.	n.d.	n.d.	<5	
		2015	n.d.	9	n.d.	n.d.	7	5	5	7	7	5	10	n.d.	n.d.	n.a.	30	n.d.	n.d.	20	n.d.	n.d.	
		2004	10	10	10	10	<5	10	<5	<5	<5	<5	n.a.	n.a.	<5	<5	n.a.	10	5	n.a.	10	10	n.d.

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
18	Dihydromethyljasmonate	2020	40	30	30	20	10	20	10	6	10	40	40	30	20	20	20	20	20	20	10	10	20
		2015	30	40	30	20	30	20	20	30	<5	20	30	20	20	70	n.a.	70	50	30	40	30	30
		2004	n.d.	n.d.	6	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.a.	n.a.	6	n.d.	n.d.	n.a.	6	n.d.	n.a.	10	n.d.	20
19	Cineol	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2015	n.d.	5	<5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	40	n.d.	n.d.	n.d.
		2004	<5	<5	n.d.	10	<5	<5	<5	<5	<5	<5	n.a.	n.a.	<5	<5	n.a.	<5	<5	n.a.	n.d.	<5	160
20	Coumarin	2020	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	5	30	30	20	20	20	20	20	20	20	10	20	20	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	10	7	5	n.a.	8	9	10	8	5	8	
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.
21	4-tert-Butylcyclohexanone	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6	5	5	5	6	9	10	10	8	<5	7	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8	n.d.	n.d.	n.d.	n.a.	n.a.	<5	<5	n.a.	<5	20	n.a.	7	8	6
22	Benzophenone	2020	<5	<5	<5	6	<5	<5	5	<5	<5	30	10	20	10	20	20	20	10	10	10	10	
		2015	n.d.	40	10	20	20	50	60	60	80	20	100	60	10	80	n.a.	90	10	6	20	9	10
		2004	30	10	10	20	20	280	10	30	70	30	n.a.	n.a.	20	20	n.a.	90	30	n.a.	40	20	50
23	Isopropylaurate	2020	170	170	200	110	90	170	200	260	140	60	300	140	330	220	200	90	160	150	110	80	100
		2015	3800	1100	4100	3600	1300	7400	1400	5100	3200	1100	2200	3800	16900	7100	1700	15000	15000	16200	16200	12700	9500
		2004	20	30	20	250	30	30	30	500	40	20	80	30	30	30	20	30	20	20	n.a.	30	20
24	Isopropylpalmitate	2020	40	40	40	30	10	10	20	20	40	10	70	30	60	50	30	20	20	10	20	20	20
		2015	70	1700	80	50	90	40	3800	50	1200	210	780	70	380	100	40	110	110	410	60	40	n.d.
		2004	160	130	30	150	180	370	40	80	90	90	360	330	280	50	120	80	50	n.a.	120	80	80
25	Methyl dehydroabietate	2020	1200	850	2000	850	1100	1100	1900	2400	2000	610	3000	1800	3800	1400	980	540	690	950	590	280	880
		2015	710	1200	5500	5400	430	190	1500	430	2000	290	780	830	17700	800	n.a.	440	4900	4600	1300	1100	1300
		2004	280	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.d.

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
	Pesticides and biocides																					
26	N,N-Diethyltoluamide, DEET	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	20	20	20	20	20	10	20	20	20	20
		2015	n.d.	<5	n.d.	n.d.	<5	n.d.	<5	6	<5	<5	5	<5	7	n.a.	7	9	7	9	10	8
		2004	n.d.	<5	n.d.	<5	<5	<5	<5	<5	<5	n.a.	n.a.	<5	10	n.a.	<5	<5	n.a.	10	10	20
27	4,4'-Dichlorobenzophenone, DBP	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	180	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	240	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.
	Technical additives, plasticizers and other industrial compounds																					
28	Di-iso-propyl naphthalenes, DIPN	2020	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	n.d.	n.d.	n.d.
		2015	n.d.	390	30	40	30	20	n.d.	110	30	50	30	70	60	n.a.	50	60	80	70	n.d.	n.d.
		2004	10	10	10	30	30	10	10	10	20	n.a.	n.a.	20	20	n.a.	20	10	n.a.	20	10	20
29	N-Butylbenzenesulfonamide, NBBS	2020	n.d.	n.d.	6	20	6	5	7	7	<5	<5	110	50	60	50	40	30	40	40	40	40
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10	<5	<5	6	<5	7	n.a.	5	10	n.d.	n.d.	5
		2004	n.d.	20	10	<5	10	10	10	10	10	n.a.	n.a.	40	20	n.a.	30	30	n.a.	40	40	50
30	2,4,4-Tri methyl pentane-1,3-dioldi-iso-butylate, TXIB	2020	40	20	30	20	20	30	50	50	30	10	70	40	40	50	40	20	30	40	20	20
		2015	3700	1700	510	1200	140	n.d.	40	70	190	70	90	70	180	290	n.a.	90	320	280	180	200
		2004	20	20	20	30	20	30	30	20	20	20	n.a.	n.a.	20	20	n.a.	10	10	n.a.	30	5
31	2,4,7,9-Tetra methyl -5-decyne-4,7-diol, TMDD	2020	130	120	160	40	20	20	30	60	20	40	23600	11900	11400	16100	15700	15200	10500	10900	10800	13400
		2015	710	330	610	550	120	100	100	140	820	380	16500	10900	7000	63900	n.a.	24600	17000	14200	9000	12100
		2004	10	10	20	10	10	20	10	10	50	10	n.a.	n.a.	1700	1500	n.a.	1600	1700	n.a.	1700	1200
32	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	2020	n.d.	20	110	30	6	n.d.	6	n.d.	<5	6	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	520	1100	80	70	470	210	870	990	150	300	800	850	40	1400	n.a.	1500	70	60	30	20
		2004	<5	n.d.	<5	<5	<5	<5	<5	<5	<5	<5	n.a.	n.a.	n.d.	<5	n.a.	<5	<5	n.a.	<5	<5

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
33	Triethylcitrate	2020	5	20	20	30	8	6	10	10	<5	5	120	60	60	60	50	30	30	40	40	50	60
		2015	n.d.	30	n.d.	n.d.	20	10	20	20	540	110	60	40	n.d.	100	n.a.	70	130	80	140	170	110
		2004	<5	<5	<5	<5	<5	n.d.	<5	<5	<5	n.a.	n.a.	40	10	n.a.	30	30	n.a.	30	40	10	
34	Acetyl tributylcitrate	2020	340	240	6	<5	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2015	n.d.	90	n.d.	n.d.	20	30	80	20	30	200	100	60	540	40	n.a.	130	90	90	40	70	50
		2004	<5	20	10	<5	30	40	<5	<5	<5	10	n.a.	n.a.	40	30	n.a.	30	<5	n.a.	10	<5	10
35	Triacetin	2020	11800	7600	9400	1600	2100	3800	4200	5900	6100	5500	5600	7500	8100	4800	2500	300	870	1500	360	1800	2400
		2015	1600	460	1000	1800	380	200	190	80	900	460	40	780	1000	810	n.a.	470	1900	1900	800	n.d.	380
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	100	n.d.	n.a.	n.d.	n.d.	n.d.
36	Triethylphosphate	2020	n.d.	n.d.	n.d.	10	10	<5	7	10	<5	6	220	110	110	160	160	120	110	140	140	170	210
		2015	n.d.	n.d.	n.d.	20	6	10	10	10	20	30	60	100	70	140	n.a.	70	210	170	180	100	140
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9	10	20	20	n.a.	n.a.	60	50	n.a.	50	90	n.a.	120	120	160
37	Tributylphosphate	2020	10	10	<5	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	20	10	8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	200	150	200	280	110	n.d.	100	460	200	860	660	2500	1500	n.a.	1400	4300	4200	1500	1200	740
		2004	120	10	60	120	130	240	160	80	150	170	n.a.	n.a.	440	460	n.a.	480	520	n.a.	730	220	430
38	Tris(2-chloroethyl)phosphate, TCEP	2020	n.d.	n.d.	n.d.	<5	<5	<5	<5	n.d.	n.d.	10	9	7	8	7	<5	<5	6	8	<5	9	10
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	70	5	<5	5	<5	<5	n.a.	<5	7	5	<5	6	<5
		2004	n.d.	n.d.	<5	<5	<5	9	9	9	9	9	n.a.	n.a.	20	20	n.a.	20	40	n.a.	40	40	60
39	Tris(chloropropyl)phosphate, TCP	2020	<5	<5	6	10	6	<5	7	8	<5	<5	110	60	60	60	60	50	40	50	50	60	60
		2015	30	50	n.d.	n.d.	n.d.	60	160	90	1200	270	260	210	140	320	n.a.	270	400	320	340	410	240
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	40	30	n.a.	6	7	n.a.	10	8	10
40	Triphenylphosphate	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	10	n.d.	n.d.	8	n.d.	n.d.	n.d.	160	60	80	30	20	10	n.a.	20	7	9	10	10	7
		2004	<5	<5	<5	<5	<5	10	<5	<5	<5	<5	n.a.	n.a.	5	5	n.a.	5	<5	n.a.	5	<5	<5

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
41	Triphenylphosphine oxide	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	260	250	130	150	170	110	60	100	80	70	70
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60	40	40	50	n.a.	30	20	50	60	60	50
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.
42	Dimethyl phthalate	2020	70	30	30	20	8	20	20	10	10	30	20	20	30	20	20	70	70	60	20	20
		2015	1000	540	40	90	390	150	180	340	390	140	330	360	30	760	n.a.	670	120	40	80	40
		2004	n.d.	< 5	< 5	< 5	< 5	10	< 5	< 5	< 5	< 5	n.a.	n.a.	< 5	10	n.a.	< 5	< 5	n.a.	10	< 5
43	Diethyl phthalate	2020	150	120	220	120	50	90	120	100	70	180	50	140	150	140	110	140	140	110	110	140
		2015	2000	1600	350	n.d.	490	120	730	1200	880	170	480	1400	130	2500	n.a.	2300	610	160	140	150
		2004	350	240	280	480	230	490	200	220	260	190	n.a.	n.a.	590	290	n.a.	370	250	n.a.	700	180
44	Di-iso-butyl phthalate	2020	260	210	400	100	80	130	170	260	260	230	350	370	460	130	70	50	70	50	30	90
		2015	610	470	3900	540	340	200	350	290	2100	670	590	170	1400	970	n.a.	350	2600	1400	570	670
		2004	60	120	90	50	40	90	70	10	40	40	n.a.	n.a.	40	30	n.a.	40	10	n.a.	60	< 5
45	Di-n-butyl phthalate	2020	890	660	690	500	130	270	280	400	500	540	570	810	1200	250	100	80	270	130	90	470
		2015	740	440	2600	2300	290	210	1100	570	790	500	430	250	1100	520	n.a.	740	1100	630	280	470
		2004	220	620	200	290	200	320	280	210	280	290	n.a.	n.a.	420	230	n.a.	290	190	n.a.	320	130
46	Benzyl butyl phthalate	2020	20	40	9	20	7	8	10	n.d.	10	< 5	20	6	20	5	10	7	6	7	5	< 5
		2015	n.d.	n.d.	90	150	30	10	50	40	160	30	60	70	100	30	n.a.	40	20	30	n.d.	30
		2004	70	60	20	30	30	360	20	20	40	70	n.a.	n.a.	110	30	n.a.	70	20	n.a.	20	n.d.
47	Bis(2-ethylhexyl) phthalate, DEHP	2020	840	1100	730	1300	1200	1100	1400	780	840	590	890	230	720	760	460	520	600	1400	350	410
		2015	600	1600	520	770	330	190	1600	390	3200	450	880	790	4400	600	n.a.	1600	230	180	820	950
		2004	120	560	n.d.	360	40	760	n.d.	160	160	250	n.a.	n.a.	340	260	n.a.	130	n.d.	n.a.	230	n.d.
48	2,2-Dimethoxy-1,2-diphenylethanone, DMPA	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	5	5	< 5	5	< 5	< 5	< 5	< 5	< 5	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
49	Diphenoxyethane	2020	n.d.	n.d.	< 5	n.d.	< 5	< 5	10	n.d.	n.d.	7	< 5	< 5	< 5	< 5	n.d.	n.d.	n.d.	< 5	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	90	< 5	n.d.	n.d.	20	7	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	40
	Miscellaneous contaminants																					
	Halogenated compounds																					
50	Dichloroaniline	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	< 5	< 5	< 5	5	6	8	8	6	< 5
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	< 5	n.a.	n.a.	< 5	< 5	n.a.	< 5	10	n.a.	10	< 5	10
51	1,1,2,2-Tetrachloroethane	2020	n.d.	n.d.	120	120	160	220	190	220	250	280	370	310	250	240	8	5	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	5	n.a.	< 5	6	n.d.	n.d.	5
		2004	10	6	n.d.	< 5	< 5	n.d.	n.d.	9	n.d.	20	n.a.	n.a.	20	n.d.	n.a.	20	n.d.	n.a.	n.d.	< 5
52	4-Bromoanisole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	40	10	10	90	< 5	180	20	30	10	90	n.a.	n.a.	20	< 5	n.a.	10	10	n.a.	20	< 5
53	2,4-Dibromoanisole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	< 5	n.d.	< 5	< 5	< 5	20	< 5	< 5	< 5	10	n.a.	n.a.	< 5	< 5	n.a.	< 5	< 5	n.a.	< 5	< 5
54	2,4,6-Tribromoanisole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	n.a.	n.a.	< 5	< 5	n.a.	< 5	< 5	n.a.	< 5	< 5	< 5
	S-containing compounds																					
55	Diphenylsulfone	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	10	10	10	20	20	20	8	10	10	10
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	40	30	40	n.a.	40	40	80	60	50	40
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
56	Methylphenylsulfone	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	10	10	30	20	<5	7	7	<5	8	20
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	20	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.
57	Benzothiazole	2020	5	5	n.d.	5	<5	<5	n.d.	<5	<5	6	<5	<5	<5	<5	6	6	8	5	<5	n.d.
		2015	n.d.	<5	<5	<5	<5	<5	20	<5	6	<5	5	9	<5	n.a.	6	10	10	20	6	10
		2004	<5	<5	<5	10	10	10	<5	10	10	n.a.	n.a.	10	10	n.a.	10	10	n.a.	10	10	20
58	2-Methylthiobenzothiazole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	70	30	30	20	30	30	40	40	40	30	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	20	n.d.	40	n.a.	20	50	40	40	40	30
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	<5	n.a.	<5	<5	<5
59	N-Phenylbenzenesulfonamide	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	20	30	30	30	20	20	20	30	20	20
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10	<5	6	5	5	<5	<5	n.a.	<5	<5	<5	<5	5	<5
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	<5	n.a.	n.a.	10	n.d.	n.a.	<5	<5	n.a.	<5	<5	10
60	N-Ethyl-o-toluenesulfonamide	2020	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	n.d.	180	80	60	80	90	50	30	50	40	50	40
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	<5	<5	<5	<5	<5	n.a.	<5	<5	<5	<5	<5	<5
		2004	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	<5	n.a.	n.a.	10	10	n.a.	10	10	n.a.	20	20	30
61	N-Ethyl-p-toluenesulfonamide	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	250	70	70	80	60	50	40	50	30	40	40
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	90	40	20	60	n.a.	50	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	80	40	n.a.	60	80	n.a.	110	110	120
62	2-Aminodiphenylsulfone	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2004	n.d.	<5	<5	<5	<5	<5	<5	<5	<5	n.a.	n.a.	<5	<5	n.a.	10	<5	n.a.	<5	<5	<5
63	N-containing compounds 2-Methylbenzotriazole																					
		2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	100	60	90	60	60	140	130	220	170	130	290
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	7	n.d.	6	n.a.	6	10	<5	10	9	10
		2004	n.d.	n.d.	<5	<5	10	10	10	10	10	10	n.a.	n.a.	10	10	n.a.	10	20	n.a.	20	30

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
64	Quinoline	2020	n.d.	n.d.	n.d.	< 5	< 5	n.d.	< 5	< 5	5	7	7	7	10	9	5	8	10	8	10	20	
		2015	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	10	n.d.	n.a.	< 5	7	7	9	< 5	< 5	
		2004	< 5	< 5	< 5	< 5	< 5	10	< 5	10	10	n.a.	n.a.	< 5	< 5	< 5	n.a.	< 5	10	< 5	< 5	10	
65	Quinoxaline	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2004	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	< 5	< 5	n.a.	n.a.	< 5	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	
66	2,3-Diethyl-2,3-dimethylsuccinonitrile	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	n.a.	< 5	< 5	< 5	< 5	< 5	< 5	
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	7	n.d.	7	7	n.a.	n.a.	n.a.	90	70	n.a.	60	150	n.a.	80	70	170
67	Phenylisocyanate	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	210	80	100	140	130	80	10	30	30	50	90	
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.
68	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1300	190	180	230	240	200	170	420	130	150	170	
		2015	n.d.	9	n.d.	40	n.d.	n.d.	n.d.	n.d.	n.d.	40	70	60	50	120	n.a.	90	n.d.	90	n.d.	n.d.	n.d.
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	60	50	n.a.	50	70	n.a.	70	50	40
69	N,N-Dibutylformamide	2020	250	240	280	140	120	280	370	640	250	130	540	280	320	560	400	130	240	180	190	240	
		2015	70	30	50	80	100	8	7	9	70	30	20	20	390	50	n.a.	20	750	430	290	250	250
		2004	160	80	40	20	90	20	30	70	20	140	n.a.	n.a.	80	140	n.a.	70	100	n.a.	80	150	120
70	O-containing compounds 2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone																						
		2020	40	10	< 5	< 5	< 5	< 5	n.d.	< 5	< 5	< 5	20	< 5	5	< 5	5	< 5	5	< 5	< 5	< 5	
		2015	20	10	10	20	10	10	10	10	40	20	40	30	70	50	n.a.	40	90	90	100	90	60
		2004	7	n.d.	n.d.	6	n.d.	9	9	< 5	7	10	n.a.	n.a.	7	10	n.a.	8	7	n.a.	10	6	10

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
71	Butylated hydroxytoluene, Ionole	2020	10	9	5	6	< 5	9	10	9	9	5	10	10	20	10	20	10	20	6	10	10	6
		2015	90	50	20	40	30	6	< 5	9	50	20	30	20	n.d.	50	n.a.	30	330	180	160	140	110
		2004	20	40	20	10	30	10	20	40	10	20	n.a.	n.a.	9	20	n.a.	20	20	n.a.	30	20	20
72	1,3,3-Trimethylindole	2020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	8	9	10	9	7	6	6	< 5	6	5	5
		2015	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9	8	6	10	n.a.	10	10	10	6	7	7
		2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.

n.d. (not detected) means the concentration was below detection limit (< 1 ng/L);

< 5 means the concentration was below limit of quantification and above detection limit (1-5 ng/L); n.a. (not analyzed)

Table A5 Loads [g/d] of organic compounds detected in Rur river water samples (taken in November 2020, March 2015, and November/December 2004).

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
	Pharmaceuticals																					
1		2020	0	0	0	0	<2	3	6	<2	3	48	41	57	57	63	51	41	62	124	58	49
		2015	0	1	0	0	0	0	5	29	6	38	118	100	102	n.a.	100	71	142	153	225	200
		2004	0	3	2	0	33	106	70	85	49	17	n.a.	n.a.	13	102	n.a.	102	102	n.a.	169	92
2	Oxcarbazepine	2020	0	0	0	0	0	0	0	0	0	17	6	9	5	5	5	6	5	6	5	<4
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	0
3	Caffeine	2020	0	0	3	13	11	16	20	21	18	93	110	104	76	51	44	58	72	52	46	60
		2015	4	1	1	<1	2	4	16	8	<3	18	37	25	29	n.a.	46	34	31	87	61	61
		2004	0	0	<1	0	31	47	52	52	57	n.a.	n.a.	89	86	n.a.	86	171	n.a.	205	205	410
4	Chlorobutanol	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	<1	<1	0	<2	16	<5	<6	<6	<7	n.a.	n.a.	1004	3235	n.a.	747	1178	n.a.	93	1450	368
5	Iminostilbene	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	<4	<5	<6	<6	<7	n.a.	n.a.	41	<10	n.a.	<10	59	n.a.	71	24	47
6	Lidocaine	2020	0	0	0	0	0	0	0	0	0	125	66	74	71	76	54	46	80	99	74	67
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	7	11	12	24	13	n.a.	n.a.	20	39	n.a.	79	79	n.a.	259	212	259
7	Acetylsalicylic acid	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	<10	<10	n.a.	<10	<10	n.a.	<12	<12	0
8	Diclofenac	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		2004	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
9	Tocopheryl acetate	2020	11	25	1	48	3	2	16	<3	0	<3	<4	<4	12	6	<4	6	12	0	0	6
		2015	0	1	0	0	<1	0	0	11	<3	7	<7	9	8	n.a.	<7	0	0	<6	0	<6
		2004	3	15	0	24	0	174	0	12	50	n.a.	n.a.	348	39	n.a.	158	0	n.a.	94	24	47
	Personal care products																					
10	N,N,N',N''-Tetraacetylenediamine, TAED	2020	0	0	0	0	0	0	0	7	24	25	43	49	40	39	23	25	26	29	38	59
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	117	247	83	237	188	107
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	164	39	n.a.	138	98	n.a.	118	142	0
11	4-Methoxycinnamic acid 2-ethylhexylester	2020	0	0	0	0	0	0	0	0	0	<3	0	0	0	<4	<4	<4	0	0	<4	0
		2015	0	1	0	0	<1	0	5	0	<3	<5	<7	20	0	n.a.	0	0	0	0	0	0
		2004	17	17	11	28	115	120	36	48	50	n.a.	n.a.	450	335	n.a.	217	79	n.a.	118	47	94
12	Drometrizole	2020	0	0	0	0	0	0	0	1	0	0	<4	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	126
13	Galaxolide	2020	1	1	<1	2	<1	3	4	0	3	<2	25	28	32	30	35	33	38	52	54	56
		2015	1	2	<1	<1	2	6	12	14	25	13	29	59	44	106	n.a.	92	112	99	112	113
		2004	6	4	3	10	7	44	60	48	25	26	n.a.	184	177	n.a.	256	197	n.a.	401	283	259
14	Tonalide	2020	<1	<1	0	<1	<1	<2	<3	0	<2	0	<3	<4	<4	<4	<4	4	4	5	<4	<4
		2015	<1	1	<1	<1	<1	<2	<3	<3	3	<3	5	<7	<7	12	n.a.	9	8	7	11	8
		2004	<1	<1	<1	<2	<4	11	12	<6	<6	<7	n.a.	n.a.	20	n.a.	39	20	n.a.	71	47	24
15	4-Oxoisophorone	2020	1	2	1	2	<1	<2	3	3	<2	3	5	12	11	10	9	5	8	7	4	11
		2015	2	1	1	1	2	4	3	<3	7	6	9	27	17	29	n.a.	14	50	57	51	32
		2004	9	19	33	6	62	38	103	41	43	90	n.a.	106	102	n.a.	102	204	n.a.	163	122	122
16	Lilial	2020	0	0	0	0	0	0	0	0	0	0	<4	<4	<4	<4	<4	0	0	0	0	<4
		2015	0	1	0	0	2	2	3	4	4	3	14	0	0	n.a.	41	0	0	20	0	0
		2004	1	2	3	3	<4	11	<6	<6	<6	<7	n.a.	<10	<10	n.a.	20	<10	n.a.	24	24	0

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
17	Viridine	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	n.a.	n.a.	<10	<10	<10	n.a.	<10	<10	n.a.	<12	<12	<12
18	Dihydromethyljasmonate	2020	6	4	5	4	3	9	12	7	3	5	21	29	22	14	13	12	15	13	11	8
		2015	3	4	3	5	8	6	12	16	<3	12	26	23	33	92	n.a.	85	68	29	51	38
		2004	0	0	2	0	0	0	0	0	<6	0	n.a.	n.a.	12	0	n.a.	11	0	n.a.	27	0
19	Gineol	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	1	<1	0	0	0	0	0	0	<5	0	0	0	n.a.	0	0	49	0	0	0
		2004	<1	<1	0	3	<4	<5	<6	<6	<6	<7	n.a.	n.a.	<10	<10	<10	<10	n.a.	0	<12	377
20	Coumarin	2020	0	0	0	0	0	<2	<3	<3	2	12	18	13	16	19	19	14	12	12	11	14
		2015	0	0	0	0	0	0	0	0	0	<5	14	10	7	n.a.	11	12	12	9	6	9
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	0
21	4-tert-Butylcyclohexanone	2020	0	0	0	0	0	0	0	0	0	4	4	4	4	5	7	9	9	6	<4	5
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	<10	<10	n.a.	<10	41	n.a.	17	19	14
22	Benzophenone	2020	<1	<1	<1	1	<1	<2	3	<3	<2	18	11	12	11	14	12	12	10	8	8	9
		2015	0	4	1	3	6	20	38	39	49	11	106	79	14	102	n.a.	113	16	7	20	11
		2004	4	2	3	7	14	305	12	36	88	39	n.a.	n.a.	41	39	n.a.	177	59	n.a.	94	118
23	Isopropylaurate	2020	25	25	28	22	22	74	106	136	62	28	183	117	271	170	154	69	123	110	82	62
		2015	414	116	444	767	332	3182	850	3146	2087	709	2329	5505	24231	9318	n.a.	2293	19677	19045	18998	14876
		2004	3	5	6	85	22	30	39	593	45	20	n.a.	n.a.	160	49	n.a.	55	39	n.a.	68	47
24	Isopropylpalmitate	2020	6	6	6	6	3	6	10	11	16	4	41	26	48	35	20	15	12	11	11	16
		2015	7	180	9	11	22	16	2372	33	791	133	810	96	549	131	n.a.	46	150	478	74	41
		2004	21	27	9	52	131	401	45	99	118	120	n.a.	n.a.	745	644	n.a.	556	91	n.a.	278	193

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
25	Methyl dehydroabietate	2020	173	122	286	163	275	467	1002	1264	858	266	1837	1436	3078	1100	764	419	536	720	445	214	665
		2015	76	125	594	1153	112	82	950	268	1317	185	811	1196	25386	1049	n.a.	578	6417	5398	1481	1295	1543
		2004	36	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	0
	Pesticides and biocides																						
26	N,N-Diethyltoluamide, DEET	2020	0	0	0	0	0	0	0	0	0	0	27	15	17	16	15	12	11	14	17	14	14
		2015	0	<1	0	0	<2	0	<3	4	<3	<3	<5	7	<7	9	n.a.	9	12	8	11	12	9
		2004	0	<1	0	<2	<4	<5	<6	<6	<7	<7	n.a.	n.a.	<10	20	n.a.	<10	<10	n.a.	24	24	47
27	4,4'-Dichlorobenzophenone, DBP	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	128	0	0	0	0	0	n.a.	n.a.	0	477	n.a.	0	0	n.a.	0	0	0
	Technical additives, plasticizers and other industrial compounds																						
28	Di-iso-propylnaphthalenes, DIPN	2020	0	0	0	0	<1	0	0	0	0	0	<3	0	0	0	0	<4	<4	<4	0	0	0
		2015	0	42	3	8	7	8	0	0	72	19	55	44	99	72	n.a.	62	79	94	80	0	0
		2004	1	2	3	4	24	37	14	14	14	30	n.a.	n.a.	47	45	n.a.	45	22	n.a.	54	27	54
29	N-Butylbenzenesulfonamide, NBBS	2020	0	0	1	3	2	2	4	4	<2	<2	67	39	39	44	40	30	23	30	31	27	29
		2015	0	0	0	0	0	0	0	0	8	<3	<5	9	<7	9	n.a.	7	13	7	0	0	6
		2004	0	4	3	<2	7	11	12	12	13	13	n.a.	n.a.	82	39	n.a.	59	59	n.a.	94	94	118
30	2,4,4-Trimethylpentane-1,3-diol di-iso-butyrate, TXIB	2020	6	3	4	3	4	13	24	26	12	6	42	29	34	37	33	12	26	30	14	10	11
		2015	400	183	55	247	35	0	25	42	122	43	92	102	252	385	n.a.	122	419	330	214	237	142
		2004	2	4	6	10	16	27	32	27	24	27	n.a.	n.a.	41	41	n.a.	20	20	n.a.	66	12	47
31	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	2020	19	17	23	7	4	8	18	30	10	18	14294	9657	9239	12498	12169	11840	8143	8277	8206	10165	9283
		2015	77	35	66	115	32	43	62	88	533	246	17068	15633	10045	83863	n.a.	32287	22271	16632	10546	14177	13289
		2004	1	2	7	3	7	27	12	12	61	13	n.a.	n.a.	3546	3027	n.a.	3219	3315	n.a.	4027	2819	1668

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
32	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	2020	0	2	16	6	1	0	3	0	<2	2	14	0	0	0	0	0	0	0	0	0	
		2015	56	114	8	15	122	91	540	613	98	194	825	1218	62	1849	n.a.	1967	88	66	40	21	110
		2004	<1	0	<1	<2	<4	<5	<6	<6	<6	<7	n.a.	n.a.	0	<10	n.a.	<10	<10	n.a.	<12	<12	<12
33	Triethylcitrate	2020	1	3	3	6	2	3	5	5	<2	2	70	45	52	47	36	22	23	30	27	36	44
		2015	0	4	0	0	5	6	9	12	351	70	58	63	0	126	n.a.	96	171	93	163	197	126
		2004	<1	<1	<1	<2	<4	<5	0	<6	<6	<7	n.a.	n.a.	82	20	n.a.	59	59	n.a.	71	94	24
34	Acetyl tributylcitrate	2020	48	34	1	<1	0	0	0	0	0	11	0	0	0	0	0	0	0	0	0	0	
		2015	0	9	0	0	4	12	46	14	21	130	102	92	774	46	n.a.	164	117	108	49	83	60
		2004	<1	4	3	<2	22	44	<6	<6	<6	13	n.a.	n.a.	82	59	n.a.	59	<10	n.a.	24	<12	24
35	Triacetin	2020	1683	1089	1351	298	542	1644	2213	3121	2673	2390	3370	6118	6579	3764	1956	234	679	1155	273	1363	1858
		2015	168	49	108	374	100	88	120	51	583	299	39	1113	1492	1061	n.a.	620	2474	2209	945	0	443
		2004	0	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	197	0	n.a.	0	0	0
36	Triethylphosphate	2020	0	0	0	2	3	<2	4	6	<2	3	134	93	92	128	121	93	84	109	103	130	158
		2015	0	0	0	4	2	6	8	7	14	19	60	146	100	189	n.a.	96	281	195	207	112	161
		2004	0	0	0	0	0	0	11	17	20	20	n.a.	n.a.	125	95	n.a.	104	173	n.a.	276	292	366
37	Tributylphosphate	2020	2	2	<1	0	0	0	0	0	<2	0	13	9	6	0	0	0	0	0	0	0	0
		2015	0	21	16	43	71	47	0	62	297	132	888	948	3646	2017	n.a.	1824	5638	4882	1713	1372	866
		2004	16	2	16	41	93	266	192	99	189	224	n.a.	n.a.	894	912	n.a.	953	1024	n.a.	1717	515	1006
38	Tris(2-chloroethyl)phosphate, TCEP	2020	0	0	0	<1	<1	<2	<3	<3	0	0	8	7	6	6	5	<4	5	6	<4	7	8
		2015	0	0	0	0	0	0	0	0	43	3	<5	7	<7	<7	n.a.	<7	9	6	<6	7	<6
		2004	0	0	<1	<2	<4	10	11	11	12	12	n.a.	n.a.	38	36	n.a.	36	72	n.a.	87	87	130
39	Tris(chloropropyl)phosphate, TCP	2020	<1	<1	1	2	2	<2	4	4	<2	<2	68	48	45	47	47	37	33	40	40	45	49
		2015	3	5	0	0	0	24	101	58	769	172	272	301	199	418	n.a.	349	520	381	398	483	287
		2004	0	0	0	0	0	0	0	0	0	0	n.a.	n.a.	74	55	n.a.	12	14	n.a.	26	19	33

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
40	Triphenylphosphate	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	1	0	0	2	0	0	105	40	87	40	32	16	n.a.	28	9	11	14	14	8
		2004	< 1	< 1	< 2	< 4	11	< 6	< 6	< 6	< 7	n.a.	n.a.	10	10	n.a.	10	< 10	n.a.	12	< 12	< 12
41	Triphenylphosphine oxide	2020	0	0	0	0	0	0	0	0	0	157	206	107	114	135	86	49	79	63	49	52
		2015	0	0	0	0	0	0	0	0	0	60	62	50	70	n.a.	34	26	59	68	73	56
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	0
42	Dimethyl phthalate	2020	10	5	5	3	2	7	13	13	5	17	18	18	21	16	12	52	50	47	17	14
		2015	112	59	5	20	100	64	112	207	249	88	345	515	37	995	n.a.	873	151	52	95	47
		2004	0	< 1	< 1	< 2	< 4	11	< 6	< 6	< 6	< 7	n.a.	n.a.	< 10	20	n.a.	< 10	n.a.	24	< 12	24
43	Diethyl phthalate	2020	22	17	31	22	12	39	62	63	45	29	109	42	117	113	108	89	107	105	80	103
		2015	219	176	38	0	128	53	453	755	571	112	499	1963	184	3233	n.a.	3014	796	190	160	179
		2004	45	52	77	164	166	531	234	261	331	247	n.a.	n.a.	1200	561	n.a.	721	494	n.a.	1644	422
44	Di-iso-butyl phthalate	2020	38	30	56	20	19	58	90	139	112	98	210	299	370	99	54	41	54	56	39	24
		2015	65	51	420	115	88	88	215	179	1374	431	608	240	2062	1269	n.a.	456	3375	1654	673	791
		2004	8	26	25	17	29	98	83	12	50	52	n.a.	n.a.	82	59	n.a.	79	20	n.a.	142	< 12
45	Di-n-butyl phthalate	2020	127	95	99	94	33	115	149	213	215	236	344	656	970	192	80	62	206	97	71	55
		2015	80	47	283	484	76	89	687	350	515	325	450	361	1562	676	n.a.	974	1501	744	325	556
		2004	29	134	55	101	141	343	328	248	356	376	n.a.	n.a.	850	447	n.a.	573	368	n.a.	764	314
46	Benzyl butyl phthalate	2020	3	5	1	3	2	3	6	0	6	< 2	12	5	12	4	9	5	5	4	< 4	5
		2015	0	0	10	31	8	4	30	25	101	21	58	95	143	43	n.a.	58	21	33	0	33
		2004	9	13	7	12	21	386	19	27	44	89	n.a.	n.a.	229	57	n.a.	132	47	n.a.	47	0
47	Bis(2-ethylhexyl) phthalate, DEHP	2020	120	153	105	252	320	478	746	414	367	255	535	186	587	588	358	402	468	1060	263	312
		2015	65	175	56	162	86	83	998	240	2042	294	908	1127	6245	792	n.a.	2082	307	213	964	1116
		2004	16	121	0	124	29	827	0	191	200	326	n.a.	n.a.	696	512	n.a.	256	0	n.a.	543	0

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
48	2,2-Dimethoxy-1,2-diphenylethanone, DMPA	2020	0	0	0	0	0	0	0	0	0	24	4	4	<4	4	<4	<4	<4	<4	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	n.a.	0	0	0
49	Diphenoxethane	2020	0	0	<1	0	0	<2	<3	6	0	4	<4	<4	<4	<4	<4	0	0	0	<4	0
		2015	0	0	0	18	0	<2	0	0	14	5	0	0	0	0	n.a.	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	104
	Miscellaneous contaminants																					
50	Halogenated compounds																					
		2020	0	0	0	0	0	0	0	0	0	<3	0	<4	<4	<4	<4	4	5	6	6	5
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0
		2004	0	0	0	0	<4	<5	<6	<6	<6	<7	n.a.	n.a.	<10	<10	n.a.	<10	20	n.a.	24	<12
51	1,1,2,2-Tetrachloroethane	2020	0	0	17	22	42	94	99	116	111	121	226	253	204	187	6	4	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	<7	<7	7	n.a.	<7	8	6	0	6
		2004	1	1	0	<2	<4	0	0	11	0	26	n.a.	n.a.	33	0	n.a.	45	0	n.a.	0	<12
52	4-Bromoanisole	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0
		2004	5	1	2	31	<4	197	18	34	10	118	n.a.	n.a.	32	<10	n.a.	21	29	n.a.	36	<12
53	2,4-Dibromoanisole	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0
		2004	<1	0	<1	<2	<4	16	<6	<6	<6	14	n.a.	n.a.	<10	<10	n.a.	<10	<10	n.a.	<12	<12
54	2,4,6-Tribromoanisole	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0
		2004	<1	<1	<1	<2	<4	<5	<6	<6	<6	<7	n.a.	n.a.	<10	<10	n.a.	<10	<10	n.a.	<12	<12

No.	Compounds		Site no.																				
			R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
	S-containing compounds																						
55	Diphenylsulfone	2020	0	0	0	0	0	0	0	0	0	0	13	9	10	11	14	14	6	10	8	8	8
		2015	0	0	0	0	0	0	0	0	0	34	57	43	51	n.a.	58	104	72	59	52	51	51
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	0	n.a.	0	0	n.a.	0	0	0
56	Methylphenylsulfone	2020	0	0	0	0	0	0	0	0	0	25	11	8	19	16	<4	5	5	<4	6	14	14
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	45	0	n.a.	0	0	n.a.	0	0	0	0
57	Benzothiazole	2020	1	1	0	1	1	<2	<3	0	<2	4	<4	<4	<4	<4	<4	5	5	6	4	<4	0
		2015	0	<1	<1	<1	<1	<2	<3	<3	15	4	<5	7	13	<7	n.a.	8	14	12	18	7	15
		2004	<1	<1	<1	3	7	11	12	<6	13	13	n.a.	n.a.	20	20	n.a.	20	20	n.a.	24	24	47
58	2-Methylthiobenzothiazole	2020	0	0	0	0	0	0	0	0	0	42	21	24	19	26	24	27	28	30	23	0	0
		2015	0	0	0	0	0	0	0	0	0	40	26	0	47	n.a.	21	63	45	47	49	33	33
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	<10	n.a.	<12	<12	<12	<12
59	N-Phenylbenzenesulfonamide	2020	0	0	0	0	0	0	0	0	0	24	19	21	25	23	16	15	18	22	18	17	17
		2015	0	0	0	0	0	0	0	0	8	<3	6	7	<7	<7	n.a.	<7	<7	<6	<6	6	<6
		2004	0	0	0	0	0	0	0	<6	0	<7	n.a.	n.a.	20	0	n.a.	<10	<10	n.a.	<12	<12	24
60	N-Ethyl- <i>o</i> -toluenesulfonamide	2020	0	0	0	0	<1	0	0	0	0	111	63	50	61	73	38	26	40	27	35	30	30
		2015	0	0	0	0	0	0	0	0	13	<3	<5	<7	<7	<7	n.a.	<7	<7	<6	<6	<6	<6
		2004	0	0	0	0	<4	<5	<6	<6	<6	<7	n.a.	n.a.	23	22	n.a.	22	22	n.a.	53	53	80
61	N-Ethyl- <i>p</i> -toluenesulfonamide	2020	0	0	0	0	0	0	0	0	0	149	58	53	59	48	37	31	39	26	30	29	29
		2015	0	0	0	0	0	0	0	0	0	93	50	32	77	n.a.	64	0	0	0	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	160	87	n.a.	122	156	n.a.	269	252	288	288
62	2-Aminodiphenylsulfone	2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0
		2004	0	<1	<1	<2	<4	<5	<6	<6	<6	<7	n.a.	n.a.	<10	<10	n.a.	12	<10	n.a.	<12	<12	<12

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	
63	N-containing compounds 2-Methylbenzotriazole																						
		2020	0	0	0	0	0	0	0	0	0	60	46	75	44	50	106	100	163	131	101	217	
		2015	0	0	0	0	0	0	0	0	<3	<5	11	0	8	n.a.	8	18	<6	14	11	14	
		2004	0	0	<1	<2	7	11	12	12	13	13	n.a.	n.a.	20	20	n.a.	20	39	n.a.	47	47	71
64	Quinoline																						
		2020	0	0	0	2	<1	0	<3	<3	2	4	6	6	8	7	4	6	8	6	9	15	
		2015	0	0	0	<1	0	0	0	<3	<3	<5	<7	15	0	n.a.	<7	10	9	11	<6	<6	
		2004	<1	<1	<1	<2	<4	<5	12	<6	13	13	n.a.	n.a.	<10	<10	n.a.	<10	20	n.a.	<12	<12	24
65	Quinoxaline																						
		2020	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0	
		2004	<1	0	0	0	0	0	0	<6	0	<7	n.a.	n.a.	<10	0	n.a.	0	0	n.a.	0	0	0
66	2,3-Diethyl-2,3-dimethylsuccinonitrile																						
		2020	0	0	0	0	0	0	0	0	0	0	0	<4	0	0	0	0	0	0	0	<4	
		2015	0	0	0	0	0	0	0	0	0	<5	<7	<7	<7	n.a.	<7	<7	<6	<6	<6	<6	
		2004	0	0	0	0	0	7	0	8	8	9	n.a.	n.a.	189	143	n.a.	117	299	n.a.	187	171	389
67	Phenylisocyanate																						
		2020	0	0	0	0	0	0	0	0	0	129	67	78	106	100	65	9	26	23	36	66	
		2015	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	0	0	0	0	0	0	
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	n.a.	0	0	n.a.	0	0	0	0
68	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN																						
		2020	0	0	0	0	0	0	0	0	0	756	155	146	182	183	153	134	315	100	113	128	
		2015	0	1	0	9	0	0	0	0	0	26	75	92	76	155	n.a.	122	0	101	0	0	0
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	115	91	n.a.	89	132	n.a.	172	116	97	
69	N,N-Dibutylformamide																						
		2020	36	34	40	26	30	121	196	340	108	56	328	225	258	432	309	100	187	139	145	146	180
		2015	8	3	5	16	25	3	4	6	42	20	18	27	561	68	n.a.	32	989	501	345	291	291
		2004	20	17	12	7	64	22	30	82	29	183	n.a.	n.a.	154	284	n.a.	130	197	n.a.	196	363	278

No.	Compounds		Site no.																				
			R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21
70	O-containing compounds																						
	2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone	2020	5	1	< 1	< 1	< 2	< 3	0	< 2	< 2	10	< 4	4	< 4	4	< 4	< 4	4	< 4	< 4	< 4	< 4
		2015	2	1	1	4	4	5	6	7	26	13	39	42	95	60	n.a.	50	113	100	118	107	69
		2004	1	0	0	2	0	10	11	< 6	9	14	n.a.	n.a.	14	20	n.a.	16	14	n.a.	31	14	31
71																							
	Butylated hydroxytoluene, Ionole	2020	1	1	1	1	< 1	4	6	5	4	2	8	11	13	10	12	9	12	5	11	8	5
		2015	10	5	2	8	8	3	< 3	6	29	10	31	30	0	71	n.a.	39	435	206	193	166	125
		2004	2	9	5	4	22	11	27	47	16	26	n.a.	n.a.	18	39	n.a.	33	30	n.a.	75	57	40
72																							
	1,3,3-Trimethoxyindole	2020	0	0	0	0	0	0	0	0	0	16	6	7	8	7	5	5	5	5	< 4	5	4
		2015	0	0	0	0	0	0	0	0	0	9	11	9	16	n.a.	14	16	12	7	8	8	8
		2004	0	0	0	0	0	0	0	0	0	n.a.	n.a.	0	0	0	n.a.	0	0	n.a.	0	0	0
n.a. (not analyzed)																							

n.a. (not analyzed)

Appendix to Chapter 5

“Distribution, Remobilization and Accumulation of Organic Contaminants by Flood Events in a Meso-Scaled Catchment System”

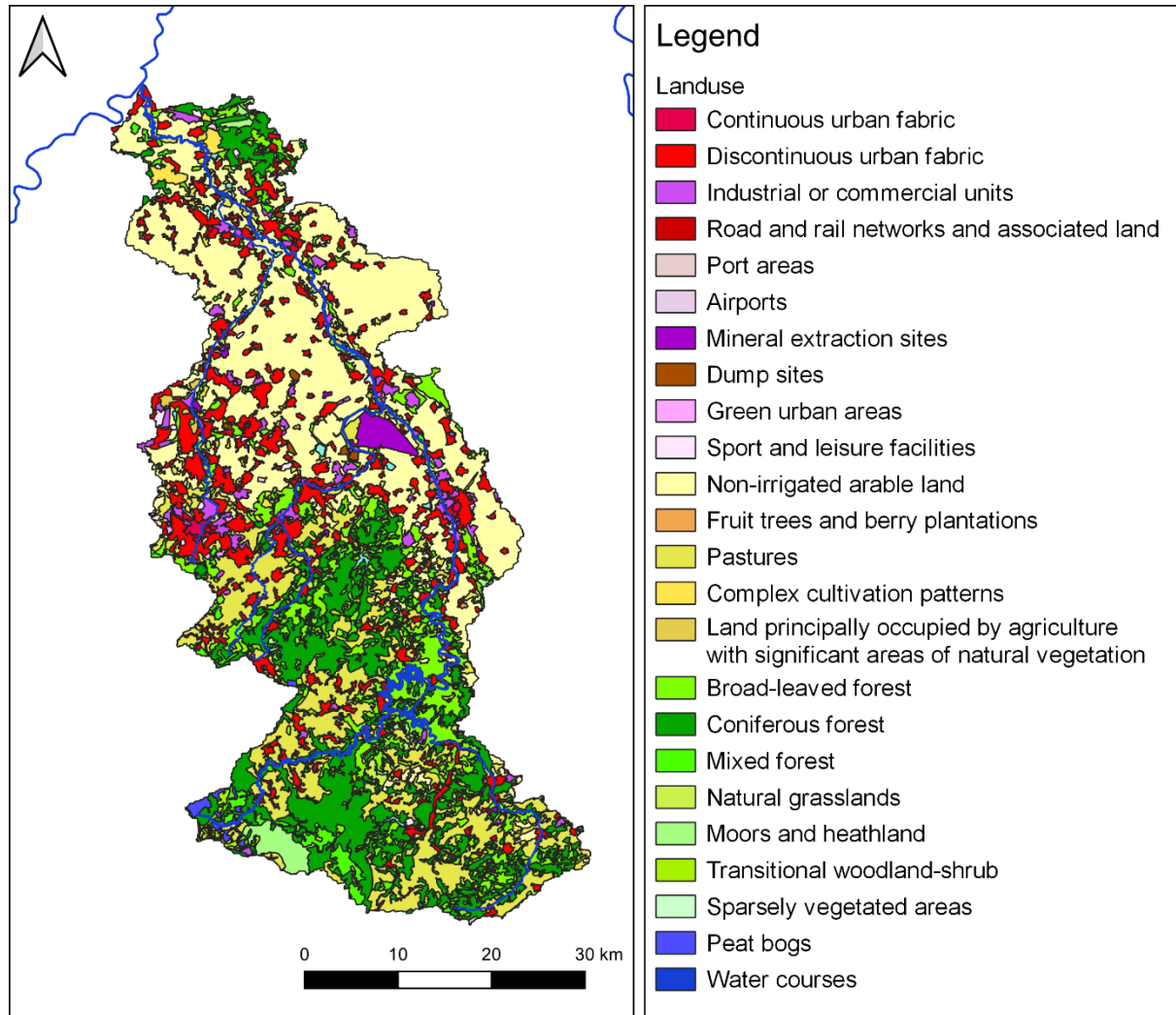


Figure A1 Land use in the catchment of the Rur river according to CORINE Land Cover data. The southern part is mainly covered by forest and grassland, while the northern part is more anthropogenically and agriculturally used.

Table A6 Standard parameters including grain size distribution and TOC content. (*) R5 to R7 were not sampled in February.

Site no.	River km	Grain size distribution						TOC [%]	
		2000 – 63 µm [%]		63 – 2 µm [%]		< 2 µm [%]			
		February	July	February	July	February	July	February	July
R1	152.8	53	90	39	8	8	2	5.9	0.5
R2	136.1	94	89	5	9	1	2	0.7	1.5
R3	129.3	91	86	6	11	3	3	2.4	5.7
R4	98.6	58	36	34	53	8	11	1.3	3.1
R5*	89.6	n.a.	69	n.a.	25	n.a.	6	n.a.	0.5
R6*	85.1	n.a.	83	n.a.	13	n.a.	4	n.a.	1.8
R7*	80.7	n.a.	50	n.a.	42	n.a.	8	n.a.	7.6
R8	71.0	56	26	36	62	8	12	6.8	4.5
R9	66.9	57	37	36	53	7	10	6.8	2.1
R10	61.4	88	60	9	33	3	7	4.1	1.0
R11	59.6	76	84	19	13	5	3	1.5	0.6
R12	51.2	83	94	14	4	3	2	1.3	0.9
R13	34.7	61	81	33	15	6	4	1.1	0.3
R14	26.6	68	96	28	3	4	1	2.9	1.0
R15	26.1	82	87	15	10	3	3	2.4	0.2
R16	24.2	77	97	19	2	4	1	2.0	1.5

n.a. (not analyzed)

Table A7 Concentrations [ng/g_{TOC}] of different pollutants/pollutant groups in the Rur catchment after a regular flood event in January/February 2021. (*) R5 to R7 were not sampled in February.

Compounds	Site no.															
	R1	R2	R3	R4	R5*	R6*	R7*	R8	R9	R10	R11	R12	R13	R14	R15	R16
Linear alkylbenzenes (LABs)																
Phenyldecenes	5	5	n.d.	81	n.a.	n.a.	n.a.	38	37	110	140	240	210	300	510	230
Phenylundecanes	22	33	30	47	n.a.	n.a.	n.a.	170	210	610	700	1600	1200	1500	2200	1200
Phenyldodecanes	26	44	37	46	n.a.	n.a.	n.a.	200	220	720	790	1900	1400	1800	2400	1400
Phenyltridecanes	18	60	39	49	n.a.	n.a.	n.a.	140	150	510	570	1200	1100	1300	1800	1100
Σ LABs	71	142	106	223	n.a.	n.a.	n.a.	548	617	1950	2200	4940	3910	4900	6910	3930
I/E ratio	0.82	1.18	1.48	0.96	n.a.	n.a.	n.a.	1.31	1.45	2.03	1.69	1.80	2.02	1.83	1.66	1.91
Polycyclic aromatic hydrocarbons (PAHs)																
Naphthalene	190	1900	1700	2100	n.a.	n.a.	n.a.	1800	1700	1700	2300	5100	5900	6000	14600	6300
Acenaphthylene	58	1000	850	600	n.a.	n.a.	n.a.	240	370	260	500	1100	760	190	270	300
Acenaphthene	130	900	940	1400	n.a.	n.a.	n.a.	800	350	330	37	940	640	780	1300	2000
Fluorene	130	380	1200	1200	n.a.	n.a.	n.a.	560	380	350	720	930	430	650	1300	1200
Phenanthrene	3200	24600	10800	25100	n.a.	n.a.	n.a.	6700	4700	7800	14300	25200	9600	6300	7500	9900
Anthracene	190	4300	2700	2000	n.a.	n.a.	n.a.	1600	1100	910	790	2400	1100	940	1500	2500
Fluoranthene	10400	37600	18300	50200	n.a.	n.a.	n.a.	8700	8100	14300	23100	46900	19200	7500	8700	12600
Pyrene	6400	30200	12300	40900	n.a.	n.a.	n.a.	7300	6000	11100	16000	36500	15700	7400	7100	9800
Benzo[<i>a</i>]anthracene	3900	11100	1900	25400	n.a.	n.a.	n.a.	3500	2100	6200	5800	22200	8900	2600	3600	4500
Chrysene	5400	14800	1900	30900	n.a.	n.a.	n.a.	4200	2400	8200	7800	29600	11400	3700	4900	5200
Benzo[<i>b</i>]fluoranthene	11200	18800	940	40500	n.a.	n.a.	n.a.	5300	2300	8900	560	42500	15900	5300	5800	2300
Benzo[<i>k</i>]fluoranthene	440	720	46	1400	n.a.	n.a.	n.a.	210	67	450	62	1800	1000	290	330	87
Benzo[<i>a</i>]pyrene	3000	5800	240	11900	n.a.	n.a.	n.a.	1500	640	3500	270	13800	5600	2000	1900	660
Indeno[1,2,3- <i>cd</i>]pyrene	4500	3600	150	8600	n.a.	n.a.	n.a.	1000	570	1300	85	11300	4300	1700	1200	76
Dibenzo[<i>a,h</i>]anthracene	630	530	15	1000	n.a.	n.a.	n.a.	23	100	170	< 5	1500	730	320	230	15
Benzo[<i>g,h,i</i>]perylene	2800	1800	76	4100	n.a.	n.a.	n.a.	660	290	670	37	5600	3000	1400	720	46
Σ EPA 16	52568	158030	54057	247300	n.a.	n.a.	n.a.	44093	31167	66140	72361	247370	104160	47070	60950	57484

Compounds	Site no.															
	R1	R2	R3	R4	R5*	R6*	R7*	R8	R9	R10	R11	R12	R13	R14	R15	R16
C ₁ phenanthrenes and anthracenes	820	4400	5300	8300	n.a.	n.a.	n.a.	2600	1900	2400	2300	5900	3100	1900	2600	2800
C ₁ fluoranthenes and pyrenes	2100	7500	2700	20700	n.a.	n.a.	n.a.	2800	1800	4500	3600	13600	5600	2500	3000	3500
Biphenyl	29	130	170	150	n.a.	n.a.	n.a.	130	41	88	160	530	260	1000	1900	1600
Retene	17	26	11	110	n.a.	n.a.	n.a.	87	28	150	110	330	110	80	37	39
Benzo[<i>a</i>]pyrene	3500	5000	220	11100	n.a.	n.a.	n.a.	1600	590	2600	300	12000	5200	2200	1800	530
Perylene	760	1200	34	1700	n.a.	n.a.	n.a.	300	110	510	130	2400	1300	570	570	99
NSO-PAHs																
Carbazole	39	1000	58	260	n.a.	n.a.	n.a.	83	43	29	44	40	25	16	58	130
Dibenzothiophene	< 5	360	230	150	n.a.	n.a.	n.a.	91	n.d.	n.d.	75	200	59	67	n.d.	98
Dibenzofuran	130	1100	1100	810	n.a.	n.a.	n.a.	610	420	480	1000	1500	520	1800	4500	4100
Hopanes																
trisnorhopane (Ts)	< 5	12	11	7	n.a.	n.a.	n.a.	n.d.	< 5	< 5	8	< 5	13	< 5	< 5	< 5
trisnorhopane (Tm)	7	31	25	17	n.a.	n.a.	n.a.	n.d.	5	< 5	8	6	14	< 5	< 5	6
C ₂₉ -hopanes	30	120	97	97	n.a.	n.a.	n.a.	< 5	20	6	20	16	39	< 5	14	14
C ₃₀ -hopanes	23	96	76	67	n.a.	n.a.	n.a.	n.d.	17	9	13	11	27	< 5	8	10
C ₃₁ -hopanes	150	75	100	140	n.a.	n.a.	n.a.	< 5	17	< 5	20	15	27	< 5	8	15
C ₃₂ -hopanes	42	33	40	25	n.a.	n.a.	n.a.	< 5	6	< 5	6	5	7	< 5	< 5	7
C ₃₃ -hopanes	13	10	12	20	n.a.	n.a.	n.a.	< 5	< 5	< 5	< 5	< 5	< 5	n.d.	< 5	< 5
C ₃₄ -hopanes	n.d.	< 5	58	10	n.a.	n.a.	n.a.	< 5	< 5	< 5	< 5	< 5	< 5	n.d.	< 5	< 5
C ₃₅ -hopanes	n.d.	< 5	8	< 5	n.a.	n.a.	n.a.	< 5	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	< 5
Σ C₂₉ - C₃₅ hopanes	258	334	391	359	n.a.	n.a.	n.a.	-	60	15	59	47	100	-	30	46

Compounds	Site no.															
	R1	R2	R3	R4	R5*	R6*	R7*	R8	R9	R10	R11	R12	R13	R14	R15	R16
Polychlorinated biphenyls (PCBs)																
PCB 28	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	110	85	94	150	280	220	120	72	170
PCB 52	n.d.	n.d.	n.d.	13	n.a.	n.a.	n.a.	93	28	84	82	150	91	53	20	57
PCB 101	< 5	11	< 5	150	n.a.	n.a.	n.a.	290	100	240	310	510	340	110	43	78
PCB 138	22	120	41	690	n.a.	n.a.	n.a.	930	48	660	980	2100	1100	310	120	230
PCB 153	18	110	52	640	n.a.	n.a.	n.a.	900	380	730	1000	2000	1200	350	120	240
PCB 180	8	330	42	520	n.a.	n.a.	n.a.	630	240	370	620	1100	680	180	73	140
Σ PCBs (6 congeners)	48	571	135	2013	n.a.	n.a.	n.a.	2953	881	2178	3142	6140	3631	1123	448	915
Various																
Mesamoll ®	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	750	97	160	400	180	260	290	350	190
Di-iso-propylnaphthalenes (DIPN)	47	75	1000	24	n.a.	n.a.	n.a.	850	1000	1700	2100	4100	1900	1200	400	770
1,2-diphenoxyethane (DPE)	< 5	13	n.d.	n.d.	n.a.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Butylated hydroxytoluene (BHT)	n.d.	< 5	n.d.	n.d.	n.a.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-benzylformamide	n.d.	n.d.	n.d.	< 5	n.a.	n.a.	n.a.	< 5	< 5	< 5	< 5	< 5	< 5	< 5	n.d.	< 5
Methyltriclosan	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.d.	n.d.	< 5	n.d.	n.d.	18	10	20	24

n.d. (not detected) means that the concentration was below the detection limit (< 1 ng/g_{TOC});

< 5 means that the concentration was below the limit of quantification and above the detection limit (1-5 ng/g_{TOC}); n.a. (not analyzed)

Table A8 Concentrations [ng/g_{TOC}] of different pollutants/pollutant groups in the Rur catchment after an extreme flood event in July 2021.

Compounds	Site no.															
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16
Linear alkylbenzenes (LABs)																
Phenyldecenes	16	< 5	n.d.	< 5	10	7	n.d.	< 5	10	52	38	47	99	170	180	130
Phenylundecanes	92	28	14	21	160	100	45	71	300	700	320	370	780	980	1400	910
Phenyldodecanes	130	45	42	30	260	160	86	100	400	1000	410	580	980	1200	1500	1100
Phenyltridecanes	130	83	5	62	500	160	80	81	320	760	410	440	850	980	1300	800
LABs	368	156	61	113	930	427	211	252	1030	2512	1178	1437	2709	3330	4380	2940
I/E ratio	0.66	0.75	0.35	0.94	1.00	1.30	2.25	2.12	1.43	1.61	1.16	1.67	1.06	1.81	1.51	1.90
Polycyclic aromatic hydrocarbons (PAHs)																
Naphthalene	840	110	< 5	16	9	960	9	36	n.d.	210	22	400	n.d.	160	320	280
Acenaphthylene	560	1200	250	51	310	310	54	460	180	940	790	240	560	210	920	490
Acenaphthene	310	1300	180	86	580	1100	120	520	290	910	240	210	720	1500	4900	1800
Fluorene	600	2600	370	140	1100	1500	250	1100	520	2100	720	270	1900	2800	8300	1400
Phenanthrene	16200	42000	5100	4400	28800	27300	5000	8100	11400	20600	19800	13400	16600	14100	39500	11000
Anthracene	2200	12700	1700	800	4400	5000	1100	3200	2600	5300	2500	1400	2400	1300	5200	2500
Fluoranthene	32100	26500	32300	10400	31700	32000	6500	3800	8400	29800	30800	39700	45600	20600	42700	10800
Pyrene	31000	30900	3900	10100	31000	33900	6800	10000	10100	25100	36500	32800	31000	14800	43700	13200
Benzo[a]anthracene	23500	51300	6400	8200	34100	32600	6100	8200	12200	27200	32500	25500	22100	7700	24500	11200
Chrysene	28900	42200	3900	10000	40700	40600	7700	7800	14500	36100	40800	38300	36600	12900	37200	13600
Benzo[b]fluoranthene	54700	103000	15900	17000	71400	69500	13500	23200	26000	62900	76500	68300	60500	18300	63700	23500
Benzo[k]fluoranthene	4000	15900	2900	1700	7000	7500	1400	3200	3700	5000	6300	3600	3100	720	2900	2400
Benzo[a]pyrene	23100	47800	7000	7200	32500	29600	5900	10000	12400	24000	30400	24800	17700	5500	21700	9500
Indeno[1,2,3-cd]pyrene	28700	61700	10600	9000	45800	38200	7500	15200	17000	36600	44800	32300	25400	16000	47600	18500
Di benzo[a,h]anthracene	5000	18500	3300	1900	11600	8700	1500	4100	4300	6400	9100	5800	2500	1200	5700	3200
Benzo[g,h,i]perylene	23600	42500	7300	6500	32200	27500	5400	10300	11700	25900	32200	24100	11000	5600	24900	10700
Σ EPA 16	275310	500210	101100	87493	373199	356270	68833	109216	135290	309060	363972	311120	277680	123390	373740	134070

Compounds	Site no.															
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16
C1 phenanthrenes and anthracenes	4800	22200	4800	2300	10200	12700	1700	6300	4300	15400	8200	4900	4700	4600	15100	7900
C1 fluoranthenes and pyrenes	11500	57200	12400	6300	26000	26700	4500	13500	9800	23700	25100	13800	11700	5200	17000	13600
Biphenyl	68	220	53	57	96	250	19	140	140	680	280	160	980	3000	8600	25800
Retene	56	280	63	180	110	900	550	610	470	680	290	250	36	47	360	290
Benzo[e]pyrene	23000	46600	7100	7000	33400	28900	5700	10100	11900	26700	32200	28000	21300	7000	26100	10100
Perylene	8200	22200	3400	2600	15000	12700	2700	4700	5800	7800	11500	6900	7000	2300	12200	5100
NSO-PAHs																
Carbazole	200	380	240	83	430	450	61	290	130	670	340	97	260	230	850	270
Dibenzothiophene	62	530	11	15	450	100	56	48	230	160	54	160	100	580	210	350
Dibenzofuran	850	3100	460	250	1200	1900	280	1200	1400	3300	1700	730	3800	12400	32400	9200
Hopanes																
trisnormeohopane (Ts)	54	46	15	50	260	51	44	64	66	36	50	90	70	37	230	18
trisnorhopane (Tm)	130	120	33	110	450	100	69	97	120	120	99	140	140	58	500	19
C ₂₉ -hopanes	850	660	200	770	2100	480	400	790	730	940	610	820	1000	430	2700	140
C ₃₀ -hopanes	970	710	200	690	2100	620	400	560	720	910	540	950	860	450	2500	150
C ₃₁ -hopanes	1700	1300	360	910	2200	710	420	840	1100	1500	860	1300	1100	480	2700	200
C ₃₂ -hopanes	650	430	140	570	1400	350	220	370	430	520	260	420	320	190	1200	99
C ₃₃ -hopanes	500	290	90	500	1100	160	170	300	320	310	230	290	380	160	980	72
C ₃₄ -hopanes	350	180	58	360	750	150	110	230	240	220	110	170	230	84	650	17
C ₃₅ -hopanes	450	190	55	450	880	170	110	220	230	220	180	170	88	88	740	40
Σ C₂₉ - C₃₅ hopanes	5470	3760	1103	4250	10530	2640	1830	3310	3770	4620	2790	4120	3978	1882	11470	718

Compounds	Site no.															
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16
Polychlorinated biphenyls (PCBs)																
PCB 28	< 5	30	< 5	n.d.	n.d.	44	82	110	210	310	160	99	400	700	1800	540
PCB 52	< 5	n.d.	< 5	n.d.	n.d.	120	25	14	78	150	40	89	82	170	250	130
PCB 101	9	74	54	40	11	1300	72	80	690	660	180	550	230	240	260	190
PCB 138	30	380	250	130	160	4700	260	420	3100	3100	980	2800	920	530	730	670
PCB 153	24	280	220	150	130	4200	270	470	2700	3100	990	2800	1000	700	770	700
PCB 180	11	280	170	79	84	3400	200	250	2200	2000	670	2300	590	480	360	460
Σ PCBs (6 congeners)	74	1044	694	399	385	13764	909	1344	8978	9320	3020	8638	3222	2820	4170	2690
Various																
Mesamoll ®	n.d.	n.d.	48	780	570	1300	n.d.	90	670	n.d	200	77	n.d	280	160	8
Di-iso-propylnaphthalenes (DIPN)	180	340	n.d.	n.d.	2600	230	140	220	14200	3800	3000	2500	4100	4200	10000	2400
1,2-diphenoxyethane (DPE)	39	< 5	n.d.	n.d.	41	16	n.d.	< 5	< 5	66	220	n.d.	66	33	800	26
Butylated hydroxytoluene (BHT)	1000	n.d.	n.d.	n.d.	53	8	n.d.	87	n.d.	330	2300	n.d.	230	n.d.	200	n.d.
N-benzylformamide	< 5	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	< 5	< 5	5	16	n.d.	6	7	47	n.d.
Methyltriclosan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22	n.d.	n.d.	81	15	n.d.

n.d. (not detected) means that the concentration was below the detection limit (< 1 ng/g_{TOC});

< 5 means that the concentration was below the limit of quantification and above the detection limit (1-5 ng/g_{TOC}); n.a. (not analyzed)

Table A9 PAH diagnostic ratios and hopane maturity indicators in samples of the Rur catchment after two flood events in January/February (Feb) and July (Jul) 2021. (*) R5 to R7 were not sampled in February.

Site no.	PAH diagnostic ratios												Hopane maturity indicators			
	An/(An+Ph)		Fl/(Fl+Py)		BaA/(BaA+Ch)		IP/(IP+Bghi)		C ₀ /(C ₀ +C ₁)		C ₀ /(C ₀ +C ₁)		Ts/(Ts+Tm)		22S/(22S+22R)	
	Feb	Jul	Feb	Jul	Feb	Jul	Feb	Jul	Feb	Jul	Feb	Jul	Feb	Jul	Feb	Jul
R1	0.06	0.12	0.62	0.51	0.42	0.45	0.62	0.55	0.89	0.85	0.81	1.40	0.22	0.29	1.00	0.68
R2	0.15	0.23	0.55	0.46	0.43	0.55	0.67	0.59	0.90	0.50	0.87	1.09	0.28	0.28	0.47	0.72
R3	0.20	0.25	0.60	0.89	0.50	0.62	0.66	0.59	0.92	0.74	0.72	0.88	0.31	0.31	0.67	0.71
R4	0.07	0.15	0.55	0.51	0.45	0.45	0.68	0.58	0.81	0.76	0.77	1.17	0.29	0.31	0.85	0.47
R5*	-	0.13	-	0.51	-	0.46	-	0.59	-	0.71	-	1.33	-	0.37	-	0.49
R6*	-	0.15	-	0.49	-	0.45	-	0.58	-	0.71	-	1.21	-	0.34	-	0.54
R7*	-	0.18	-	0.49	-	0.44	-	0.58	-	0.75	-	1.28	-	0.39	-	0.55
R8	0.19	0.28	0.54	0.28	0.45	0.51	0.60	0.60	0.85	0.51	0.76	0.92	n.d.	0.40	0.58	0.63
R9	0.19	0.19	0.57	0.45	0.47	0.46	0.66	0.59	0.89	0.65	0.75	1.25	0.38	0.35	0.70	0.64
R10	0.10	0.2	0.56	0.54	0.43	0.43	0.66	0.59	0.85	0.70	0.78	1.00	0.40	0.23	0.64	0.66
R11	0.05	0.11	0.59	0.46	0.43	0.44	0.70	0.58	0.92	0.73	0.87	1.30	0.50	0.34	0.69	0.63
R12	0.09	0.09	0.56	0.55	0.43	0.40	0.67	0.57	0.86	0.84	0.82	1.36	0.40	0.39	0.79	0.72
R13	0.10	0.13	0.55	0.60	0.44	0.38	0.59	0.70	0.86	0.87	0.78	1.40	0.48	0.33	0.62	0.60
R14	0.13	0.08	0.50	0.58	0.41	0.37	0.55	0.74	0.86	0.87	0.79	1.41	0.50	0.39	0.65	0.64
R15	0.17	0.12	0.55	0.49	0.42	0.40	0.63	0.66	0.84	0.84	0.78	1.32	0.40	0.32	0.45	0.49
R16	0.20	0.19	0.56	0.45	0.46	0.45	0.62	0.63	0.86	0.64	0.82	1.03	0.25	0.49	0.52	0.62

Appendix to Chapter 6

“Dynamic Transport and Distribution of Organic Pollutants
in Water and Sediments of the Rur River”

Table A10 Loads [g/d] of organic compounds detected in Rur river water samples (taken in November 2020).

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Pharmaceuticals																						
1	Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	<2	3	6	<2	3	48	41	57	57	63	51	41	62	124	58	49	
2	Oxcarbazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17	6	9	5	5	5	6	5	6	5	<4	
3	Caffeine	n.d.	n.d.	3	13	11	16	20	21	11	18	93	110	104	76	51	44	58	72	52	46	60	
4	Lidocaine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	125	66	74	71	76	54	46	80	99	74	67	
	Personal care products																						
5	Tocopheryl acetate	11	25	1	48	3	2	16	<3	<2	n.d.	<3	<4	<4	12	6	<4	6	12	n.d.	n.d.	6	
6	N,N,N',N'-Tetraacetylenediamine, TAED	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7	24	25	43	49	40	39	23	25	26	29	38	59	
7	4-Methoxynnicamic acid 2-ethylhexylester	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	n.d.	n.d.	n.d.	<4	<4	<4	n.d.	n.d.	<4	n.d.	
8	Drometrizole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1	n.d.	n.d.	n.d.	<4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
9	Galaxolide	1	1	<1	2	<1	3	4	n.d.	3	<2	25	28	32	30	35	33	38	52	54	51	56	
10	Tonalide	<1	<1	n.d.	<1	<1	<2	<3	n.d.	<2	n.d.	<3	<4	<4	<4	<4	<4	4	4	5	<4	<4	
11	4-Oxoisophorone	1	2	1	2	<1	<2	3	3	<2	3	5	12	11	10	9	5	8	7	4	8	11	
12	Lilial	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<4	<4	<4	<4	<4	n.d.	n.d.	n.d.	<4	n.d.	
13	Dihydromethyljasmonate	6	4	5	4	3	9	12	7	3	5	21	29	22	14	13	12	15	13	11	8	15	
14	Coumarin	n.d.	n.d.	n.d.	n.d.	n.d.	<2	<3	<3	2	12	18	13	16	19	19	14	12	12	11	14	15	
15	4-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4	4	4	4	5	7	9	9	6	<4	5	
16	Benzophenone	<1	<1	<1	1	<1	<2	3	<3	<2	<2	18	11	12	11	14	12	12	10	8	8	9	
17	Isopropylaurate	25	25	28	22	22	74	106	136	62	28	183	117	271	170	154	69	123	110	82	62	77	
18	Isopropylpalmitate	6	6	6	6	3	6	10	11	16	4	41	26	48	35	20	15	12	11	11	11	16	
19	Methyl dehydroabietate	173	122	286	163	275	467	1002	1264	858	266	1837	1436	3078	1100	764	419	536	720	445	214	665	
	Pesticides and biocides																						
20	N,N-Diethyl-m-toluamide, DEET	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27	15	17	16	15	12	11	14	17	14	14	

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Technical additives, plasticizers and other industrial compounds																					
21	Di-iso-propylnaphthalenes, DIPNs	n.d.	n.d.	n.d.	n.d.	<1	n.d.	n.d.	n.d.	n.d.	n.d.	<3	n.d.	n.d.	n.d.	n.d.	<4	<4	<4	n.d.	n.d.	n.d.
22	N-Butylbenzenesulfonamide, NBBS	n.d.	n.d.	1	3	2	2	4	4	<2	<2	67	39	39	44	40	30	23	30	31	27	29
23	2,4,4-Trimethylpentane-1,3-diol di-iso-butyrate, TXIB	6	3	4	3	4	13	24	26	12	6	42	29	34	37	33	12	26	30	14	10	11
24	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	19	17	23	7	4	8	18	30	10	18	14294	9657	9239	12498	12169	11840	8143	8277	8206	10165	9283
25	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	n.d.	2	16	6	1	n.d.	3	n.d.	<2	2	14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	Triethyl citrate	1	3	3	6	2	3	5	5	<2	2	70	45	52	47	36	22	23	30	27	36	44
27	Acetyl tributyl citrate	48	34	1	<1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
28	Triacetin	1683	1089	1351	298	542	1644	2213	3121	2673	2390	3370	6118	6579	3764	1956	234	679	1155	273	1363	1858
29	Triethyl phosphate	n.d.	n.d.	n.d.	2	3	<2	4	6	<2	3	134	93	92	128	121	93	84	109	103	130	158
30	Tributyl phosphate	2	2	<1	n.d.	n.d.	n.d.	n.d.	n.d.	<2	n.d.	13	9	6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
31	Tris(2-chloroethyl)phosphate, TCEP	n.d.	n.d.	n.d.	<1	<1	<2	<3	<3	n.d.	n.d.	8	7	6	6	5	<4	5	6	<4	7	8
32	Tris(chloropropyl)phosphates, TCP	<1	<1	1	2	2	<2	4	4	<2	<2	68	48	45	47	47	37	33	40	40	45	49
33	Triphenyl phosphate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
34	Triphenyl phosphine oxide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	157	206	107	114	135	86	49	79	63	49	52
35	Dimethyl phthalate	10	5	5	3	2	7	13	13	5	5	17	18	18	21	16	12	52	50	47	17	14
36	Diethyl phthalate	22	17	31	22	12	39	62	63	45	29	109	42	117	113	108	89	107	105	80	80	103
37	Di-iso-butyl phthalate	38	30	56	20	19	58	90	139	112	98	210	299	370	99	54	41	54	56	39	24	69
38	Di-n-butyl phthalate	127	95	99	94	33	115	149	213	215	236	344	656	970	192	80	62	206	97	71	55	355
39	Benzyl butyl phthalate	3	5	1	3	2	3	6	n.d.	6	<2	12	5	12	4	9	5	5	5	4	<4	5
40	Bis(2-ethylhexyl) phthalate, DEHP	120	153	105	252	320	478	746	414	367	255	535	186	587	588	358	402	468	1060	263	312	429
41	2,2-Dimethoxy-1,2-diphenylethane, DMPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	4	4	<4	4	<4	<4	<4	<4	n.d.	n.d.
42	Diphenoxethane, DPE	n.d.	n.d.	<1	n.d.	n.d.	<2	<3	6	n.d.	n.d.	4	<4	<4	<4	<4	n.d.	n.d.	n.d.	<4	n.d.	n.d.

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Miscellaneous contaminants																						
	Halogenated compounds																						
43	Dichloroaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	n.d.	<4	<4	<4	4	5	6	6	5	<4	
44	1,1,2,2-Tetrachloroethane	n.d.	n.d.	17	22	42	94	99	116	111	121	226	253	204	187	6	4	n.d.	n.d.	n.d.	n.d.	n.d.	
	S-containing compounds																						
45	Diphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13	9	10	11	14	14	6	10	8	8	8	
46	Methylphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25	11	8	19	16	<4	5	5	<4	6	14	
47	Benzothiazole	1	1	n.d.	1	1	<2	<3	n.d.	<2	<2	4	<4	<4	<4	<4	5	5	6	4	<4	n.d.	
48	2-Methylthiobenzothiazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	42	21	24	19	26	24	27	28	30	23	n.d.	
49	N-Phenylbenzenesulfonamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	19	21	25	23	16	15	18	22	18	17	
50	N-Ethyl-o-toluenesulfonamide	n.d.	n.d.	n.d.	n.d.	<1	n.d.	n.d.	n.d.	n.d.	n.d.	111	63	50	61	73	38	26	40	27	35	30	
51	N-Ethyl-p-toluenesulfonamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	149	58	53	59	48	37	31	39	26	30	29	
	N-containing compounds																						
52	2-Methylbenzotriazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60	46	75	44	50	106	100	163	131	101	217	
53	Quinoline	n.d.	n.d.	n.d.	2	<1	n.d.	<3	<3	<2	2	4	6	6	8	7	4	6	8	6	9	15	
54	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<4	
55	Phenylisocyanate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	129	67	78	106	100	65	9	26	23	36	66	
56	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	756	155	146	182	183	153	134	315	100	113	128	
57	N,N-Dibutyformamide	36	34	40	26	30	121	196	340	108	56	328	225	258	432	309	100	187	139	145	146	180	
	O-containing compounds																						
58	2,6-Di-tert-butyl-1,4-benzoquinone, BHT quinone	5	1	<1	<1	<1	<2	<3	n.d.	<2	<2	10	<4	4	<4	4	<4	<4	4	<4	<4	<4	
59	Butylated hydroxytoluene, BHT	1	1	1	1	<1	4	6	5	4	2	8	11	13	10	12	9	12	5	11	8	5	
60	1,3,3-Trimethyloxindole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16	6	7	8	7	5	5	5	<4	5	4	
		n.d. (not detected)																					

n.d. (not detected)

Table A11 Loads [g/d] of organic compounds detected in Rur river water samples (taken in June 2021).

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Pharmaceuticals																						
1	Carbamazepine	n.d.	<0.2	<0.2	n.s.	<2	5	7	7	6	5	19	48	50	32	21	47	44	44	45	55	49	
2	Oxcarbazepine	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<6	<6	<5	<5	<5	<5	n.d.	n.d.	n.d.	n.d.	
3	Caffeine	1	n.d.	0.3	n.s.	6	72	90	70	87	85	49	112	133	73	50	88	60	54	52	53	79	
4	Lidocaine	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	72	87	96	65	60	69	
	Personal care products																						
5	Tocopheryl acetate	1	2	2	n.s.	21	26	44	523	58	54	7	16	n.d.	n.d.	23	6	10	n.d.	9	<5	n.d.	
6	N,N,N'-Tetraacetylenediamine, TAED	n.d.	n.d.	1	n.s.	n.d.	27	18	16	16	9	17	39	16	17	35	n.d.	n.d.	16	12	16	13	
7	4-Methoxycinnamic acid 2-ethylhexylester	2	3	1	n.s.	11	22	<4	8	8	10	15	15	6	<5	5	<5	15	9	11	10	11	
8	Drometrizole	n.d.	<0.2	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
9	Galaxolide	0.3	1	<0.2	n.s.	3	22	17	34	26	8	34	64	49	40	43	48	44	53	68	78	48	
10	Tonalide	<0.2	<0.2	<0.2	n.s.	<2	<4	<4	<4	<4	<4	<5	<6	<6	<5	<5	<5	<5	<5	5	6	<5	
11	4-Oxoisophorone	1	1	1	n.s.	3	<4	7	5	15	9	5	13	9	9	10	8	12	5	5	<5	<5	
12	Lilial	<0.2	<0.2	n.d.	n.s.	<2	<4	<4	<4	n.d.	<4	<5	6	5	6	7	11	12	9	14	19	10	
13	Dihydromethyljasmonate	1	2	3	n.s.	11	33	10	23	18	21	18	31	32	18	27	25	72	19	9	14	10	
14	Coumarin	<0.2	<0.2	n.d.	n.s.	<2	<4	<4	<4	<4	<4	n.d.	<6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	n.d.	n.d.	
15	4-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<6	<6	<5	<5	<5	<5	<5	<5	n.d.	<5	
16	Benzophenone	0.3	0.5	0.2	n.s.	2	4	4	5	<4	<4	6	6	7	5	7	6	<5	<5	<5	<5	<5	
17	Isopropyl laurate	14	22	7	n.s.	53	426	219	498	129	209	282	169	471	169	261	299	131	153	26	115	100	
18	Isopropyl palmitate	18	18	30	n.s.	96	173	294	978	324	266	174	287	93	65	102	121	36	21	103	98	37	
19	Methyl dehydroabietate	35	108	23	n.s.	424	1272	677	2275	959	1934	1045	1324	5543	1452	8	2068	357	357	134	208	222	
	Pesticides and biocides																						
20	N,N-Diethyl-m-toluamide, DEET	1	1	1	n.s.	6	6	4	8	6	9	18	29	28	31	38	43	36	33	45	33	35	

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Technical additives, plasticizers and other industrial compounds																					
221	Di-iso-propylnaphthalenes, DIPNs	n.d.	<0.2	n.d.	n.s.	n.d.	<4	n.d.	<4	<4	n.d.	<5	<6	<6	<5	<5	<5	<5	<5	<5	<5	<5
222	N-Butylbenzenesulfonamide, NBBS	0.3	0.3	1	n.s.	5	12	7	6	6	5	21	32	25	15	13	17	12	12	9	11	10
223	2,4,4-Trimethylpentane-1,3-diol di-iso-butyrate, TXIB	<0.2	2	0.5	n.s.	5	14	7	24	21	55	33	24	102	31	32	30	8	9	n.d.	5	<5
224	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	4	6	169	n.s.	110	160	172	162	88	87	14556	15408	12541	12666	12665	12187	10687	10521	8601	4545	9806
225	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	3	1	1	n.s.	41	8	n.d.	7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
226	Triethylcitrate		1	1	n.s.	10	31	19	15	17	16	31	44	26	25	28	29	24	24	13	7	14
227	Acetyl tributylcitrate	1	16	4	n.s.	4	28	<4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
228	Triacetin	189	28	62	n.s.	n.d.	n.d.	n.d.	252	n.d.	n.d.	670	n.d.	403	n.d.	6383	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
229	Triethylphosphate	2	1	1	n.s.	6	23	27	22	31	18	150	174	173	125	144	120	104	93	114	89	98
230	Tributylphosphate	n.d.	n.d.	<0.2	n.s.	n.d.	n.d.	n.d.	<4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6	6	6	9	6	5	6
231	Tris(2-chloroethyl)phosphate, TCEP	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5
232	Tris(chloropropyl)phosphates, TCP	0.3	0.4	0.3	n.s.	5	11	10	10	13	12	27	61	32	31	29	38	30	37	19	24	29
233	Triphenylphosphate	<0.2	<0.2	n.d.	n.s.	<2	<4	<4	n.d.	n.d.	n.d.	<5	<6	<6	<5	<5	<5	<5	<5	<5	<5	<5
234	Triphenylphosphine oxide	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	73	50	32	17	50	31	57	28	32	79
235	Dimethyl phthalate	3	5	2	n.s.	26	54	24	57	4	17	14	15	12	13	11	12	5	5	7	7	8
236	Diethyl phthalate	9	16	8	n.s.	79	105	71	149	51	86	168	129	126	82	89	80	39	36	26	72	60
237	Di-iso-butyl phthalate	9	9	11	n.s.	81	202	88	133	87	77	159	130	451	221	244	101	50	58	44	78	33
238	Di-n-butyl phthalate	28	24	34	n.s.	307	703	287	275	122	184	370	236	242	342	235	159	70	58	77	71	63
239	Benzyl butyl phthalate	1	6	1	n.s.	13	34	27	56	6	n.d.	22	23	12	16	15	10	10	11	15	12	22
240	Bis(2-ethylhexyl) phthalate, DEHP	42	26	26	n.s.	258	1580	n.d.	501	n.d.	n.d.	n.d.	344	n.d.	n.d.	n.d.	n.d.	25	n.d.	n.d.	n.d.	n.d.
241	2,2-Dimethoxy-1,2-diphenylethane, DMPA	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<6	<6	<5	n.d.	<5	<5	<5	<5	<5	<5
242	Diphenoxethane, DPE	<0.2	1	<0.2	n.s.	<2	4	7	7	6	<4	7	7	7	<5	<5	<5	<5	<5	<5	<5	<5

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Miscellaneous contaminants																					
	Halogenated compounds																					
43	Dichloroaniline	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	<4	n.d.	<4	<4	<5	<6	<6	7	6	8	11	11	12	15	10
44	1,1,2,2-Tetrachloroethane	1	2	1	n.s.	<2	<4	<4	<4	<4	<4	<5	<6	<6	<5	<5	10	26	28	18	n.d.	15
	S-containing compounds																					
45	Diphenylsulfone	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<6	n.d.	<5	<5	<5	<5	<5	<5	<5	n.d.
46	Methylphenylsulfone	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6	7	<6	<5	6	6	5	<5	6	<5	<5
47	Benzothiazole	<0.2	<0.2	<0.2	n.s.	<2	<4	<4	<4	<4	<4	<5	6	6	7	7	7	7	6	5	5	5
48	2-Methylthiobenzothiazole	<0.2	<0.2	<0.2	n.s.	<2	<4	<4	<4	<4	<4	15	25	28	21	24	18	16	20	29	32	25
49	N-Phenylbenzenesulfonamide	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	251	6	<5
50	N-Ethyl- <i>o</i> -toluenesulfonamide	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18	32	26	14	16	27	17	13	11	14	11
51	N-Ethyl- <i>p</i> -toluenesulfonamide	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16	25	21	13	14	20	12	10	6	9	9
	N-containing compounds																					
52	2-Methylbenzotriazole	n.d.	n.d.	n.d.	n.s.	<2	4	5	7	7	7	35	48	48	49	58	70	52	55	66	35	50
53	Quinoline	<0.2	0.2	0.2	n.s.	<2	n.d.	<4	<4	<4	<4	<5	6	<6	<5	<5	<5	<5	<5	<5	<5	<5
54	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
55	Phenylisocyanate	n.d.	n.d.	n.d.	n.s.	n.d.	14	<4	n.d.	n.d.	n.d.	<5	<6	<6	<5	<5	<5	n.d.	<5	<5	<5	<5
56	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	173	114	131	107	125	113	73	62	54	31	39
57	N,N-Dibutylformamide	15	20	6	n.s.	98	258	103	256	101	338	161	152	375	119	200	205	46	45	18	36	51
	O-containing compounds																					
58	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone, BHT quinone	<0.2	0.2	<0.2	n.s.	<2	<4	<4	<4	<4	9	6	7	17	<5	6	5	<5	<5	<5	<5	<5
59	Butylated hydroxytoluene, BHT	2	2	1	n.s.	14	27	17	33	17	43	33	31	36	21	27	17	10	14	8	17	11
60	1,3,3-Trimethyloxindole	n.d.	n.d.	n.d.	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<6	<6	<5	<5	<5	<5	<5	n.d.	<5	<5
		n.s. (not sampled); n.d. (not detected)																				

n.s. (not sampled); n.d. (not detected)

Table A12 Loads [g/d] of organic compounds detected in Rur river water samples (taken in November 2021).

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Pharmaceuticals																						
1	Carbamazepine	n.d.	<0.4	<0.4	1	4	18	<3	16	11	7	62	32	34	84	101	87	54	77	82	41	107	
2	Oxcarbazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<4	<4	n.d.	n.d.	<5	<5	n.d.	n.d.	
3	Caffeine	n.d.	3	5	<1	21	48	16	52	26	30	39	40	32	20	53	51	24	49	61	31	142	
4	Lidocaine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	233	62	32	23	32	52	26	59	65	37	33	
	Personal care products																						
5	Tocopheryl acetate	n.d.	2	2	12	15	n.d.	n.d.	89	53	<3	31	25	217	445	71	1019	588	792	997	7	554	
6	N,N,N'-Tetraacetylenediamine, TAED	n.d.	n.d.	n.d.	n.d.	n.d.	31	6	20	11	25	17	25	14	5	24	14	11	22	37	15	18	
7	4-Methoxycinnamic acid 2-ethylhexylester	<0.4	<0.4	<0.4	4	2	<3	4	7	<3	<3	<3	<3	<3	<4	n.d.	n.d.	<4	<5	<5	n.d.	n.d.	
8	Drometrizole	<0.4	n.d.	n.d.	n.d.	n.d.	<3	n.d.	n.d.	n.d.	<3	4	<3	<3	<4	4	<4	<4	<5	6	<5	<5	
9	Galaxolide	<0.4	<0.4	1	4	12	19	28	63	26	21	57	75	94	124	59	61	91	183	223	149	97	
10	Tonalide	n.d.	n.d.	<0.4	<1	<2	<3	<3	5	<3	<3	5	<3	4	5	<4	<4	<4	7	9	<5	<5	
11	4-Oxoisophorone	<0.4	1	1	<1	<2	<3	<3	3	4	7	6	8	4	<4	6	5	4	7	9	8	6	
12	Lilial	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	n.d.	<3	n.d.	n.d.	n.d.	n.d.	<5	n.d.	<5	<5	
13	Dihydromethyljasmonate	1	3	4	4	57	64	35	20	27	28	47	23	24	21	14	17	13	43	27	45	23	
14	Coumarin	n.d.	<0.4	<0.4	n.d.	n.d.	n.d.	n.d.	<3	<3	<3	5	6	4	<4	<4	<4	<4	6	7	6	5	
15	4-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	<3	<3	<4	<4	n.d.	<4	<5	<5	n.d.	<5	
16	Benzophenone	<0.4	3	1	1	4	5	6	5	5	5	15	10	20	8	6	6	6	13	13	7	8	
17	Isopropyl laurate	3	5	15	21	104	89	97	159	42	114	179	183	346	174	122	53	55	278	292	65	100	
18	Isopropyl palmitate	4	1	2	18	26	12	48	157	56	95	n.d.	48	87	12	7	n.d.	41	115	66	n.d.	15	
19	Methyl dehydroabietate	32	19	54	114	557	263	1492	11907	1305	3864	1544	1462	2450	569	524	621	434	1771	1986	609	300	
	Pesticides and biocides																						
20	N,N-Diethyl- <i>m</i> -toluamide, DEET	n.d.	<0.4	n.d.	n.d.	<2	11	6	10	4	9	13	9	4	<4	13	9	6	13	17	10	13	

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Technical additives, plasticizers and other industrial compounds																						
21	Di-iso-propylnaphthalenes, DIPNs	n.d.	n.d.	<0.4	<1	<2	n.d.	<3	n.d.	n.d.	n.d.	<3	<3	<3	<4	n.d.	n.d.	n.d.	<5	<5	n.d.	n.d.	
22	N-Butylbenzenesulfonamide, NBBS	<0.4	0.5	0.5	<1	2	30	10	31	13	21	40	23	20	18	35	27	16	32	36	16	27	
23	2,4,4-Trimethylpentane-1,3-diol di-iso-butyrate, TXIB	<0.4	0.5	0.5	<1	2	<3	10	6	<3	6	26	9	18	5	<4	n.d.	<4	6	<5	n.d.	<5	
24	2,4,7,9-Tetramethyl-5-decyno-4,7-diol, TMDD	5	2	3	<1	11	33	17	36	13	32	18287	4920	4286	8076	7552	9086	6055	6925	5734	7267	8025	
25	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	2	6	19	12	36	87	31	13	98	48	87	74	147	44	41	81	74	23	9	51	292	
26	Triethylcitrate	0.5	1	1	<1	5	30	3	20	4	16	31	20	7	<4	25	15	5	29	30	19	19	
27	Acetyl tributylcitrate	4	<0.4	0.4	<1	3	19	<3	<3	<3	n.d.	<3	<3	n.d.	<4	<4	<4	n.d.	<5	<5	n.d.	6	
28	Triacetin	435	244	101	34	205	934	204	193	n.d.	129	299	156	71	n.d.	169	n.d.	n.d.	n.d.	n.d.	65	892	
29	Triethylphosphate	n.d.	<0.4	<0.4	n.d.	3	31	20	28	21	33	196	125	95	68	113	92	92	158	171	182	95	
30	Tributylphosphate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
31	Tris(2-chloroethyl)phosphate, TCEP	n.d.	<0.4	<0.4	n.d.	<2	81	19	71	26	50	52	33	17	23	50	34	18	41	53	22	23	
32	Tris(chloropropyl)phosphates, TCP	<0.4	1	1	n.d.	5	77	20	71	31	59	130	75	36	42	83	64	35	84	101	57	68	
33	Triphenylphosphate	n.d.	n.d.	<0.4	<1	<2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5	5	n.d.	n.d.	
34	Triphenylphosphine oxide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	n.d.	140	39	33	29	95	111	51	56	40	26	96	
35	Dimethyl phthalate	<0.4	2	2	2	2	34	12	12	26	21	24	27	35	4	16	22	25	16	5	19	17	
36	Diethyl phthalate	2	11	16	8	31	103	81	22	114	97	118	107	164	82	56	91	91	81	64	106	189	
37	Di-iso-butyl phthalate	18	13	10	10	40	78	90	105	62	97	102	74	88	63	44	87	44	106	102	88	100	
38	Di-n-butyl phthalate	81	70	23	56	114	298	103	189	164	136	153	103	140	96	78	179	123	195	209	260	169	
39	Benzyl butyl phthalate	0.4	<0.4	1	2	11	4	3	n.d.	<3	n.d.	3	<3	5	n.d.	n.d.	n.d.	n.d.	14	8	n.d.	<5	
40	Bis(2-ethylhexyl) phthalate, DEHP	50	17	48	272	255	206	102	675	411	305	134	13	274	13	n.d.	443	199	552	391	470	119	
41	2,2-Dimethoxy-1,2-diphenylethane, DMPA	<0.4	<0.4	<0.4	<1	<2	<3	<3	<3	<3	<3	16	<3	3	<4	n.d.	n.d.	<4	5	<5	n.d.	<5	
42	Diphenoxethane, DPE	<0.4	0.5	0.4	2	8	8	18	20	8	11	7	6	12	20	12	<4	<4	9	6	n.d.	8	

No.	Compounds	Site no.																					
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	
	Miscellaneous contaminants																						
	Halogenated compounds																						
43	Dichloroaniline	n.d.	n.d.	n.d.	<1	<2	n.d.	n.d.	n.d.	n.d.	3	<3	<3	<4	<4	<4	n.d.	<4	<5	6	<5	<5	
44	1,1,2,2-Tetrachloroethane	<0.4	8	4	6	10	19	88	62	71	78	56	94	155	n.d.	n.d.	n.d.	167	101	122	154	80	
	S-containing compounds																						
45	Diphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<3	<3	<3	4	9	8	4	8	9	5	8	
46	Methylphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	6	n.d.	n.d.	7	<4	n.d.	<4	<5	5	6	n.d.	
47	Benzothiazole	n.d.	1	<0.4	<1	2	<3	3	5	<3	<3	4	4	<3	6	<4	n.d.	<4	<5	<5	n.d.	n.d.	
48	2-Methylthiobenzothiazole	n.d.	<0.4	<0.4	<1	<2	<3	<3	<3	<3	48	12	15	22	12	12	8	15	29	41	19	15	
49	N-Phenylbenzenesulfonamide	n.d.	n.d.	2	<1	n.d.	13	<3	6	<3	4	5	4	4	<4	11	7	4	7	13	6	15	
50	N-Ethyl- <i>o</i> -toluenesulfonamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	66	18	9	4	28	14	7	22	31	15	13		
51	N-Ethyl- <i>p</i> -toluenesulfonamide	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	1	7	n.d.	5	57	17	8	4	28	13	5	17	23	10	13	
	N-containing compounds																						
52	2-Methylbenzotriazole	n.d.	n.d.	n.d.	<1	<2	n.d.	<3	4	<3	<3	84	31	22	22	34	25	27	50	68	67	37	
53	Quinoline	n.d.	n.d.	<0.4	n.d.	n.d.	n.d.	n.d.	n.d.	<3	<3	<3	<3	<3	<4	<4	<4	<4	<5	<5	<5	<5	
54	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
55	Phenylisocyanate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	664	120	232	125	94	49	205	64	57	15	42		
56	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	445	60	76	247	66	228	258	44	134	173	526		
57	N,N-Dibutylformamide	1	2	3	4	11	13	22	23	9	37	72	44	65	8	20	13	13	30	37	42	22	
	O-containing compounds																						
58	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone, BHT quinone	1	11	4	4	13	12	22	31	10	24	48	49	91	36	24	13	13	44	54	18	23	
59	Butylated hydroxytoluene, BHT	1	6	2	4	8	11	10	25	13	17	24	16	30	19	8	9	12	19	20	16	9	
60	1,3,3-Trimethyloxindole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8	<3	<3	<4	<4	<4	<4	<5	<5	<5	<5	
		n.d. (not detected)																					

n.d. (not detected)

Table A13 Loads [g/d] of organic compounds detected in Rur river water samples (taken in May 2022).

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Pharmaceuticals																					
1	Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2	58	30	29	38	26	43	41	44	76	73	115
2	Oxcarbazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3	Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	56	86	81	34	56	31	89	34	45	35	71	54	60	47	100	133
4	Lidocaine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21	27	74	34	40	28	35	68	48
	Personal care products																					
5	Tocopheryl acetate	n.d.	n.d.	n.d.	n.d.	400	703	n.d.	167	1355	377	n.d.	n.d.	n.d.	n.d.	n.d.	380	815	n.d.	n.d.	n.d.	n.d.
6	N,N,N'-Tetraacetylenediamine, TAED	n.d.	n.d.	n.d.	<0.5	n.d.	8	8	5	<2	4	n.d.	n.d.	7	<3	<3	6	4	5	5	8	6
7	4-Methoxycinnamic acid 2-ethylhexylester	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8	Drometrizole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9	Galaxolide	<0.5	0.5	<0.5	1	3	13	6	8	6	2	31	26	12	33	33	30	30	24	63	46	33
10	Tonalide	n.d.	<0.5	n.d.	<0.5	n.d.	<2	<2	<2	<2	n.d.	9	<2	<2	<3	3	<3	<3	<4	7	4	<4
11	4-Oxoisophorone	1	1	1	1	2	<2	5	6	7	9	5	7	3	<3	<3	<3	<3	<4	<4	6	<4
12	Lilial	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
13	Dihydromethyljasmonate	4	6	5	6	23	53	41	28	16	18	6	23	16	25	15	153	48	27	46	47	25
14	Coumarin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6	3	<2	n.d.	<3	<3	<3	<4	<4	<4	n.d.
15	4-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
16	Benzophenone	<0.5	4	2	4	4	5	4	4	4	3	12	30	6	12	13	23	13	13	27	21	16
17	Isopropyl laurate	2	47	24	46	120	182	152	131	148	141	138	472	214	97	129	1337	507	394	810	474	341
18	Isopropylpalmitate	n.d.	n.d.	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
19	Methyl dehydroabietate	47	246	80	224	470	2162	626	306	386	658	265	1045	709	300	287	3860	1578	658	2678	1163	490
	Pesticides and biocides																					
20	N,N-Diethyl-m-toluamide, DEET	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	23	8	8	7	10	14	20	24	34	55	30

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Technical additives, plasticizers and other industrial compounds																					
21	Di-iso-propylnaphthalenes, DIPNs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<2	<2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
22	N-Butylbenzenesulfonamide, NBBS	1	0.5	n.d.	n.d.	n.d.	3	3	2	<2	3	79	29	25	24	20	27	27	29	28	40	32
23	2,4,4-Trimethylpentane-1,3-diol di-iso-butyrate, TXIB	1	13	4	9	20	31	39	17	43	35	9	62	41	15	23	101	92	58	99	55	47
24	2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	2	1	14	5	10	268	60	79	23	45	12194	3842	5226	5994	4876	4109	3928	4254	4151	4644	3663
25	(1-Hydroxycyclohexyl)phenylketone, Irgacure 184	7	4	11	11	45	117	30	28	54	19	49	38	90	48	47	102	107	50	46	41	126
26	Triethyl citrate	73	45	45	16	234	135	254	204	121	174	104	132	80	515	173	730	295	382	322	1027	683
27	Acetyl tributyl citrate	19	2	1	n.d.	5	57	15	21	20	43	26	35	9	3	3	235	30	7	72	22	20
28	Triacetin	97	755	666	209	285	3576	1907	560	766	909	n.d.	954	3610	n.d.	58	6133	5339	3152	5004	2076	990
29	Triethyl phosphate	n.d.	<0.5	n.d.	n.d.	<1	3	4	2	<2	6	135	53	45	49	69	47	53	61	65	147	67
30	Tributyl phosphate	n.d.	13	5	4	2	95	6	22	<2	8	12	19	47	17	9	259	132	14	200	60	18
31	Tris(2-chloroethyl)phosphate, TCEP	4	<0.5	<0.5	n.d.	<1	<2	<2	<2	<2	<2	18	4	8	<3	<3	<3	4	<4	<4	8	7
32	Tris(chloropropyl)phosphates, TCP	3	<0.5	1	<0.5	3	6	6	5	4	7	72	40	33	25	26	35	38	37	49	63	60
33	Triphenyl phosphate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
34	Triphenyl phosphine oxide	n.d.	n.d.	n.d.	n.d.	n.d.	<2	<2	<2	<2	<2	130	45	24	25	32	31	28	27	25	71	57
35	Dimethyl phthalate	1	1	1	1	3	5	10	5	10	5	6	12	6	6	8	13	10	17	12	10	20
36	Diethyl phthalate	6	9	10	13	45	91	52	32	58	37	53	95	93	60	46	112	94	68	94	68	100
37	Di-iso-butyl phthalate	20	42	28	38	62	282	109	123	54	137	288	91	280	58	68	599	334	183	535	234	132
38	Di-n-butyl phthalate	84	51	49	97	66	253	116	123	95	147	317	83	368	190	132	473	280	211	414	185	251
39	Benzyl butyl phthalate	1	3	<0.5	3	3	13	7	7	<2	4	86	17	3	9	6	24	8	<4	19	17	13
40	Bis(2-ethylhexyl) phthalate, DEHP	210	46	51	132	99	66	586	371	86	80	n.d.	n.d.	463	254	1134	478	320	n.d.	28	n.d.	922
41	2,2-Dimethoxy-1,2-diphenylethane, DMPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	23	13	7	18	10	5	5	5	8	7	5
42	Diphenoxethane, DPE	2	5	5	6	12	12	11	10	9	7	8	39	16	39	7	47	29	26	48	55	94

No.	Compounds	Site no.																				
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22
	Miscellaneous contaminants																					
	Halogenated compounds																					
43	Dichloroaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
44	1,1,2,2-Tetrachloroethane	n.d.	n.d.	n.d.	8	n.d.	8	9	n.d.	<2	<2	<2	n.d.	n.d.	<3	<3	5	108	104	98	44	<4
	S-containing compounds																					
45	Diphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2613	1031	1540	745	16	544	256	423	<4	169	5
46	Methylphenylsulfone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22	8	<2	n.d.	14	<3	4	<4	n.d.	13	n.d.
47	Benzothiazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<4
48	2-Methylthiobenzothiazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22	16	<2	20	n.d.	n.d.	n.d.	13	76	25	19
49	N-Phenylbenzenesulfonamide	n.d.	n.d.	n.d.	114	4	4	6	n.d.	n.d.	n.d.	10	4	6	n.d.	n.d.	3	4	4	n.d.	11	9
50	N-Ethyl- <i>o</i> -toluenesulfonamide	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	49	22	16	8	16	16	19	19	12	29	16
51	N-Ethyl- <i>p</i> -toluenesulfonamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	69	17	16	10	6	15	22	19	14	31	18
	N-containing compounds																					
52	2-Methylbenzotriazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27	14	4	<3	11	7	13	14	14	45	15
53	Quinoline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
54	2,3-Diethyl-2,3-dimethylsuccinonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
55	Phenylisocyanate	n.d.	<0.5	n.d.	<0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	275	67	66	89	47	57	73	82	73	149	72
56	Azobisisobutyronitrile, AIBN / Tetramethylsuccinonitrile, TMSN	n.d.	n.d.	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.	n.d.	216	87	58	73	92	60	63	89	82	101	46
57	N,N-Dibutylformamide	2	93	53	43	124	161	364	114	283	193	164	65	317	113	156	540	369	399	356	433	236
	O-containing compounds																					
58	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone, BHT quinone	1	15	3	9	13	24	22	14	31	27	40	88	29	53	59	119	72	52	80	87	69
59	Butylated hydroxytoluene, BHT	1	3	6	8	20	35	29	22	36	20	6	7	11	5	25	124	64	36	91	51	41
60	1,3,3-Trimethyloxindole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7	3	<2	<3	<3	<3	<3	<4	<4	4	<4
n.d. (not detected)																						

n.d. (not detected)

Table A14 Amounts [ng/g_{TOC}] of organic compounds detected in Rur riverbed samples (taken in November 2020).

No.	Compounds	Site no.																R19	R20
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18		
	Linear alkylbenzenes, LABs																		
1	Phenyldecane (C ₁₀)	n.s.	25	16	n.d.	< 5	32	15	35	140	n.d.	n.d.	110	400	140	220	170	190	49
2	Phenylundecane (C ₁₁)	n.s.	150	110	43	55	260	140	210	760	1300	45	600	2400	750	1000	910	920	250
3	Phenyltridecane (C ₁₃)	n.s.	220	150	99	110	430	220	330	940	1100	120	750	2900	990	1100	1200	990	330
4	Phenyltridecane (C ₁₃)	n.s.	280	200	170	150	590	250	760	1000	630	120	810	1800	820	810	1100	800	340
	Σ LABs	-	675	476	312	315	1312	625	1335	2840	3030	285	2270	7500	2700	3130	3380	2900	969
	Polychlorinated biphenyls, PCBs																		
5	Cl ₃ -PCB (PCB 28)	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	35	370	330	2300	7	120	670	190	1200	290	360	59
6	Cl ₄ -PCB (PCB 52)	n.s.	n.d.	n.d.	n.d.	5	n.d.	60	67	120	690	< 5	54	290	74	310	91	84	31
7	Cl ₅ -PCB (PCB 101)	n.s.	75	18	10	56	n.d.	160	270	240	660	14	210	270	190	440	500	110	130
8	Cl ₆ -PCB (PCB 138)	n.s.	440	87	46	280	13	420	1300	660	1600	110	900	260	760	1200	1900	330	490
9	Cl ₆ -PCB (PCB 153)	n.s.	450	88	39	240	9	400	1200	610	2000	100	840	350	710	1200	1700	310	470
10	Cl ₇ -PCB (PCB 180)	n.s.	400	70	15	230	9	190	1200	410	800	41	640	45	430	610	1200	170	350
	Σ PCBs (6 representative congeners)	-	1365	263	110	811	31	1265	4407	2370	8050	272	2764	1885	2354	4960	5681	1364	1530
	Polycyclic aromatic hydrocarbons, PAHs																		
11	Acenaphthylene	n.s.	1400	1400	84	300	2100	340	220	350	780	150	460	170	260	1000	390	600	270
12	Acenaphthene	n.s.	2900	890	44	320	1200	1800	420	280	1800	89	400	280	990	3400	1300	2600	780
13	Fluorene	n.s.	3200	1200	86	620	2700	2000	560	800	3100	170	820	570	990	5300	1600	4100	1400
14	Phenanthrene	n.s.	36400	19800	2700	9100	45400	17300	18500	11200	23500	2500	14000	4200	11900	19100	19500	14100	8100
15	Anthracene	n.s.	5100	1600	370	2100	1400	2000	1000	2200	2100	560	2400	750	2300	5100	1400	3100	3200
16	Fluoranthene	n.s.	48300	35600	6300	13800	73300	33500	40600	21600	30800	10000	26800	9500	15900	24100	27400	15500	8000
17	Pyrene	n.s.	33300	27900	4800	11100	57400	24000	31500	16400	21600	7100	21800	7300	12600	20400	22500	12700	6400
18	Benz[<i>a</i>]anthracene	n.s.	16600	17500	2700	7500	22600	5400	20500	6500	8500	4400	13100	3900	7200	15100	9200	7700	4100
19	Triphenylene / Chrysene	n.s.	18900	21300	4300	9200	29100	6400	22700	8900	12700	5000	16300	5400	9900	18500	13800	10400	5900
20	Benz[<i>b</i>]fluoranthene	n.s.	25200	27200	6800	11900	9700	13100	24600	7700	9200	3700	25700	7900	11400	26300	17700	15100	7800
21	Benz[<i>k</i>]fluoranthene	n.s.	1800	1300	510	940	570	450	830	270	280	220	1700	510	660	1800	390	850	570
22	Benz[<i>a</i>]pyrene	n.s.	8500	8000	2700	5300	3300	2100	7100	2300	1900	1300	10200	2500	3500	9000	4100	4900	2900
23	Naphthalene	n.s.	2300	2100	600	1200	4500	680	3800	3600	6600	730	1200	2200	3000	20900	7300	16000	6400
24	Indeno[1,2,3- <i>cd</i>]pyrene	n.s.	5200	5900	3100	3500	1300	7300	2300	1400	1400	740	10400	2100	3500	8000	4000	5100	3300
25	Benz[<i>g,h,i</i>]perylene	n.s.	2800	3400	2600	2800	880	4300	1400	1300	690	580	6800	1300	2200	5600	2900	3500	2500
26	Dibenz[<i>a,h</i>]anthracene	n.s.	700	970	510	740	530	2200	460	110	210	120	2000	310	600	1700	610	960	630
	Σ EPA 16 PAHs	-	212600	176060	38204	80420	255980	122870	176490	84910	125160	37359	154080	48890	86900	185300	134090	117210	62250

No.	Compounds	Site no.																	
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
	Industrial compounds																		
27	Di-iso-propylnaphthalenes, DIPNs	n.s.	24	76	16	38	370	440	240	6200	1200	330	1300	5800	3700	2800	2200	1800	260
28	Diphenoxyethane, DPE	n.s.	n.d.	16	25	33	120	13	37	110	44	30	18	19	24	24	56	36	8
29	Mesamoll®	n.s.	n.d.	130	200	310	n.d.	n.d.	110	130	200	19	24	300	140	190	150	230	66
30	Butylated hydroxytoluene, BHT	n.s.	71	< 5	9	< 5	67	8	42	7	n.d.	14	11	< 5	18	13	78	20	n.d.
31	Dichlorobenzenes (Cl ₂)	n.s.	n.d.	8	n.d.	< 5	< 5	< 5	35	51	86	17	40	123	49	266	84	498	60
32	Trichlorobenzenes (Cl ₃)	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	10	56	n.d.	16	89	17	119	31	247	24
33	Tetrachlorobenzenes (Cl ₄)	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	5	n.d.	< 5	< 5	< 5	< 5	n.d.	11	< 5
34	Pentachlorobenzene (Cl ₅)	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5	n.d.	< 5	< 5	< 5	< 5	n.d.	< 5	< 5
35	Hexachlorobenzene (Cl ₆)	n.s.	n.d.	n.d.	< 5	< 5	n.d.	< 5	< 5	< 5	10	n.d.	< 5	< 5	< 5	7	n.d.	< 5	< 5
	Σ Chlorinated benzenes (Cl ₂ to Cl ₆)	-	n.d.	8	n.d.	n.d.	n.d.	n.d.	35	61	157	17	56	212	66	392	115	756	84
	Pesticide residues																		
36	Dichlorodiphenyldichloroethylene, DDE	n.s.	n.d.	n.d.	14	9	6	< 5	10	180	n.d.	n.d.	n.d.	11	< 5	10	n.d.	n.d.	< 5
37	Dichlorodiphenyldichloroethane, DDD	n.s.	n.d.	160	10930	85	280	16	130	n.d.	88	21	42	14	86	78	130	100	80
	Σ DDX	-	n.d.	160	10944	94	286	16	140	180	88	21	42	25	86	88	130	100	80
	Personal care products																		
38	Methyltridosan	n.s.	n.d.	< 5	n.d.	n.d.	6	n.d.	n.d.	n.d.	< 5	n.d.	13	34	14	160	44	160	14
39	Octocrylene	n.s.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		n.s. (not sampled); n.d. (not detected)																	

n.s. (not sampled); n.d. (not detected)

Table A15 Amounts [ng/g_{TOC}] of organic compounds detected in Rur riverbed samples (taken in June 2021).

No.	Compounds	Site no.																R19	R20
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18		
	Linear alkylbenzenes, LABs																		
1	Phenyldecane (C ₁₀)	n.d.	n.d.	76	40	110	n.d.	5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	88	n.d.	220	n.s.	n.d.
2	Phenylundecane (C ₁₁)	17	62	69	100	85	18	32	73	150	1200	240	250	440	900	98	1200	n.s.	55
3	Phenyldecane (C ₁₂)	52	140	92	150	50	27	58	93	310	2000	450	500	1000	1200	160	1500	n.s.	160
4	Phenyltridecane (C ₁₃)	99	240	170	250	52	27	120	94	440	1900	650	560	1000	1100	150	1200	n.s.	160
	Σ LABs	168	442	407	540	297	72	215	260	900	5100	1340	1310	2440	3288	408	4120	-	375
	Polychlorinated biphenyls, PCBs																		
5	Cl ₃ -PCB (PCB 28)	n.d.	340	n.d.	8	n.d.	n.d.	65	82	1300	620	160	n.d.	18	15	88	720	n.s.	n.d.
6	Cl ₄ -PCB (PCB 52)	n.d.	n.d.	n.d.	46	n.d.	n.d.	210	31	200	150	250	n.d.	9	40	7	310	n.s.	n.d.
7	Cl ₅ -PCB (PCB 101)	10	n.d.	<5	470	13	7	2400	170	680	460	120	140	20	210	70	890	n.s.	12
8	Cl ₆ -PCB (PCB 138)	54	n.d.	69	1500	33	32	10000	1100	2900	1400	370	760	250	770	480	3300	n.s.	200
9	Cl ₆ -PCB (PCB 153)	30	n.d.	59	1400	31	34	9500	1100	2600	1400	360	740	260	780	410	3100	n.s.	190
10	Cl ₇ -PCB (PCB 180)	n.d.	n.d.	29	1100	18	20	7000	730	1600	650	240	480	81	540	230	2100	n.s.	110
	Σ PCBs (6 representative congeners)	94	340	157	4524	95	93	29175	3213	9280	4680	1500	2120	638	2355	1285	10420	-	512
	Polycyclic aromatic hydrocarbons, PAHs																		
11	Acenaphthylene	170	130	2600	170	260	190	220	9900	790	450	480	36	140	56	110	290	n.s.	150
12	Acenaphthene	1200	1900	3300	710	550	1500	1600	5900	710	1500	1100	210	230	340	300	2400	n.s.	610
13	Fluorene	1400	2400	5300	1200	1100	3700	2200	16400	1000	2200	1500	360	510	870	820	3500	n.s.	990
14	Phenanthrene	42300	65400	71300	58900	11500	9200	50600	168000	41400	44300	42100	15700	6400	15300	9900	54200	n.s.	4800
15	Anthracene	4100	7000	22400	19800	3500	5300	18400	43200	2900	6600	8100	2200	1300	2300	1300	9200	n.s.	1200
16	Fluoranthene	70000	116000	25500	228000	32700	12700	109000	79200	70900	60100	69200	39400	7400	22700	12100	69200	n.s.	2900
17	Pyrene	57700	95200	73700	196000	20900	8900	58400	119000	55300	54100	61500	31200	8200	18400	9500	54600	n.s.	5200
18	Benz[<i>a</i>]anthracene	49600	70400	42400	165000	22800	12000	54800	56300	27600	34300	51600	21800	7600	13400	8900	32000	n.s.	4900
19	Triphenylene / Chrysene	60500	91000	26400	196000	27100	13400	63100	72400	44100	43400	57800	30800	9900	17400	12200	43200	n.s.	5900
20	Benz[<i>b</i>]fluoranthene	102000	127000	78800	303000	42600	22900	118000	125000	72000	62700	99500	56800	16600	28700	22100	67200	n.s.	10300
21	Benz[<i>k</i>]fluoranthene	7100	7900	13900	24700	4400	4100	11900	9500	3700	5000	9600	3300	1700	2000	1400	4600	n.s.	1100
22	Benz[<i>a</i>]pyrene	40800	46200	37800	128000	19100	10800	48400	54900	24800	29400	48700	20700	7100	11400	8000	26600	n.s.	4400
23	Naphthalene	640	820	1700	5200	280	680	2200	3500	7700	5500	6400	2100	1000	3100	3500	11700	n.s.	4300
24	Indeno[1,2,3- <i>cd</i>]pyrene	38700	40900	40000	113000	18000	10300	47200	55100	24000	21200	38100	23200	7200	8600	9100	21900	n.s.	5000
25	Benz[<i>g,h,i</i>]perylene	30400	32100	29800	79800	13800	7700	37100	44700	19300	16700	29300	19300	5500	7200	7200	18800	n.s.	3800
26	Dibenz[<i>a,h</i>]anthracene	7100	7200	12300	19100	4000	3100	10800	9700	3100	3600	6900	4200	1700	1300	2000	3400	n.s.	1200
	Σ EPA 16 PAHs	513710	711550	487200	1538580	222590	126470	633920	872700	399300	391050	531880	271306	82480	153066	108430	422790	-	56750

No.	Compounds	Site no.																	
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
	Industrial compounds																		
27	Di-iso-propylnaphthalenes, DIPNs	450	2300	150	850	n.d.	n.d.	240	180	570	3500	2900	1700	590	1000	340	8300	n.s.	n.d.
28	Diphenoxyethane, DPE	25	n.d.	150	260	18	< 5	33	33	200	71	49	n.d.	n.d.	13	n.d.	n.d.	n.s.	7
29	Mesamoll®	3600	n.d.	930	7900	510	600	1000	760	1000	420	190	n.d.	200	n.d.	210	180	n.s.	110
30	Butylated hydroxytoluene, BHT	11	n.d.	71	130	< 5	< 5	n.d.	45	110	40	13	n.d.	n.d.	n.d.	< 5	n.d.	n.s.	< 5
31	Dichlorobenzenes (Cl ₂)	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	7	30	64	30	< 5	n.d.	11	45	57	n.s.	n.d.
32	Trichlorobenzenes (Cl ₃)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	16	24	n.s.	n.d.
33	Tetrachlorobenzenes (Cl ₄)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.s.	n.d.
34	Pentachlorobenzene (Cl ₅)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.s.	n.d.
35	Hexachlorobenzene (Cl ₆)	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.s.	n.d.
	Σ Chlorinated benzenes (Cl ₂ to Cl ₆)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7	30	64	30	n.d.	n.d.	11	61	81	-	n.d.
	Pesticide residues																		
36	Dichlorodiphenyldichloroethylene, DDE	n.d.	n.d.	18	17	13	< 5	180	84	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	46	n.s.	11
37	Dichlorodiphenyldichloroethane, DDD	n.d.	n.d.	n.d.	n.d.	9	39	n.d.	33	630	160	100	n.d.	n.d.	40	180	85	n.s.	71
	Σ DDX	n.d.	n.d.	18	17	22	39	180	117	681	160	100	n.d.	n.d.	40	180	131	-	82
	Personal care products																		
38	Methyltridosan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.s.	11
39	Octocrylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27	n.d.	n.d.	8	n.d.	n.d.	n.d.	n.d.	n.d.	n.s.	n.d.
n.s. (not sampled); n.d. (not detected)																			

n.s. (not sampled); n.d. (not detected)

Table A16 Amounts [ng/g_{TOC}] of organic compounds detected in Rur riverbed samples (taken in November 2021).

No.	Compounds	Site no.																R19	R20
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18		
1	Linear alkylbenzenes, LABs																		
2	Phenyldecane (C ₁₀)	17	< 5	18	n.d.	n.d.	n.d.	10	32	92	120	15	55	80	11	< 5	41	120	19
3	Phenylundecane (C ₁₁)	74	62	95	5	30	24	140	330	1500	2400	630	1000	2100	880	580	960	1700	430
4	Phenyltridecane (C ₁₃)	120	93	120	14	56	46	280	430	1600	2600	870	1600	2500	1400	880	1400	2200	620
5	Σ LABs	170	120	120	20	97	110	260	470	1100	2500	750	1500	1600	1200	650	1200	3400	560
6		381	275	353	39	183	180	690	1262	4292	7620	2265	4155	6280	3491	2110	3601	7420	1629
7	Polychlorinated biphenyls, PCBs																		
8	Cl ₃ -PCB (PCB 28)	8	n.d.	n.d.	n.d.	n.d.	n.d.	22	900	630	1300	170	180	260	170	240	400	670	59
9	Cl ₄ -PCB (PCB 52)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8	670	240	290	38	200	110	35	8	180	140	10
10	Cl ₅ -PCB (PCB 101)	< 5	8	7	n.d.	n.d.	n.d.	120	4100	730	820	230	790	410	110	42	440	220	43
11	Cl ₆ -PCB (PCB 138)	17	50	37	n.d.	n.d.	< 5	400	15800	2700	2800	800	4300	1500	460	190	990	610	190
12	Cl ₇ -PCB (PCB 153)	20	50	39	n.d.	n.d.	< 5	400	17200	2900	3000	860	4400	1700	530	210	1100	610	190
13	Σ PCBs (6 representative congeners)	12	38	16	n.d.	n.d.	n.d.	220	13100	2200	2500	430	3400	1000	250	74	510	380	100
14		57	146	99	n.d.	n.d.	n.d.	1148	51770	9400	10710	2528	13270	4980	1555	764	3620	2630	592
15	Polycyclic aromatic hydrocarbons, PAHs																		
16	Acenaphthylene	8	150	2500	720	210	69	47900	150	750	220	540	390	35	63	360	140	500	380
17	Acenaphthene	130	1100	620	890	17	1700	34800	1300	71	3800	520	270	220	330	3700	1800	3200	1900
18	Fluorene	5	2000	2500	1200	320	4100	90400	2700	3500	24700	1300	1100	320	680	3800	2800	4600	2100
19	Phenanthrene	7400	64400	70400	20400	16100	34500	269000	55200	42200	109000	32700	28700	16000	7900	17800	45000	37100	16300
20	Anthracene	1100	9800	6900	2500	2000	6300	296000	13500	9500	127000	10200	6300	3200	1900	3400	7400	6500	2900
21	Fluoranthene	41200	75600	79700	12000	45900	43900	248000	161000	23300	120000	112000	133000	81200	25300	21900	73600	74500	18700
22	Pyrene	31100	93700	86700	13500	32000	37400	230000	68500	21800	77200	88700	90700	37600	19500	19800	54900	64900	15300
23	Benz[<i>a</i>]anthracene	16900	84700	73700	14900	18200	28400	314000	96700	49400	281000	51700	54100	38300	11100	12100	27700	37100	9800
24	Triphenylene / Chrysene	25000	102000	102000	19400	24500	34900	277000	121000	61200	328000	76100	90200	54200	17000	16800	39600	57300	15300
25	Benz[<i>b</i>]fluoranthene	40800	149000	147000	31300	32000	58600	623000	189000	69800	361000	98500	142000	86500	27200	25200	52100	87300	22000
26	Benz[<i>k</i>]fluoranthene	2000	12800	10200	2900	1700	5100	74900	14400	7600	31100	6300	9000	6500	1400	2000	3500	6000	1500
27	Benz[<i>a</i>]pyrene	13800	61200	49500	13100	12100	24300	233000	82000	39800	161000	36600	58600	36900	9700	10600	21300	36100	9200
28	Naphthalene	100	510	1000	570	160	250	3400	180	n.d.	n.d.	710	620	220	1400	6300	3100	5500	8700
29	Indeno[1,2,3- <i>cd</i>]pyrene	17100	56200	68100	17500	11400	27800	295000	80100	38100	109000	28300	57000	39500	11000	10700	19500	39100	8600
30	Benz[<i>g,h,i</i>]perylene	14000	40000	50400	13400	7800	20100	189000	64000	29000	76200	17900	47000	33100	9000	8100	15000	29800	6500
31	Dibenz[<i>a,h</i>]anthracene	2500	12100	12900	3400	1500	5200	62600	14600	7200	17100	4500	9000	6500	1400	1900	3200	6200	1500
32	Σ EPA 16 PAHs	213143	765260	764120	167680	205907	332619	3288000	964330	403221	1826320	566570	727980	440295	144873	164460	370640	495700	140680

No.	Compounds	Site no.																	
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
	Industrial compounds																		
27	Di-iso-propylnaphthalenes, DIPNs	240	180	230	5	130	< 5	780	2400	12200	33000	3700	3800	4300	2300	1800	1500	2300	470
28	Diphenoxymethane, DPE	12	350	160	< 5	2200	13	11	750	25	n.d.	16	n.d.	n.d.	< 5	15	6	230	11
29	Mesamoll®	610	340	400	14	1900	660	< 5	520	470	11	37	n.d.	n.d.	n.d.	30	790	280	n.d.
30	Butylated hydroxytoluene, BHT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
31	Dichlorobenzenes (Cl ₂)	< 5	< 5	9	n.d.	n.d.	n.d.	n.d.	5	79	76	19	55	40	65	31	71	329	51
32	Trichlorobenzenes (Cl ₃)	< 5	< 5	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	42	n.d.	6	9	5	< 5	14	117	15
33	Tetrachlorobenzenes (Cl ₄)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
34	Pentachlorobenzene (Cl ₅)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
35	Hexachlorobenzene (Cl ₆)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Σ Chlorinated benzenes (Cl ₂ to Cl ₆)	n.d.	n.d.	9	n.d.	n.d.	n.d.	n.d.	5	79	118	19	61	49	70	31	85	446	66
	Pesticide residues																		
36	Dichlorodiphenyldichloroethylene, DDE	n.d.	n.d.	n.d.	5	n.d.	14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	29	24	24
37	Dichlorodiphenyldichloroethane, DDD	n.d.	n.d.	n.d.	5	n.d.	540	n.d.	450	n.d.	n.d.	n.d.	990	n.d.	n.d.	n.d.	n.d.	62	31
	Σ DDX	n.d.	n.d.	n.d.	10	n.d.	554	n.d.	450	n.d.	n.d.	n.d.	990	n.d.	n.d.	n.d.	29	86	55
	Personal care products																		
38	Methyltrichlorosil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
39	Octocrylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d. (not detected)																		

n.d. (not detected)

Table A17 Amounts [ng/g_{TOC}] of organic compounds detected in Rur riverbed samples (taken in May 2022).

No.	Compounds	Site no.																R19	R20
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18		
	Linear alkylbenzenes, LABs																		
1	Phenyldecane (C ₁₀)	n.d.	n.d.	n.d.	17	n.d.	< 5	< 5	19	64	280	130	130	200	210	81	120	150	27
2	Phenylundecane (C ₁₁)	< 5	40	56	56	31	28	89	120	740	1800	1300	1400	1500	1600	660	1000	1000	190
3	Phenyltridecane (C ₁₃)	6	85	60	54	67	32	140	190	890	1900	1900	2100	2100	2400	740	1200	1500	260
4	Phenyltridecane (C ₁₃)	n.d.	120	88	180	210	70	270	450	910	1600	2800	2100	2300	2300	670	1000	1600	280
	Σ LABs	6	245	204	307	308	130	499	779	2604	5580	6130	5730	6100	6510	2151	3320	4250	757
	Polychlorinated biphenyls, PCBs																		
5	Cl ₃ -PCB (PCB 28)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	200	630	620	780	560	130	410	320	350	490	170	65
6	Cl ₄ -PCB (PCB 52)	n.d.	n.d.	18	19	n.d.	< 5	310	140	280	260	320	40	180	540	140	160	55	25
7	Cl ₅ -PCB (PCB 101)	n.d.	n.d.	190	290	130	25	2600	140	790	470	350	270	750	1200	220	270	120	72
8	Cl ₆ -PCB (PCB 138)	n.d.	66	730	930	580	120	8600	360	3000	1400	1200	1200	2800	2800	560	870	460	430
9	Cl ₆ -PCB (PCB 153)	n.d.	63	760	1000	610	110	9900	360	3400	1400	1300	1300	3000	3000	590	890	450	410
10	Cl ₇ -PCB (PCB 180)	n.d.	15	510	660	370	98	6500	150	1900	920	890	760	1700	1800	340	600	280	490
	Σ PCBs (6 representative congeners)	n.d.	144	2208	2899	1690	353	28110	1780	9990	5230	4620	3700	8840	9660	2200	3280	1535	1492
	Polycyclic aromatic hydrocarbons, PAHs																		
11	Acenaphthylene	37	1400	3700	280	8700	130	1600	1000	2200	420	280	300	320	200	270	250	220	270
12	Acenaphthene	65	10100	2100	400	1300	920	1500	2100	4300	940	560	460	470	830	1500	2500	1200	840
13	Fluorene	67	3600	4300	700	5000	1400	6000	2000	6200	2400	1300	380	900	1500	6600	3800	3000	1200
14	Phenanthrene	4700	64800	53400	20600	172000	13800	155000	43800	115000	27100	27000	17700	22900	15200	23500	45100	21200	10700
15	Anthracene	900	32300	23600	9100	31500	5200	22800	22900	28600	8300	7000	5700	4400	3200	5400	10700	5200	1800
16	Fluoranthene	13500	25300	33000	27400	109000	15100	143000	29400	89400	19900	82900	52100	45100	38800	28100	58900	33400	8400
17	Pyrene	9700	51100	35900	30100	110000	17600	177000	33200	93900	21600	60000	42800	40000	30200	23400	48500	28100	8700
18	Benz[<i>a</i>]anthracene	8900	33700	50500	26000	141000	13300	138000	48500	85600	24400	53800	26000	30500	19800	17300	36300	25500	6400
19	Triphenylene / Chrysene	12700	31100	44500	30200	182000	14500	181000	44200	114000	30500	77200	39600	44500	26900	24400	47300	33400	8900
20	Benz[<i>b</i>]fluoranthene	20900	75200	122000	48600	275000	28400	282000	81200	166000	46400	123000	67200	67400	44300	36200	70900	49200	13600
21	Benz[<i>k</i>]fluoranthene	1500	14800	25100	6400	35000	4500	27600	13100	18900	6400	9500	5300	5800	2600	2700	5800	5300	1100
22	Benz[<i>a</i>]pyrene	8700	39900	61700	22900	147000	14200	134000	40300	83200	23600	57800	31300	31200	17100	14400	32700	23300	5900
23	Naphthalene	120	n.d.	n.d.	< 5	n.d.	11	150	n.d.	550	n.d.	n.d.	10	< 5	< 5	n.d.	< 5	n.d.	n.d.
24	Indeno[1,2,3- <i>cd</i>]pyrene	10100	50500	79600	29500	175000	17100	161000	50200	103000	31000	63700	39100	39500	17600	24900	41500	35800	13400
25	Benz[<i>g,h,i</i>]perylene	7800	34500	54700	19400	130000	12800	116000	35600	73000	20100	47500	27000	28000	12300	13000	22100	20600	6400
26	Dibenz[<i>a,h</i>]anthracene	1700	14200	24300	5800	28200	4900	31300	12500	18800	6000	12600	6600	7300	3100	4100	6200	5700	2000
	Σ EPA 16 PAHs	101389	482500	618400	277380	1550700	163861	1577950	460000	1002650	269060	624140	361550	368290	233630	225770	432550	291120	89610

No.	Compounds	Site no.																		
		R2	R3	R4	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	
	Industrial compounds																			
27	Di-iso-propylnaphthalenes, DIPNs	80	n.d.	130	8	1200	180	770	1700	1600	11800	7400	3700	10200	3700	2000	2800	1000	460	
28	Diphenoxyethane, DPE	n.d.	n.d.	n.d.	n.d.	7	n.d.	12	< 5	140	37	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	22	n.d.	
29	Mesamol®	n.d.	n.d.	n.d.	53	680	40	1800	160	3500	1200	730	420	750	670	240	400	730	150	
30	Butylated hydroxytoluene, BHT	27	n.d.	51	< 5	170	< 5	34	22	320	37	61	140	22	n.d.	7	n.d.	< 5	n.d.	
31	Dichlorobenzenes (Cl ₂)	n.d.	n.d.	10	n.d.	n.d.	n.d.	n.d.	< 5	5	85	22	5	36	58	126	68	161	28	
32	Trichlorobenzenes (Cl ₃)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.	10	16	62	23	49	8	
33	Tetrachlorobenzenes (Cl ₄)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	
34	Pentachlorobenzene (Cl ₅)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	< 5	< 5	n.d.	< 5	n.d.	n.d.	
35	Hexachlorobenzene (Cl ₆)	n.d.	n.d.	< 5	n.d.	n.d.	< 5	n.d.	n.d.	n.d.	< 5	n.d.	n.d.	< 5	< 5	< 5	< 5	n.d.	n.d.	
	Σ Chlorinated benzenes (Cl ₂ to Cl ₆)	n.d.	n.d.	10	n.d.	n.d.	n.d.	n.d.	n.d.	5	125	22	5	46	74	188	91	210	36	
	Pesticide residues																			
36	Dichlorodiphenyldichloroethylene, DDE	n.d.	n.d.	n.d.	n.d.	44	6	90	n.d.	120	6	n.d.	n.d.	50	19	< 5	20	< 5	31	
37	Dichlorodiphenyldichloroethane, DDD	n.d.	n.d.	210	n.d.	57	88	320	n.d.	940	200	n.d.	n.d.	78	n.d.	100	36	59	20	
	Σ DDX	n.d.	n.d.	210	n.d.	101	94	410	n.d.	1060	206	n.d.	n.d.	128	19	102	56	63	51	
	Personal care products																			
38	Methyltridolan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21	36	7	
39	Octocrylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11	32	5	
	n.d. (not detected)																			

n.d. (not detected)

Table A18 Available acute toxicity data for selected organic compounds detected in Rur river water samples.

Compound	Effect concentration [mg/L]	Threshold type	Experimental organism (species)	Exposure duration [h]	Effect / Assessment endpoint	Reference
Tris(2-chloroethyl)phosphate, TCEP	51	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Shi et al. (2016); Verbruggen et al. (2006)
	330	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	190	E(L)C50	Fish (<i>Oryzias latipes</i>)	96	Mortality	
Tris(chloropropyl)phosphate, TCP	45	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Verbruggen et al. (2006)
	91	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	30	E(L)C50	Fish (<i>Poecilia reticulata</i>)	96	Mortality	
Tri- <i>n</i> -butylphosphate	4.2	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Verbruggen et al. (2006)
	3.65	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	13	E(L)C50	Fish (<i>Oryzias latipes</i>)	96	Mortality	
Tri- <i>iso</i> -butylphosphate	34	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Verbruggen et al. (2006)
	11	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	20	E(L)C50	Fish (<i>Leuciscus idus</i>)	96	Mortality	
Triethylphosphate	900	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Verbruggen et al. (2006)
	350	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	2140	E(L)C50	Fish (<i>Leuciscus idus</i>)	96	Mortality	
Triphenylphosphate	0.5	E(L)C50	Algae (<i>Scenedesmus subspicatus</i>)		Growth inhibition	Verbruggen et al. (2006)
	1.1	E(L)C50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	0.42	E(L)C50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
Diethyl phthalate	16	EC50	Algae (<i>Selenastrum capricornutum</i>)	96	Chlorophyll <i>a</i>	Adams et al. (1995); LeBlanc (1980)
	86	LC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	52	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	16.7	LC50	Fish (<i>Lepomis macrochirus</i>)	96	Mortality	
	17	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
Dimethyl phthalate	142	EC50	Algae (<i>Selenastrum capricornutum</i>)	96	Chlorophyll <i>a</i>	Adams et al. (1995); LeBlanc (1980)
	45.9	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	33	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	50	LC50	Fish (<i>Lepomis macrochirus</i>)	96	Mortality	
	39	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
Dibutyl phthalate	0.4	EC50	Algae (<i>Selenastrum capricornutum</i>)	96	Chlorophyll <i>a</i>	Adams et al. (1995)
	2.99	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	0.48	LC50	Fish (<i>Lepomis macrochirus</i>)	96	Mortality	
	0.92	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	

Compound	Effect concentration [mg/L]	Threshold type	Experimental organism (species)	Exposure duration [h]	Effect / Assessment endpoint	Reference
Benzyl butyl phthalate	0.21	EC50	Algae (<i>Selenastrum capricornutum</i>)	96	Chlorophyll <i>a</i>	Adams et al. (1995); Gledhill et al. (1980); LeBlanc (1980)
	0.4	LC50	Algae (<i>Selenastrum capricornutum</i>)	96	Cell number	
	> 0.96	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	3.7	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	92	LC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	1.5	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
	1.7	EC50	Fish (<i>Lepomis macrochirus</i>)	96	Mortality	
Bis(2-ethylhexyl) phthalate, DEHP	5.3	EC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	Adams et al. (1995)
	> 0.10	EC50	Algae (<i>Selenastrum capricornutum</i>)	96	Chlorophyll <i>a</i>	
	> 0.16	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	> 0.20	LC50	Fish (<i>Lepomis macrochirus</i>)	96	Mortality	
	> 0.67	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
Caffeine	46	EC50	Algae (<i>Selenastrum capricornutum</i>)	48	Growth inhibition	Sanderson et al. (2003); Russom et al. (1997)
	46	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality/Reproduction	
	805	EC50	Fish (<i>Pimephales promelas</i>)	96	Mortality/Reproduction	
	151	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
	> 100	EC50	Algae (<i>Pseudokirchneriella subcapitata</i>)	96	Growth inhibition	
Carbamazepine	48.9	EC50	Algae (<i>Pseudokirchneriella subcapitata</i>)	96	Growth inhibition	Harada et al. (2008); Kim et al. (2007); Ferrari et al. (2004)
	> 13.8	EC50	Crustacean (<i>Daphnia magna</i>)	48	Mortality	
	76.3	E(L)C50	Crustacean (<i>Daphnia magna</i>)	96	Immobility	
	35.4	E(L)C50	Fish (<i>Oryzias latipes</i>)	96	Mortality	
	388	EC50	Algae (<i>Chlorella protothecoides</i>)	24	Photosynthetic yield	
N,N-Diethyl-m-toluidide, DEET	4.1	EC50	Algae (<i>Pseudokirchneriella subcapitata</i>)	96	Growth inhibition	Harada et al. (2008); Costanzo et al. (2007); Seo et al. (2005); Brooke (1984)
	108	LC50	Crustacean (<i>Daphnia magna</i>)	96	Mortality	
	75.7	EC50	Fish (<i>Pimephales promelas</i>)	96	Loss of equilibrium	
	110	LC50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
	89.3	E(L)C50	Fish (<i>Pimephales promelas</i>)	96	Mortality	
N,N-Dibutylformamide	0.95	LC50	Fish (<i>Oryzias latipes</i>)	96	Mortality	Brooke (1984)
Galaxolide	1.0	LC50	Fish (<i>Oryzias latipes</i>)	96	Mortality	Yamauchi et al. (2008)
Tonalide	61	EC50	Fish (<i>Danio rerio</i>)	96	Mortality	Yamauchi et al. (2008)
2,4,7,9-Tetramethyl-5-decyl-4,7-diol, TMDD	72	LC50	Fish (<i>Danio rerio</i>)	96	Mortality	Vincze et al. (2014)
Benzothiazole	24.6	EC50	Crustacean (<i>Ceriodaphnia dubia</i>)	48	Mortality	Nawrocki et al. (2005)
2-Methylthiobenzothiazole	12.7	EC50	Crustacean (<i>Ceriodaphnia dubia</i>)	48	Mortality	Nawrocki et al. (2005)

LC50 (lethal concentration causing the death of 50% of the observed test organisms); EC50 (half-maximal effective concentration inducing a defined response of 50% of the observed test organisms)

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Table A19 Available sediment toxicity data for selected organic compounds detected in Rur riverbed samples.

Organic pollutant	Effect concentration [ng/g _{dwt}]	Threshold type	Experimental organism (species)	Effect	Reference
Total PAHs	4022 - 44792	ERL - ERM	Benthic macroinvertebrates	Adverse biological effects occasionally occur	Han et al. (2021); Long et al. (1995)
Acenaphthylene	44 - 640				
Acenaphthene	16 - 500				
Fluorene	19 - 540				
Phenanthrene	240 - 1500				
Anthracene	85.3 - 1100				
Fluoranthene	600 - 5100				
Pyrene	665 - 2600				
Benz[a]anthracene	261 - 1600				
Triphenylene / Chrysene	384 - 2800				
Benzo[a]pyrene	430 - 1600				
Naphthalene	160 - 2100				
Dibenz[a,h]anthracene	63.4 - 260				
Total PAHs	1684	TEL	Benthic macroinvertebrates	Concentrations occasionally associated with adverse effects	Macdonald et al. (1996)
Acenaphthylene	5.87				
Acenaphthene	6.71				
Fluorene	21.2				
Phenanthrene	86.7				
Anthracene	46.9				
Fluoranthene	113				
Pyrene	153				
Benz[a]anthracene	74.8				
Triphenylene / Chrysene	108				
Benzo[a]pyrene	88.8				
Naphthalene	34.6				
Dibenz[a,h]anthracene	6.22				

Organic pollutant	Effect concentration [ng/L _{dw}]	Threshold type	Experimental organism (species)	Effect	Reference
Total DDT	1.58 – 46.1	ERL - ERM	Benthic macroinvertebrates	Adverse biological effects occasionally occur	Long et al. (1995)
	3.89	TEL	Benthic macroinvertebrates	Concentrations occasionally associated with adverse effects	Macdonald et al. (1996)
Total PCBs	22.7 -180	ERL - ERM	Benthic macroinvertebrates	Adverse biological effects occasionally occur	Long et al. (1995)
	21.6	TEL	Benthic macroinvertebrates	Concentrations occasionally associated with adverse effects	Macdonald et al. (1996)
Total LABs	7.96	LC50	Nematode (Caenorhabditis elegans)	Mortality (24 h)	Johnson et al. (2007)
Bis(2-ethylhexyl) phthalate, DEHP	182	TEL	Benthic macroinvertebrates	Concentrations occasionally associated with adverse effects on the benthic community	Macdonald et al. (1996)

LC50 (lethal concentration causing the death of 50% of the observed test organisms); ERL (effects range-low; lower 10th percentile of the effects data distribution); ERM (effects range-median, 50th percentile of the effects data distribution); TEL (threshold effects level)

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