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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 with 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}–µg/g_{TOC} showing a decreasing tendency toward 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

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,

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environmental studies of the sedimentary compartment in river systems focus mainly on near-surface, contemporary pollution [33]. 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 [7]. Such studies have already been carried out worldwide, mainly in coastal environments and lacustrine systems (e.g., [53, 75, 85, 86]). The results obtained can be used to assess the effectiveness of previous or current regulations and initiatives (e.g., [10, 31]). Subsequently, these information can be used to evaluate the need for further action as restrictions, specific monitoring or other countermeasures (e.g., [7, 33]). 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 [33]. Both lipophilic organic and inorganic pollutants (e.g., heavy metals) have a high affinity to associate with particulate matter [37]. 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 [11]. 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 [47]. 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 [55, 59, 87]. 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 [19]. 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 [65]. Due to their extensive usage, some of the organic contaminants are already ubiquitously distributed in our environment (e.g., [32, 44, 87]). 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 [64]. For instance, PCBs have been produced on a large scale for industrial use since about 1930 [13]. However, due to toxic responses in humans and animals, they were banned in Germany in 1989 [69, 89].

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 [18, 39, 88]. 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 [33]. 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 [2]. Accordingly, knowledge of site-specific developments and land use is highly relevant, which is available for the Urft reservoir in western Germany (cf. Figure 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 and 1905 with a total length of 12 km and covers a catchment area of 372.6 km^2 [96]. 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 [77]. The main inflow is the Urft river with a length of 46.4 km [79]. 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 [77].

As can be seen in Fig. 1a, 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 Fig. 1a [94]. 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 [76, 93]. The city of Kall is also located directly on the Urft river (11,112 inhabitants in 2022), while the city of Hellenthal is located at its tributary Olef (7925 inhabitants in 2022) [40, 41].

Although the Urft reservoir is now located in the Eifel National Park (established in 2004, see Fig. 1a–b), there were and still are several further emission sources in

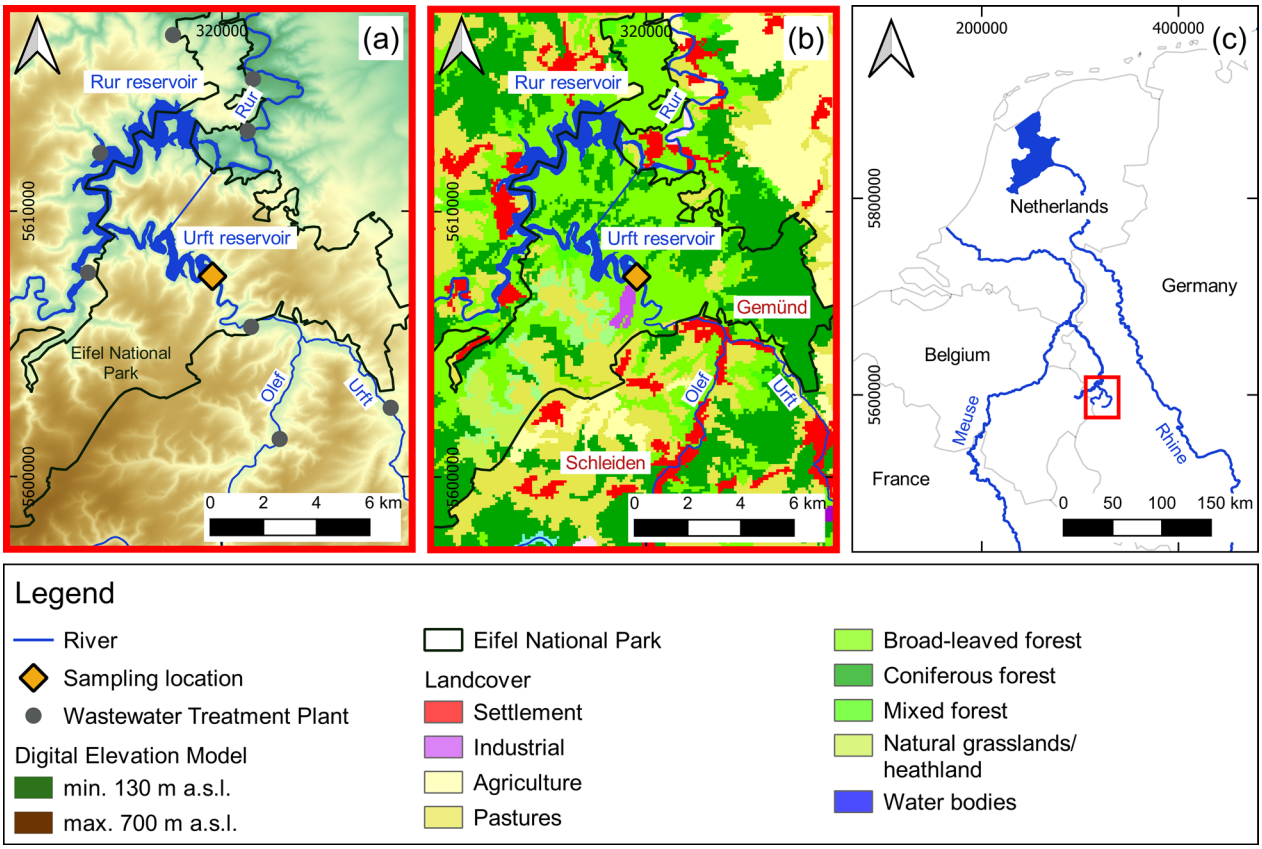

Fig. 1 **a** Overview of the Urft reservoir including the sampling location and the elevation (meters above sea level, m a.s.l.) [26]; **b** shows the landcover according to Corine Landcover [16] data,**c** shows the sampling area in a European context; Coordinate system: ETRS89 / UTM zone 32N

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 twentieth century, there were several factories mainly specialized on pulp and paper board production [50, 62]. 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 [36]. Moreover, the village of Gemünd was important for iron production for centuries, until the last company ceased production in 1966 [48]. 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. [78]. 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 nineteenth century [16, 61, 77].

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 [33]. 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 [88]. In addition, reservoirs typically show an undisturbed, continuous and homogeneous sedimentation, with conditions that are less variable than in floodplains [15]. 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 [78].

Methods

Sampling

The investigated core (U3) was taken as part of the study from Stauch et al. [77], which is focusing on the sediment deposition in the Urft reservoir (Fig. 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) [78]. 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 ℃ in the dark.

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. [78]. 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 ℃ for TOC and 1000 ℃ 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 [37, 98].

Dating

Stauch et al. [78] 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 [33]. Samples covering intervals of 2.5–5 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 [78].

Organic geochemical analysis

Sample extraction and fractionation

Aliquots of 10–15 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. [73], 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 ℃ and a pressure of 10 MPa for 5 min. Following this, the individual extracts were combined, and the aqueous phase was separated and disposed. Afterward, 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. [74] 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 ℃ 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 20–400 µL.

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 × 0.25 mm ID × 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 ℃) at 60 ℃ with a splitless time of 60 s was followed by 3 min at the initial temperature, then programmed at a rate of 3 ℃/min to 310 ℃ with an isothermal time of 20 min. MS analysis was performed in full-scan mode (EI^+, 70 eV) having a source temperature of 200 ℃, scanning from 35 to 700 amu at a rate of 1.5 scans/s.

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 [72, 73]. Blank analysis revealed neglectable background and laboratory contamination with LABs and phthalates.

Results

Standard sedimentological parameters

The grain size distribution and organic content of the samples have been analyzed as basic sedimentological parameters (see Table 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 (69–76%). In general, the TOC content varied between 1.8 and 6.0%. The highest values were detected for depths of 160–230 cm (average of 5.3%). In depths of 70–150 cm, the average was lower (2.5%); while in lower depths of 30–60 cm, it was again higher (3.9%).

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 2). For instance, polychlorinated biphenyls (PCBs) have been largely produced since about 1930 and were finally banned in Germany in 1989 [13, 89]. 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 µg/g_{TOC}. However, a clear contamination peak occurred at a depth of 121–130 cm with a PCB6 sum of 11.6 µg/g_{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)) and also indicators of wastewater pollution (e.g., linear alkylbenzenes (LABs)) were found in the drilling core. DIPNs and LABs were clearly identified in the µg/g range. Similar to the group of PCBs, both the DIPN and LAB (C_{10}

Table 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

Table 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

Compound	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**
Linear alkylbenzenes, LABs													
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	12,940	9810	12,190	18,900	10,200	4490	5360	6230	3120	5030
Polychlorinated biphenyls, PCBs													
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
Cl_6-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	11,557	2220	2762	1145	3325	703	680
Polycyclic aromatic hydrocarbons, PAHs													
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	12,000	19,200	18,900	17,100	35,300	22,200	30,000	35,400	572,000	28,600	16,600	79,100
Anthracene, An	820	2400	3100	5100	4400	7100	4500	18,200	12,500	10,100	6900	7400	25,300
Fluoranthene, Fl	5500	9300	24,900	13,300	19,700	91,500	14,400	24,900	27,500	71,300	15,200	153,000	47,000
Pyrene, Py	4500	11,300	31,700	13,100	26,300	69,200	19,600	17,800	28,800	90,700	18,100	63,000	46,700
Benzo[a]anthracene, BaA	3700	12,700	28,600	23,900	29,300	53,700	24,200	20,500	37,900	73,300	37,200	118,000	69,100
Chrysene, Ch	5600	16,500	38,500	16,600	23,300	72,300	23,600	17,800	29,700	109,000	31,100	167,000	57,100
Benzo[b]fluoranthene	9300	27,200	65,800	52,900	62,600	102,000	51,800	68,900	97,600	168,000	76,200	284,000	168,000
Benzo[k]fluoranthene	680	3700	6900	9800	10,600	9000	7600	14,600	15,400	13,300	10,900	23,500	39,600
Benzo[a]pyrene	3700	12,300	28,900	25,300	29,800	42,100	23,100	33,700	41,800	65,600	33,400	125,000	89,000
Naphthalene	490	560	1100	1700	1100	1800	2000	3500	2800	2400	4400	1100	12,100
Indeno[1,2,3-cd]pyrene, IP	5100	16,900	37,800	33,300	39,000	17,800	32,300	40,600	52,100	73,200	32,900	116,000	124,000
Benzo[g,h,i]perylene, Bghi	4300	13,000	28,400	23,700	28,200	8300	24,300	25,000	36,700	53,200	25,400	85,000	82,400
Dibenz[a,h]anthracene	850	4800	8900	11,300	12,100	4100	9600	9800	12,300	13,100	7000	22,200	39,800

Table 2 (continued)

Compound		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**
Σ EPA16 PAHs		48,256	143,600	325,120	251,330	305,910	516,070	260,920	333,400	436,800	1,319,790	331,250	1,184,940	891,600
C_1 phenanthrenes and anthracenes		1800	4700	8600	11,400	16,800	12,300	9400	42,500	34,300	30,600	13,400	13,500	46,900
C_1 fluoranthenes and pyrenes		2700	12,200	26,000	33,800	40,800	38,700	23,100	90,800	83,200	63,300	46,300	63,600	171,000
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	12,300	29,700	25,300	30,400	44,100	25,300	38,800	46,700	71,600	38,200	127,000	82,400
Perylene		1200	6700	10,800	12,000	13,400	12,600	11,300	14,900	18,600	19,200	15,600	35,100	50,500
NSO-PAHs														
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	10,900
Hopanes														
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
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
Industrial compounds														
Di-*iso*-propylnaphthalenes, DIPNs		8000	12,000	40,500	74,900	33,100	75,500	299,000	74,500	72,200	39,500	69,300	31,700	61,400
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

Table 2 (continued)

Compound	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**
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
Pesticide residues													
Dichlorodiphenyldichloroethylene, DDE	49	120	200	200	210	140	790	340	150	210	310	81	37
Dichlorodiphenyldichloroethane, 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
Personal care products													
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

to C_{13}) profiles showed their highest amounts at a depth of 121–130 cm (DIPNs: 299 µg/g_{TOC}; LABs: 18.9 µg/g_{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 µg/g_{TOC}; LABs: 0.8 µg/g_{TOC}). However, the average DIPN concentration (68.6 µg/g_{TOC}) was much higher than the average LAB concentration (7.6 µg/g_{TOC}). Other industrial compounds showed maxima in the range of 15 ng/g_{TOC} (N-benzylformamide)–2.6 µg/g_{TOC} (di-*n*-octylphthalate) (see Table 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 [4, 52]. Octocrylene is commercially used in sunscreens and further personal care products such as shampoos, hair sprays and conditioners [20, 71]. Both substances were detected at depths greater than 107 cm with maxima of 1.6 µg/g_{TOC} (methyltriclosan) and 62 ng/g_{TOC} (octocrylene).

Insecticide residues of dichlorodiphenyltrichloroethane (DDT), which has been widely used since the early 1940s, have also been found regularly [42]. 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) [30, 82]. The average sum of DDT residues (including dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD)) was 2.1 µg/g_{TOC} with a minimum of 0.2 µg/g_{TOC} (30–40 cm) and a maximum of 6.7 µg/g_{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., [1, 3, 63]). Partly, these processes result from natural mechanisms, such as wild fires, but most are caused by anthropogenic emissions [66]. The diffuse origin can be further clarified by PAH diagnostic ratios [81, 99]. The cumulative sum of EPA16 PAHs shows decreasing concentrations with decreasing depth. The maximum of 1.3 mg/g_{TOC} (180–190 cm) is more than 27 times higher than the minimum of 48.3 µg/g_{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 µg/g_{TOC} to 10.9 µg/g_{TOC} and minima ranging from 0.08 µg/g_{TOC} to 0.8 µg/g_{TOC}. Overall, PAHs are the most abundant and dominate the total contamination with the highest individual concentrations (see Table 2). Correspondingly, the concentrations of geohopanes (C_{29} to C_{35} stereoisomers) were much lower, showing a peak at a depth of 107–114 cm (3.6 µg/g_{TOC}). In contrast to the PAHs, there was an increasing tendency with decreasing depth.

Discussion

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. [78] 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 Fig. 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 [14, 83, 97]. Corresponding problems were first addressed in the late 1960s and then in the 1970s recognized by the general public [9, 68]. At that time, the first pioneering studies on organic water pollution were carried out (e.g., [43, 54]). 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

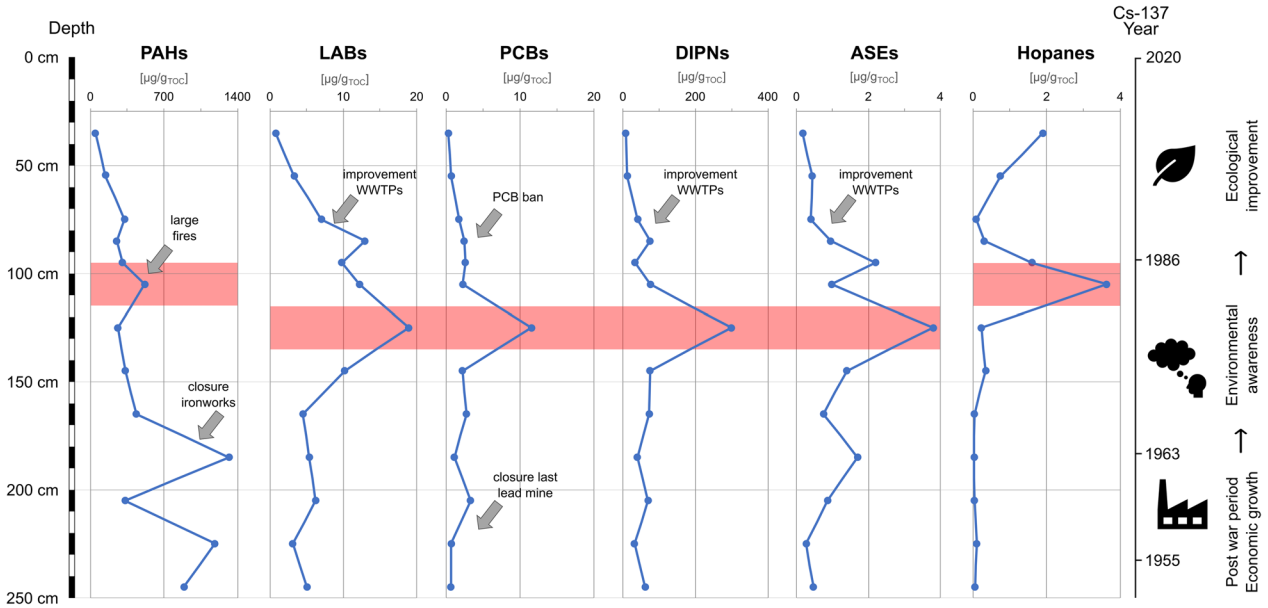

Fig. 2 Overview of different contamination profiles correlated with depth and general as well as catchment-specific time markers. The layer marked in red shows particularly high concentrations and, thus, indicates a possible extraordinary event

increase in research activities, political interest, and the establishment of several nature conservation organizations [9, 83]. 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 [68].

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 (Fig. 2). According to this trend, even lower concentrations can be estimated at the surface of the reservoir sediment. Samples from a depth of 180–250 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 [27]. For example, the ironworks in Gemünd, which had been destroyed in 1944, was rebuilt and restarted as part of this process [48]. The corresponding production may have caused higher PAH emissions, as several PAH diagnostic ratios indicate a primarily pyrogenic origin (cf. Figure 3). Most of the samples correlate with petroleum combustion as well as grass, wood, or coal combustion (cf. [81, 99]). 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 [38, 48]. 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 desulphurization systems) [83]. 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 121–130 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 [21]. 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 1–6; < 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 [24, 70], 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 nineteenth century or early twentieth century [45, 49]. However, lead ore mining in the Eifel region came to a final end with the closure of the last mine in 1957 [6]. Remobilization of corresponding sediments is therefore

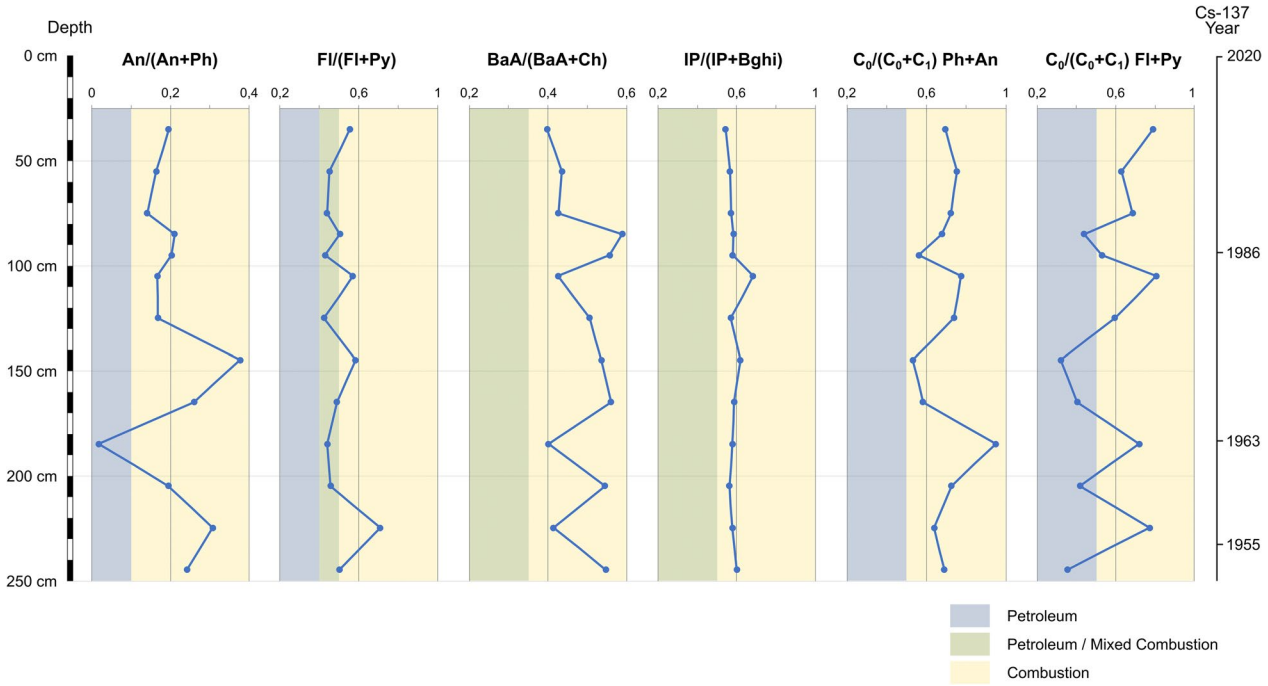

Fig. 3 Overview of different PAH diagnostic ratios based on the detected concentrations of anthracene (An), phenanthrene (Ph), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Ch), indeno[1,2,3-cd]pyrene (IP), benzo[g,h,i]perylene (Bghi), C_1 phenanthrenes and anthracenes and C_1 fluoranthenes and pyrenes correlated with depth and general time markers to differentiate and classify emission sources (petrogenic vs. pyrogenic) according to Yunker et al. [99]

a likely emission pathway for PCBs into the Urft and its tributaries. Except to the clear peak at 121–130 cm, PCB6 concentrations were at an almost similar level at depths of 80–210 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 [89]. Until then, especially the higher chlorinated PCBs were widely used in industrial applications, e.g., in electrical insulation or hydraulic equipment [91, 92]. 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., [29, 57]).

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 [22, 34]. 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 [67, 100]. 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 [34]. The highest LAB contamination at a depth of 80–150 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 [94]. In general, particularly in the last forty years, great efforts have been made in Germany to improve the efficiency of wastewater treatment [84]. 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 [20]. 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 80–210 cm (late 1950s–early 1990s). Again, respective maximum concentrations were detected for sample 7 (121–130 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 [21]. 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 [51]. 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 [29, 46].

Overall, most of the organic compounds show their main contamination at depths between 80 and 150 cm and thus in the period from the 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 toward 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 [78].

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 [73]. 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 first produced in the early 1970s. However, the original bactericide is comparatively polar and more mobile than methyltriclosan [12, 52]. 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 [5]. 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 [56]. However, octocrylene is strongly lipophilic and shows only a low water solubility [8].

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 [100]. Throughout Germany, contaminations with mineral oil products have been regularly detected at former military sites [58, 60, 80]. 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 107–114 cm (early 1980s) or 121–130 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 [21]. 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 107–114 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 [28, 35]. 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 [78].

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. [29] 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 [101]. 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 [25]. 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. [23] 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. [57] 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. [11] 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. [34] 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. [11], 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.

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 toward 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.

Abbreviations

An	Anthracene
ASEs	Alkylsulfonic acid phenyl esters
BaA	Benzo[a]anthracene
Bghi	Benzo[g,h,i]perylene
BHT	Butylated hydroxytoluene
Ch	Chrysene
Cs-137	Caesium-137
DCM	Dichloromethane
DDD	Dichlorodiphenyl-dichloroethane
DDE	Dichlorodiphenyl-dichloroethylene
DDT	Dichlorodiphenyl-trichloroethane
DEHA	Bis(2-ethylhexyl) adipate
DEHP	Bis(2-ethylhexyl) phthalate
DBP	Di-*n*-butyl phthalate
DIBP	Di-*iso*-butyl phthalate
DIPNs	Di-*iso*-propylnaphthalenes
DPE	1,2-Diphenoxyethane
EPA	U.S. Environmental Protection Agency
Fl	Fluoranthene
GC/MS	Gas chromatography/mass spectrometry
IP	Indeno[1,2,3-cd]pyrene
LABs	Linear alkylbenzenes
LASs	Linear alkylbenzene sulfonates
LOD	Limit of detection
LOQ	Limit of quantification
m a.s.l	Meters above sea level
NIST	National Institute of Standards (USA)
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCTs	Polychlorinated terphenyls
Ph	Phenanthrene
POPs	Persistent organic pollutants
Py	Pyrene
TC	Total carbon
TIC	Total inorganic carbon
Tm	17α-22,29,30-Trisnorhopane
TOC	Total organic carbon
Ts	18α-22,29,30-Trisnorneohopane
VC	Vinyl chloride
WWTP	Wastewater treatment plant

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Availability of data and materials
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Declarations

Ethical approval and consent to participate
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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