Water Research 305 (2026) 126506

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Adsorption outweighs biodegradation: Organic micropollutants exhibit compound-specific temperature responses in biologically active granular activated carbon filters

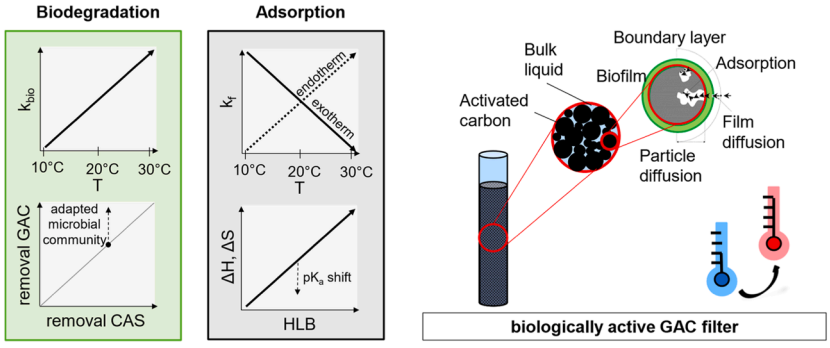
Larissa Graß [a], Daniel Hillebrandt [b], Julian Firk [b], Laurence Palmowski [a], Benedikt M. Aumeier [c], Thomas Wintgens [a,*]

[a] Institute of Environmental Engineering (ISA) RWTH Aachen University, Mies-van-der-Rohe-Str. 1, Aachen, 52074, Germany
[b] Niersverband, Am Niersverband 10, Viersen, 41747, Germany
[c] Chair of Urban Water Systems Engineering, Technical University of Munich, Am Coulombwall 3, Garching, 85748, Germany

HIGHLIGHTS

- Temperature impacts both adsorption and biodegradation in GAC filters.
- Hydrate shells influence the temperature-dependent adsorption behavior of OMPs.
- pK_a shift increases 1H-benzotriazole removal at lower temperatures in GAC filters.
- Adapted microbiology leads to high biodegradation of diclofenac in GAC filters.
- Exothermically adsorbing OMPs cause temperature-related changes in GAC filter effluent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Granular activated carbon filters
Organic micropollutants
Temperature-dependent adsorption
Biodegradation
Microbial community

ABSTRACT

In this study, we investigated the influence of water temperature fluctuations on biologically active granular activated carbon filters (GAC filters) used for advanced treatment in municipal wastewater treatment plants. In addition to adsorption, biodegradation processes influence the removal of organic micropollutants (OMPs) in GAC filters as the filter operation time increases. Both processes, adsorption and biodegradation, are individually influenced by temperature changes. However, it is largely unknown how the temperature-dependent behaviour of individual OMPs affects the combination of adsorption and biodegradation processes in GAC filters so far.

Results indicate that the influence of temperature on the OMP removal in GAC filters varies greatly depending on substance-specific properties. Regarding temperature dependency of adsorption, the number of hydrophilic groups, represented by the hydrophilic-lipophilic balance (HLB) and molecular weight, as well as the temperature-dependent shift of the dissociation constant (pK_a) were identified as decisive substance properties. The effect of the pK_a shift was evident primarily for 1H-benzotriazole, both in laboratory experiments and in two pilot-scale GAC filters operated over a period of four years. Furthermore, laboratory tests show that an adapted microbial community in GAC filters especially improves the biodegradation of diclofenac, clarithromycin and

* Corresponding author.
E-mail address: Wintgens@isa.rwth-aachen.de (T. Wintgens).

https://doi.org/10.1016/j.watres.2026.126506
Received 3 March 2026; Received in revised form 2 June 2026; Accepted 13 July 2026
Available online 15 July 2026
0043-1354/© 2026 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

amisulpride, compared to an activated sludge system. Especially for 1H-benzotriazole, elevated temperatures lead to increased effluent concentrations in the pilot scale GAC filters which can be explained that exothermic adsorption behaviour outweighs potentially increased biodegradation. With the exception of 1H-benzotriazole and ∑4-/5-methylbenzotriazole, all OMPs examined exhibit the opposite behaviour, namely a decrease in wastewater concentrations with increasing temperature.

1. Introduction

Granular activated carbon (GAC) filtration is a common advanced wastewater treatment process that is increasingly being used on full-scale wastewater treatment plants (WWTPs) to remove organic micropollutants (OMPs) (Tarigan et al., 2025). In addition to adsorption, which is considered as the main removal mechanism for many OMPs, the growth of biofilms was shown to have a major influence on the cleaning performance of GAC filters. Multiple studies were able to demonstrate a fostered OMP removal efficiency at increased operating times of GAC filters due to biological degradation processes (Fundneider et al., 2021b; Sauter et al., 2023; Sbardella et al., 2018). However, biofilm growth likely causes pore blockages and thus leads to increased pressure loss over the filter bed (Fundneider et al., 2021b; Hess and Morgenroth, 2021). Overall, the proportionate effect of adsorption, desorption, and biological degradation on the removal of OMPs in GAC filters and the mutual influence of these processes are largely unclear (Hess and Morgenroth, 2021). In addition to process settings such as empty bed contact time (EBCT) and backwash frequency, temperature was recognised as an external factor that considerably influences the removal performance of GAC filters (Fundneider et al., 2021b; Hess and Morgenroth, 2021). However, studies that have profoundly investigated the influence of temperature up to now only refer to biofiltration systems applied in drinking water treatment (Emelko et al., 2006; Hallé et al., 2015; Huck and Sozanski, 2008). In addition to biological degradation processes, however, adsorption is also significantly affected by temperature differences. Studies investigating the temperature-dependent adsorption of OMPs on activated carbon have so far not gone beyond laboratory experiments in buffered solutions (Aumeier et al., 2022; Masson et al., 2017; Nam et al., 2014). Thus, the extent to which the temperature dependence of OMP adsorption is relevant for the continuous operation of GAC filters in WWTP effluent remains still unknown. This work is the first to assess the impact of temperature on biologically active GAC filters holistically in terms of biodegradation and adsorption and in a real wastewater matrix.

The biodegradation of OMPs is generally regarded as a co-metabolic process (Ngo et al., 2020; Thuptimdang et al., 2020). The main substrate source for biological growth in GAC filters is dissolved organic carbon (DOC), whose concentration is orders of magnitude higher than that of OMPs in the effluent of biological treatment stages (Çeçen and Aktas, 2011). Significantly more biomass respectively higher biological activity was found at warm temperatures compared to cold ones (Emelko et al., 2006; Fundneider et al., 2021b; Huck and Sozanski, 2008), although the degradation of DOC in biologically active GAC filters does not show any dependence on temperature (Emelko et al., 2006; Fundneider et al., 2021b; Graß et al., 2025), In addition to temperature, filter depth and filter operation time influence the amount of biomass in biofilters (Emelko et al., 2006; Fundneider et al., 2021b; Hallé et al., 2015). Biomass decreases with increasing filter depth in top-down fed GAC filters (Fundneider et al., 2021b; Hallé et al., 2015). After an initial growth phase and a prolonged operation time, the biomass reaches a plateau, also known as steady state (Emelko et al., 2006; Simpson, 2008). In the plateau phase, biological activity is regulated by substrate availability and process settings (Basu et al., 2015; Fundneider, 2020). Above all, the backwash frequency is used to control biofilm thickness and was identified by Fundneider et al. (2021b) to be a suitable indicator for biofilm development and indirectly for biological activity. Unlike the biological degradation of DOC in GAC filters, which can be limited by its bioavailability (Graß et al., 2025), the degradation of OMPs in conventional activated sludge systems (CAS) for most parts depends on temperature fluctuations (Hai et al., 2011; Meynet et al., 2020; Sui et al., 2016). In addition to microbial growth and activity, solubility and other physicochemical properties play a role in the temperature dependence of the biodegradation of individual OMPs (Cirja et al., 2007; Price and T., 2004). Within the optimal temperature range of the specific microorganism groups, their growth rate increases gradually with rising temperature. In biological wastewater treatment, it can be roughly estimated that an increase of 10 °C leads to a two to three times higher conversion and growth rates (Chen et al., 2020). Meynet et al. (2020) showed that even short-term temperature changes not only influence microbial activity and thus enzymatic activity but also cause marked shifts in the composition of the microbial community. Increased taxonomic shifts, which can occur during long-term temperature changes, further determine the presence or abundance of specific biotransformation enzymes respectively specific biotransformation pathways (Meynet et al., 2024). Thus, OMPs that undergo a similar type of biotransformation reaction show similar responses to temperature changes (Meynet et al., 2020).

The extent to which findings on the biodegradability of OMPs in CAS can be transferred to biologically active GAC filters has not yet been extensively investigated. The study by Sauter et al. (2023) showed that the diversity of the microbial community in GAC filters changes depending on the availability of biodegradable organic substances. Furthermore, several microorganisms were identified whose enzymatic activity could also be linked to the co-metabolic degradation of OMPs (Sauter et al., 2023). Initial investigations of the influence of temperature on the degradation of OMPs in biofilters showed that less bioavailable components are more dependent on temperature fluctuations (Hallé et al., 2015). Furthermore, Fundneider et al. (2021b) reported a general improvement in OMP degradation at higher temperatures in biologically active GAC filters whereas DOC was not affected.

Regarding adsorption, enthalpic and entropic effects including the degree of dissociation, and the diffusion rate are important substance-specific variables through which temperature can influence OMP removal in GAC filters (Aumeier et al., 2022). Since adsorptive reactions are considered to be exothermic and have negative enthalpy ($\Delta H < 0$), the extent of adsorption is expected to increase as temperatures decrease (Çeçen and Aktas, 2011). However, the studies by Aumeier et al. (2022) and Masson et al. (2017) showed that and explained how certain micropollutants exhibit positive enthalpy and thus apparently endothermic behaviour. Consequently, when interpreting enthalpy, not only the adsorption reaction itself (interaction between solute and adsorbent) but also the interactions between solute and solvent and solvent and adsorbent must be considered (Aumeier et al., 2022). These interactions primarily include hydrogen bonds between the adsorbent and/or solute with water (Masson et al., 2017).

In this study, the hydrophilic-lipophilic balance (HLB) value was identified as the substance property that best reflects and quantifies these interactions with the aqueous phase. Moreover, it was chosen as the core predictor for the temperature-dependent adsorption behaviour of the investigated OMPs. The HLB value classifies surface-active moieties of the investigated molecules by quantifying their affinity to the oil and water phases (Heusch, 1970). Eq. (1) shows the calculation of the HLB value:

$$HLB = 20 * \left(\frac{MW_H}{MW_H + MW_P}\right) \quad (1)$$

MW_H: Sum of the molecular weight of all hydrophilic regarded moieties.
MW_P: Sum of the molecular weight of all hydrophobic regarded moieties.

Another decisive substance property regarding temperature-dependent adsorption behaviour is the logarithmic dissociation constant (pK_a). What is special about the pK_a in this context is that the substance property itself is influenced by temperature changes. Consequently, the pK_a of certain OMPs decreases with rising temperature, which leads to an increase in the degree of dissociation (α) (Aumeier et al., 2022). This temperature-induced pK_a shift affects the charge of the solute and thus its solubility behaviour in water and its intermolecular attraction to the adsorbent (Aumeier et al., 2022; Çeçen and Aktas, 2011). The pK_a shift primarily influences the solubility behaviour of strongly dissociated OMPs (Aumeier et al., 2022).

This work improves the understanding of temperature-dependent OMP removal in biologically active GAC filters, by extending existing research on temperature-dependency of biological and adsorptive removal processes to the corresponding wastewater matrix and filtration system. Moreover, correlations between physicochemical substance properties and temperature-dependent degradation behaviour of individual OMPs in GAC filters are investigated. Findings from long-term pilot-scale studies are further examined and discussed based on laboratory batch experiments and measurements from the full-scale CAS.

2. Material and methods

2.1. Experimental setup

2.1.1. Full-scale / pilot-scale system

This study examines the temperature-dependent behaviour of OMPs in two pilot-scale GAC filters. The two GAC filters were fed with the effluent of the WWTP Nette (86,000 PE) in North Rhine-Westphalia (NRW), Germany, which was further pre-treated by a pilot-scale ultrafiltration (UF) system. Data from the pilot-scale plant and the full-scale WWTP was collected over an operational period of 4 years (2021–2024), respectively 46,000 GAC filter bed volumes (BV). The full-scale WWTP Nette consists of a mechanical treatment stage (screens, sand and grease traps and primary clarification), a biological treatment stage (CAS with pre-anoxic denitrification) and a downstream non-biologically active flocculation filtration (24 continuously rinsed Dyna-Sand filters). The UF system (ZeeWeed 500®) consists of outside-in supported PVDF hollow fibre membranes.

The two GAC filters examined in this study were filled with Chemviron Cyclecarb® 401 and were fed top-down at a flow rate of 0.145 m^3/h and a filtration velocity of 3.15 m/h. The EBCT of both filters was set to 40 min. The relatively high EBCT was deliberately chosen to promote biological activity in the GAC filters and to minimize potentially limiting effects caused by the hydraulic retention time. According to Fundneider et al., (2021a), no further improvement in the performance of GAC filters is to be expected with an EBCT exceeding 20–30 min. However, Larasati et al. (2026) show that in biologically active GAC filters, an EBCT of >26 min should be chosen to achieve an OMP removal of over 80 %. Moreover, the two filters differed in their backwash regime. While the backwash frequency in filter A was controlled by pressure loss in the filter, filter B was backwashed once a week until October 2024. After that, backwashing was further intensified to a daily interval (Monday to Friday). The pressure-dependent backwashing of filter A resulted in a lower backwash frequency of approx. 0.4 backwash events per week. As the biofilm thickness in GAC filters is primarily regulated by backwashing (Fundneider et al., 2021b; Liao et al., 2015), it is to be expected that the lower backwash frequency in Filter A leads to increased biological activity compared to Filter B. Both GAC filters were backwashed on a regular basis after approx. 10 months of operating time. OMP samples were taken at the inlet and outlet of the GAC filters and at three intermediate bed depths (flow path from top down: 0.9 m, 1.3 m and 1.7 m). Fig. 1 shows the flow chart of the pilot-scale UF and GAC filtration.

The origin and removal of DOC (background matrix) in pilot-scale GAC filter A has already been investigated in Graß et al. (2025). Further information on the operating settings of the CAS of the WWTP Nette during the examined time period (2021–2024) and on the pilot plant can also be found in Graß et al. (2025). In addition, the competitive adsorption behaviour of OMPs in the pilot-scale GAC filters was investigated in Parniske et al. (2026). Filter A in this study corresponds to filter 1 and filter B corresponds to filter 3 in the study by Parniske et al. (2026).

2.1.2. Lab-scale adsorption experiments

The adsorption experiments were carried out as described in Graß et al. (2025), with the difference that activated carbon concentrations of 5, 10, 15 and 20 mg/L were selected for this study to be able to accurately represent the adsorption equilibrium curves of as many examined OMPs as possible. In addition, adsorption tests were carried out at three different temperatures (10, 20 and 30 °C) to investigate the thermodynamic adsorption parameters (enthalpy (ΔH) and entropy change (ΔS)) for the individual OMPs in the temperature range of the pilot-scale GAC filter columns. The adsorption tests at all three temperatures were carried out on three different feed samples (three runs) of the pilot-scale GAC filters.

2.1.3. Lab-scale biodegradation experiments

The biodegradation experiments were designed in analogy with the Zahn-Wellens test (DIN EN ISO 9888:1999–11) and as described in detail in Graß et al. (2025). In order to compare the biodegradation of OMPs in GAC filter backwash sludge with that in CAS sludge, backwash sludge samples (GAC filter A and GAC filter B) and activated sludge samples from the aerated zone of the CAS at the WWTP Nette were taken. All sludge was freed from particulate matter in a three-phase washing process. This consisted in settling and centrifuging (at 2500 rpm for 5 min) the sludge, decanting the supernatant and resuspending the pellets in tap water (Graß et al., 2025). The biological degradation test was performed in triplicates for all three sludges (CAS, GAC filter A and GAC filter B). In order to make the results of the different sludges comparable, the volatile suspended solids (VSS) were set to 0.03 g/L in all biodegradation experiments. For the biodegradation experiments, a feed sample was taken from the pilot-scale GAC filters, inoculated with the different sludges and incubated at 20 °C under stirred and aerobic conditions. The low VSS concentration and a long incubation time of 28 days in the degradation experiment were deliberately chosen to reduce the impact of adsorption on sludge flocs and to ensure that OMP biodegradation was as complete as possible.

2.2. Sampling and chemical analysis

2.2.1. Wastewater sampling from the full-scale CAS and pilot-scale system

Samples from the full-scale WWTP Nette and the pilot-scale system were collected with automatic samplers (23-h composite samples) or by manual sampling (qualitative samples). To evaluate the removal of the examined OMPs in the CAS of the WWTP Nette, samples were taken from the effluent of the primary treatment/inlet to the CAS and from the effluent of the WWTP/inlet to the pilot plant. To examine the removal of OMPs in the pilot-scale GAC filters, samples were taken at the inlet and outlet of the filters and at three intermediate bed depths. The samples on the full-scale plant as well as the inlet and outlet of the GAC filters were taken using automatic samplers. The intermediate measuring points of the GAC filters were sampled manually.

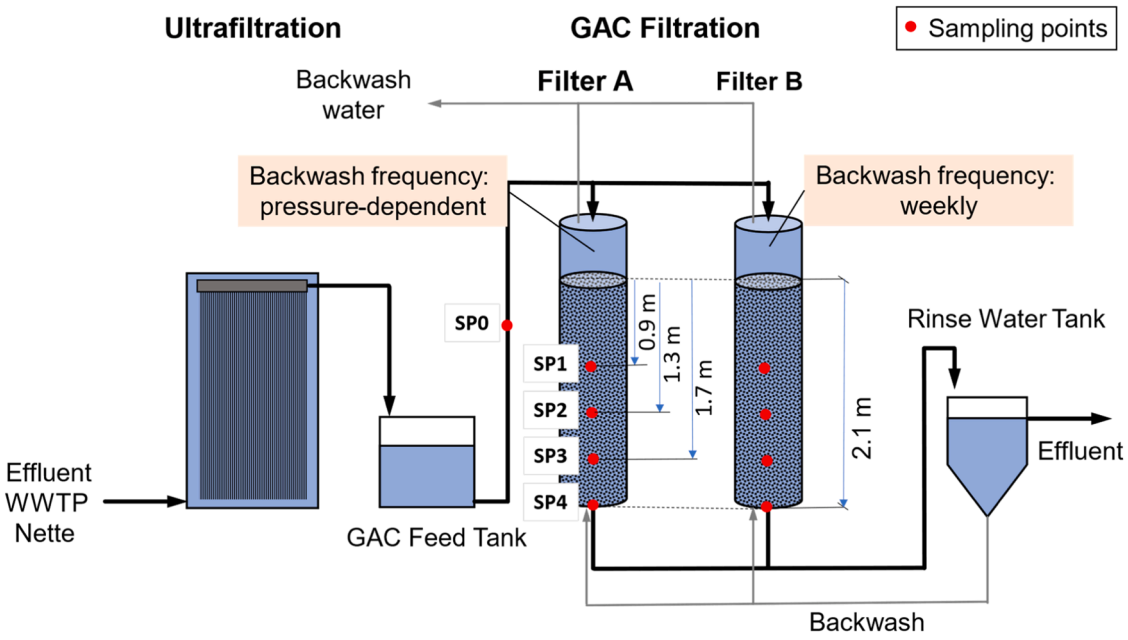


Fig. 1. Flow chart of the pilot-scale UF and GAC filtration system. Sampling points (SP0 to SP4) are marked with red dots.

2.2.2. Sampling of lab experiments

All samples taken during the adsorption experiments and the biodegradation experiments were filtered through 0.45 µm syringe filters (Labsolute ProFill, RC, Ø= 25 mm) that were pre-rinsed with 200 mL ultrapure water. After being removed from the temperature-controlled incubation shaker (LABWIT EHRK 300), the samples from the temperature-dependent adsorption tests were kept at the respective temperature using heated or cooled water baths until the activated carbon was filtered out. From the sludge samples used as inoculum for the biological degradation experiments, part of the centrifuged pellet was taken for 16S rRNA gene amplicon sequencing.

2.2.3. Sample analysis

In this study, the 12 OMPs defined as indicator substances by the 2024 revised EU Urban Wastewater Treatment Directive (European Parliament and Council of the European Union, 2024) were examined. These 12 OMPs are divided in the directive into category 1 ("substances that can be very easily treated": amisulpride, citalopram, carbamazepine, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol and venlafaxine) and category 2 ("substances that can be easily disposed of": 1H-benzotriazole, ∑4-/5-methylbenzotriazole, candesartan and irbesartan). The OMPs Σ4-/5-methylbenzotriazole, amisulpride, candesartan, citalopram, hydrochlorothiazide, irbesartan and venlafaxine were only examined from 21.02.2023 onwards and thus only in operating years 3 and 4. For the remaining OMPs (carbamazepine, clarithromycin, diclofenac, metoprolol, and 1H-benzotriazole), measurement results are available for all 4 operating years examined. The OMPs were measured using LC-MS (DIN 38,407–47:2017–07) with a Limit of Quantification (LOQ) of 0.02 µg/L. For data evaluation, values smaller than the LOQ (<LOQ) were set at half the LOQ. The microbial population in the CAS of the WWTP Nette and in GAC filter A and GAC filter B was examined using 16S rRNA gene amplicon sequencing analysis. Library construction and sequencing was carried out by the microbiological laboratory of the Chair of Urban Water Systems Engineering, TU Munich. Total DOC was analysed by using a total organic carbon analyser (SHIMADZU; TOC-L).

2.3. Calculation methods and statistical analysis

2.3.1. Statistical calculations

The removal of OMPs was calculated in relation to the inflow concentration of the respective process stage or to the initial concentration of the corresponding lab experiment. Eq. (2) shows the calculation for removal:

$$\text{Removal} = \frac{c_0 - c_i}{c_0}[-] \quad (2)$$

c_0: Inflow concentration (process stage evaluation) or initial concentration (lab experiments).
c_i: Concentration at measuring point i (process stage evaluation) or at time i (lab experiments).

The OMP removal rate constant in the CAS refers to the removal averaged over the wastewater retention time in the CAS of the corresponding day. Eq. (3) shows the calculation for the removal rate constant in the CAS (k_{bio}):

$$k_{bio} = \frac{Removal_j}{\frac{V_{CAS}}{Q_j}}[1/\text{d}] \quad (3)$$

$Removal_j$: Removal on day j [-]
V_{CAS}: CAS basin volume [m^3]
Q_j: Flow of the WWTP Nette on day j [m^3/d]

Correlation analyses were performed uniformly using Pearson's correlation. Pearson's coefficient (r) was thus used to evaluate the linear relationship between two metric variables. The quality of non-linear fits (e.g. Freundlich isotherms) was quantified using the coefficient of determination (R^2). Moreover, uncertainties of data points in measuring series were calculated using a 95% confidence interval. Summary statistics (confidence interval) were performed using Python packages Seaborn and the Errorbar toolbox.

2.3.2. Freundlich isotherms

Freundlich isotherms were used to evaluate the adsorption tests and compare the adsorption equilibrium curves at different temperatures.

Freundlich isotherms serve to describe the equilibrium state of the adsorption of a substance at an interface at a constant temperature and thus represents the amount of substance bound to the interface in relation to the amount of substance in the solution (Graß et al., 2025). Eq. (4) shows the Freundlich isotherm equation for the adsorption of substances from a liquid phase:

$$q_e = K_F \cdot c_e^{\,n} \tag{4}$$

q_e: Loading of the activated carbon in relation to the substance under consideration mg/gAC.
K_F: Freundlich-constant.
c_e: Total concentration of the substance under consideration in the solution mg/L.
n: Heterogeneity factor.

In this study, the quality of the non-linear Freundlich isotherm fit (Scipy and the Optimize toolbox) was assessed using R^2 to filter out analysis results with insufficient accuracy. Consequently, only data series from OMPs were included in further correlation analyses if R^2 was higher than 80 %. If data series were able to achieve an R^2 greater than 80 % by eliminating a single data point, these were also included in further analyses. Data series that had more than two measurement points below the LOQ were also excluded from subsequent analyses. Consequently, the quality of the results was classified as high ($R^2 > 80$ %), medium (20 % $< R^2 \leq$ 80 %) and low ($R^2 \leq 20$ % or number of values n(>LOQ) = 1) depending on the quality of the Freundlich fit.

2.3.3. Van 't Hoff plots

Van 't Hoff plots were used to calculate the apparent adsorption enthalpy ΔH during adsorption of the examined OMPs based on the procedure proposed by Aumeier et al. (2022):

$$\Delta H(q_e, T) = -R * \left(\frac{d ln\left(\frac{q_e}{c_e}\right)}{d\left(\frac{1}{T}\right)} \right)_{q_e} \tag{5}$$

q_e: Loading of the activated carbon in relation to the substance under consideration mg/g_{PAC}.
c_e: Total concentration of the substance under consideration in the solution mg/L.
T: Temperature.
R: Universal gas constant.

Since the adsorption curves determined in this study have several reference points per temperature, the mean value of the ratio of q to c was first calculated for each temperature and then further used for the van 't Hoff plots. As described above, calculated thermodynamic parameters from the van 't Hoff plots were only included in further correlation analyses if the Freundlich isotherms of the OMPs showed sufficient quality ($R^2 > 80$ % and n(>LOQ) ≥ 2) at all three temperatures investigated. In contrast, the K_F values were also determined for individual temperatures, even if the Freundlich fit was not of sufficient quality for the other temperatures. Since the three runs of the adsorption tests were carried out with different feed samples (different OMP concentrations and different background DOC matrix), the results of the three runs of the adsorption experiments were not combined but analysed separately.

2.3.4. Arrhenius plots

Based on the evaluations by Meynet et al. (2020), Arrhenius plots were used to investigate the temperature-dependent degradation behaviour of OMPs in the CAS of the WWTP Nette. k_{bio} of the CAS was calculated as described in Eq. (3) and then plotted as a natural logarithm over the inverse temperature (Arrhenius relationship). Eq. (6) shows the classic Arrhenius relationship used in this study:

$$ln\ k_{bio} = ln\ A - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{6}$$

$ln\ A$: Pre-exponential factor.
E_a: Activation energy.
T: Temperature.
R: Universal gas constant.

The activation energy (E_a) was calculated from the slope of the linear regression line of the Arrhenius plot (ln k_{bio} vs 1/T). E_a serves as a parameter for quantifying temperature-dependent removal behaviour in the CAS.

3. Results & discussion

3.1. Temperature-dependent degradation behaviour in biologically active GAC filters varies between individual OMPs

Contrary to what would be expected from biological degradation processes, especially 1H-benzotriazole exhibits higher concentrations at higher temperatures in the effluent of the pilot-scale GAC filters. Thus, the increase in biological activity expected with rising temperatures does not cause a reduction in 1H-benzotriazole effluent concentrations. However, other OMPs such as clarithromycin, metoprolol, venlafaxine, irbesartan and hydrochlorothiazide exhibit higher concentrations at lower temperatures, especially in the intermediate measuring points. Fig. 2 shows 1H- benzotriazole and clarithromycin concentrations at different bed depths of GAC filter A over the filter BV.

While both substances are removed from the water phase to concentrations below the LOQ during the first months of operation, years two to four show largely consistent behaviour with seasonal fluctuations. The decreasing effect of higher temperatures on clarithromycin concentrations gradually decreases across the depth of the filter bed. However, unlike clarithromycin, seasonal fluctuations in 1H-benzotriazole concentrations are also reflected in the pilot-scale GAC filter effluent. The contrasting influence of temperature on the removal behaviour of individual OMPs in the pilot-scale GAC filters can be attributed to the different degradation processes and different physiochemical properties. While biological degradation generally increases with rising temperatures, temperature can have either a positive or a negative effect on adsorption behaviour. Both biodegradability and temperature dependence of adsorption are decisively influenced by physicochemical properties of the individual OMPs. In the following influencing factors on temperature-dependent adsorption and biodegradation are examined to characterise what determines the temperature-dependent behaviour of each individual OMP in biologically active GAC filters.

3.2. OMPs exhibit partly endothermic and partly exothermic adsorption behaviour

In the temperature range investigated (10–30 °C), four of the twelve OMPs examined exhibited exothermic behaviour (ΔH<0), and five OMPs exhibited endothermic behaviour (ΔH>0). For three other substances, no ΔH could be determined. For the substances amisulpride and citalopram, there were not enough measurements >LOQ available to perform a reliable Freundlich fit. For candesartan, no reliable Freundlich fit was possible due to highly fluctuating measurement results in all three wastewater samples examined.

Unlike single substance adsorption curves, the adsorption of individual OMPs in the investigated wastewater matrices competes with the adsorption of other OMPs and the background DOC matrix (Parniske

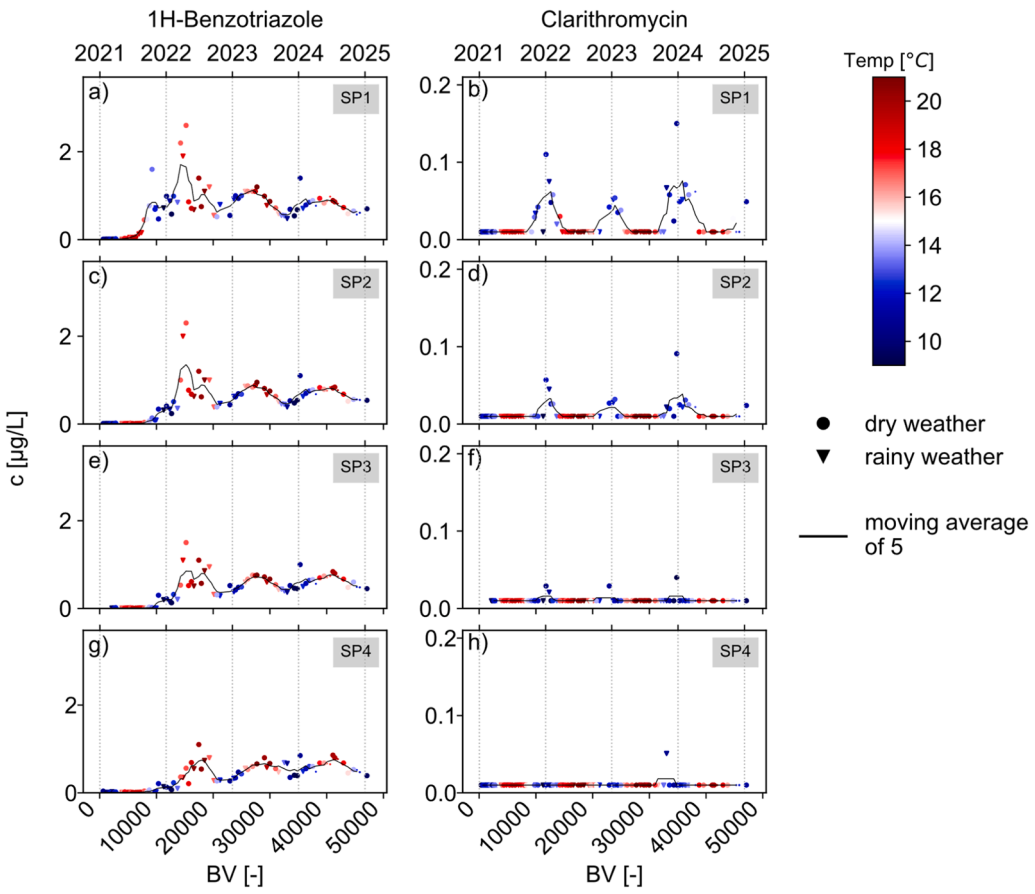


Fig. 2. Impact of temperature on 1H-benzotriazole (a, c, e and g) and clarithromycin (b, d, f and h) concentrations at different sampling points (SP1–4) of GAC filter A over BV, divided into dry weather days and rainy weather days.

et al., 2026). Thus, laboratory batch experiments with the influent wastewater of the GAC filters are a valuable intermediate step in investigating the transferability of results from literature (Aumeier et al., 2022; Masson et al., 2017) to the results of the pilot plant examined in this study. In the real wastewater adsorption experiments 1H-benzotriazole, hydrochlorothiazide, ∑4-/5-methylbenzotriazole and diclofenac exhibited exothermic adsorption behaviour in descending order. Whereas the OMPs carbamazepine, metoprolol, venlafaxine, irbesartan and clarithromycin exhibited ascending endothermic behaviour. Fig. 3 shows the determined adsorption curves and their Freundlich parameters for two apparently exothermic (1H-benzotriazole and hydrochlorothiazide) and two apparently endothermic (clarithromycin and venlafaxine) OMPs. The adsorption curves of all OMPs and all runs, as well as their van 't Hoff plots, can be found in Chapter 1 of the supplementary information (SI).

The ΔH determined for OMPs in the wastewater matrix of the influent to the GAC filters largely corresponds to the results reported in the literature for single-substance adsorption in buffer solutions. For 1H-benzotriazole, the average ΔH determined in this study is - 25 kJ/mol, which lies between the values reported by Aumeier et al. (2022) (- 14 kJ/mol) and Masson et al. (2017) (- 33 kJ/mol). The same applies to carbamazepine, whose value of + 10 kJ/mol falls between the ΔH reported by Aumeier et al. (2022) (+ 7 kJ/mol) and Masson et al. (2017) (+ 24 kJ/mol). The ΔH for metoprolol of + 12 kJ/mol determined in this study is significantly lower than that determined by Aumeier et al. (2022) (+ 50 kJ/mol). However, metoprolol shows generally endothermic behaviour in both studies. The significantly larger temperature range of 20 to 70 °C in Aumeier et al. (2022) could be another reason for the differing ΔH values between the two studies, in addition to the competitive adsorption behaviour in the real wastewater matrix. For diclofenac slightly exothermic adsorption behaviour (ΔH = - 3 kJ/mol) was determined in this study. However, literature data for diclofenac varies considerably. While Aumeier et al. (2022) reported a clearly endothermic behaviour (ΔH = + 31 kJ/mol), the results in Masson et al. (2017) indicate a clearly exothermic behaviour (ΔH = - 25 kJ/mol) for diclofenac adsorption. The K_F values and thermodynamic parameters of all OMPs examined are summarised in the SI (Table 1).

3.3. *Using the HLB value as core predictor for adsorption enthalpy*

Correlations between the determined thermodynamic variables (ΔH and ΔS) and the substance properties were examined to identify linkages between temperature-dependent adsorption behaviour and the physicochemical properties of OMPs. Overall, the HLB value has proven to be the most suitable predictor for the temperature-dependent adsorption behaviour of the OMPs investigated. Fig. 4 displays the correlation analysis of the thermodynamic parameters and substance properties of the OMPs. Hydrochlorothiazide was excluded from the correlation analysis shown in Fig. 4. The specific physicochemical properties of hydrochlorothiazide and the resulting deviation from the correlation between HLB and the thermodynamic variables are further explained below.

An alternative predictor to HLB is $\log_{Kow}$, which, has also shown a strong correlation with the thermodynamic parameters ΔS and ΔH (69 respectively 67 %) determined in this study. However, unlike $\log_{Kow}$, the HLB value reflects the potential of single OMPs to interact with the aqueous phase via individual molecular groups. Furthermore, correlation analysis of the substance properties showed that HLB has a strong positive correlation with the molecular weight (MW) of the OMPs examined. Moreover, the MW itself also correlates strongly and

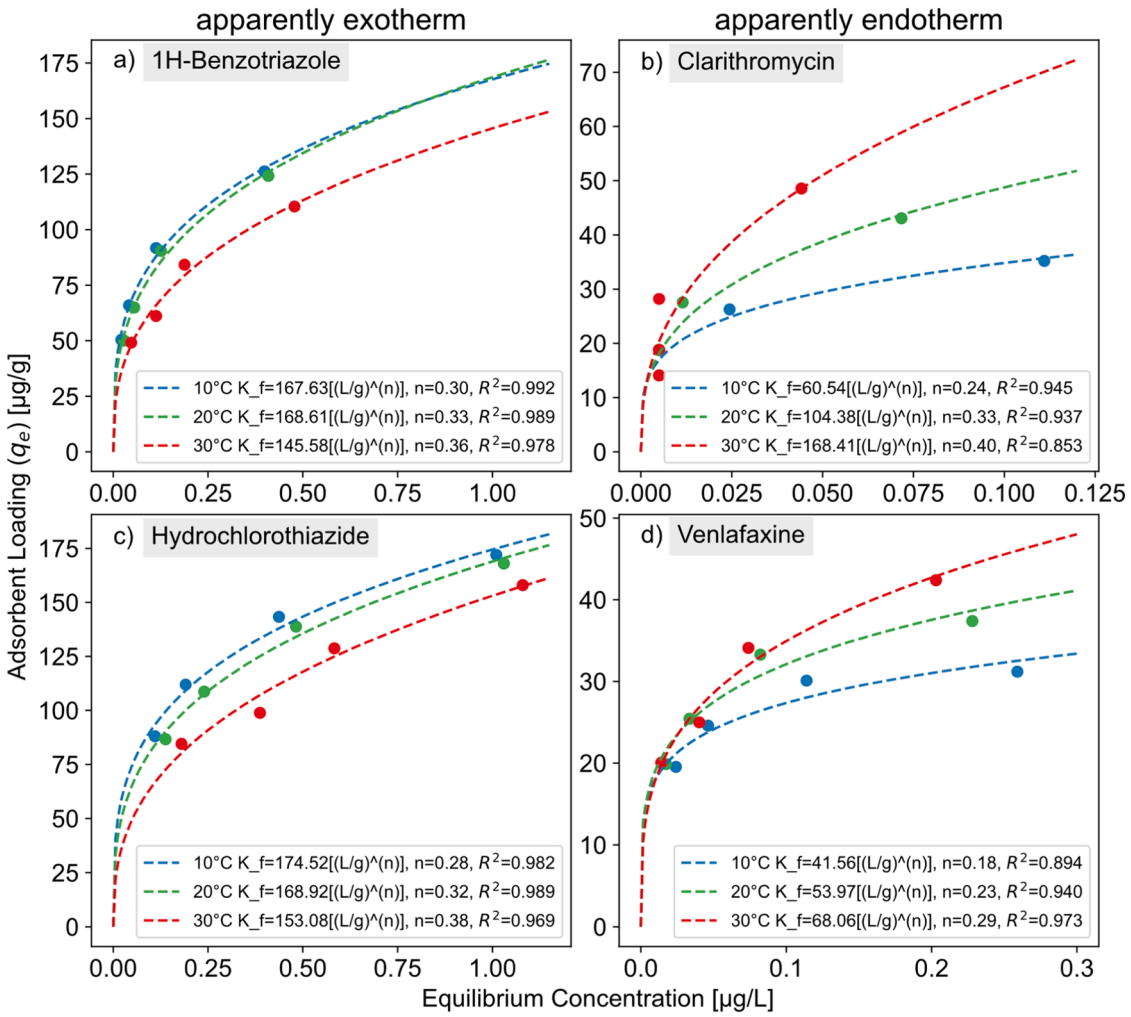


Fig. 3. Temperature-dependent adsorption curves and Freundlich parameters for 2 apparently exothermic OMPs (1H-benzotriazole (a) and hydrochlorothiazide (c)) and 2 apparently endothermic OMPs (clarithromycin (b) and venlafaxine (d)).

Table 1
Substance properties of the investigated OMPs: octanol-water partition coefficient[a] logKow, pH-dependent partition coefficient[a] logD at a pH of 7.3, hydrophilic-lipophilic balance[a] HLB, molecular weight[b] MW, dissociation constant[b] pK_a at ambient temperature T = 20 °C, and degree of dissociation α calculated at a pH of 7.3.

	$\log K_{ow}$	log*D* (pH=7.3)	HLB	MW [g/mol]	pK_a (*T* = 20 °C)	*α* (pH=7.3)
Amisulpride	0.25	−1.33	18.32	369.5	9.3	0.99%
1-H-Benzotriazole	1.30	1.28	7.70	119.1	8.4	7.84%
Candesartan	5.31	0.72	6.10	440.5	6.0[c]	95.20%
Carbamazepine	2.77	2.77	10.60	236.3	13.9	0.00%
Citalopram	3.76	0.82	10.02	324.4	9.4	0.82%
Clarithromycin	3.24	1.53	15.50	748.0	9.0	2.00%
Diclofenac	4.26	1.16	6.08	296.1	4.2	99.93%
Hydrochlorothiazide	−0.58	−0.58	20.54	297.7	7.9	20.08%
Irbesartan	5.38	4.28	13.49	428.5	4.1	99.94%
4-/5-Methylbenzotriazole	1.82	1.80	6.94	133.2	(8.8)	3.07%
Metoprolol	1.76	−0.19	13.73	267.4	9.7	0.40%
Venlafaxine	2.74	1.03	11.37	277.4	9.5	0.63%

[a] : $\log K_{ow}$, logD, and HLB were taken from Chemicalize database (ChemAxon, 2024).
[b] : MW and pK_a and Ion-Mode were taken from PubChem database (Kim et al., 2025) unless stated otherwise.
[c] : (Husain et al., 2011).

positively with ΔH and ΔS. In contrast, $\log_{Kow}$ shows the strongest correlation with the degree of dissociation (α), which, unlike MW, does not show a strong correlation with ΔH and ΔS. Consequently, the HLB value appears to primarily reflect an increasing number of functional groups capable of forming hydrogen bonds with increasing MW. Meanwhile, $\log K_{ow}$ appears to be more sensitive to the influence of dissociation behaviour on the solubility of OMPs. Further discussion on the use of $\log_{Kow}$ as an alternative predictor to the HLB value for the thermodynamic adsorption behaviour of the OMPs investigated can be found in the SI (Chapter 2). Table 1 provides an overview of the

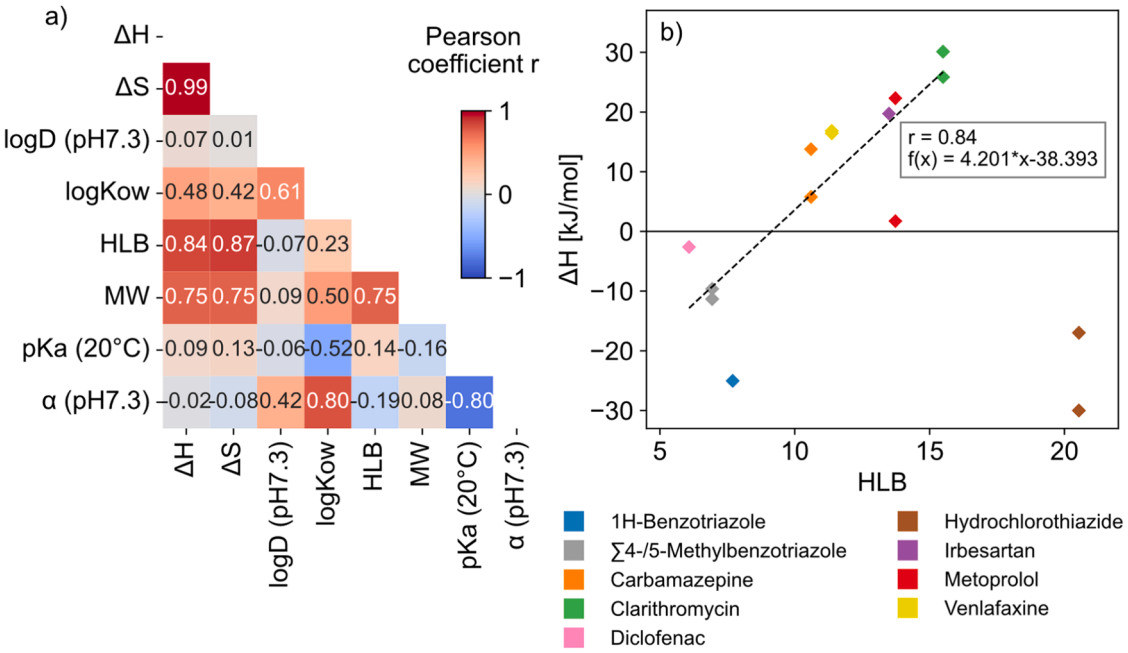


Fig. 4. Results of the correlation analysis of the thermodynamic parameters and substance properties of the OMPs investigated in this study, excluding hydrochlorothiazide. In b), the correlation between ΔH and HLB is shown, taking into account all runs (runs 1 to 3) for the individual OMPs where they exhibited a high-quality Freundlich fit (R^2 > 80%).

physicochemical properties regarding hydrophilicity, dissociation, and MW for all OMPs examined.

The positive correlation between MW, hydrophilicity, and thermodynamic parameters, as observed in the correlation with the HLB value, was also found in literature (Fontecha-Cámara et al., 2006; Masson et al., 2017). More specifically, MW and hydrophilicity favour the formation of hydrogen bonds, which in turn affects the temperature-dependent adsorption behaviour of molecules (Masson et al., 2017). The study by Masson et al. (2017) describes how molecules with a larger hydrate shell tend to exhibit endothermic behaviour. This endothermic adsorption behaviour is accompanied by an increase in ΔS, which can be interpreted as an increase in degrees of freedom in the system (Chandler, 2005). The increase in degrees of freedom during the adsorption of substances with larger hydration shells can be attributed to the breaking of the solvation sphere, which is accompanied by an increased energy requirement (increased ΔH) (Aumeier, 2020; Masson et al., 2017). Thus, this indicates that the positive correlation between HLB, MW, and ΔH, as well as the endothermic adsorption behaviour of some OMPs, is due to the more frequently occurring hydrogen bonds in larger molecules with more hydrophilic groups. Consequently, the energy absorbed to break the hydration shell (endothermic process) (Çeçen and Aktas, 2011) exceeds, for some OMPs, the energy released by binding to an adsorption site (Aumeier, 2020).

In addition to the formation of hydrate shells, this data shows, that it is the pK_a shift that determines the temperature-dependent adsorption behaviour of individual OMPs. Among the OMPs studied, especially hydrochlorothiazide is decisively influenced by the pK_a shift in its temperature-dependent adsorption behaviour. Thus, hydrochlorothiazide shows the greatest deviation from the correlation between ΔH and HLB.

*4*According to the threshold criteria proposed in Aumeier et al. (2022) ($|pH\text{-}pK_a| < 1.3$ ($\alpha > 5$ %)) in total three of the OMPs examined in this study exhibit the properties required to undergo a temperature-induced pK_a shift. In addition to candesartan ($|pH\text{-}pK_a| = 1.3$ ($\alpha = 95.2$ %)), for which no thermodynamic adsorption parameters could be determined due to poor adsorbability, these include 1H-benzotriazole ($|pH\text{-}pK_a| = 1.07$ ($\alpha = 7.84$ %)) and hydrochlorothiazide ($|pH\text{-}pK_a| = 0.6$ ($\alpha = 20.08$ %)). Alongside to the strongest deviation from the correlation between ΔH and HLB, these are the two OMPs that exhibit the most exothermic adsorption behaviour.

While 1H-benzotriazole was already identified by Aumeier et al. (2022) as the substance with the strongest pK_a shift, hydrochlorothiazide has not been examined in the comparative studies (Aumeier et al. 2022; Masson et al., 2017) previously. Unlike 1H-benzotriazole, hydrochlorothiazide also meets the stricter threshold criteria defined by Perrin et al. (1981) (pK_a shift relevant: ($|pH\text{-}pK_a| < 1$ ($\alpha > 10$ %)) suggesting an even more pronounced influence of the pK_a shift for hydrochlorothiazide than for 1H-benzotriazole. In summary, this analysis shows that the affinity for interaction with the aqueous phase (hydration shell formation) is the primary factor determining whether the adsorption of an OMP appears to be endothermic or exothermic. Additionally, certain OMPs - particularly 1H-benzotriazole and hydrochlorothiazide - are also strongly influenced by their temperature-dependent dissociation behaviour (pK_a shift). Whether these substances adsorb exothermically or endothermically can therefore only be predicted with limited accuracy based on the HLB value.

3.4. The temperature-dependent removal of OMPs in CAS does not show a strong correlation with physicochemical substance properties

Unlike adsorption, biodegradation processes in the temperature range studied (8 to 23 °C) generally show a positive correlation between temperature and conversion respectively growth rates (Chen et al., 2020). Thus, when it comes to biodegradability, the question is primarily how well a OMP is co-metabolised—not whether its breakdown is positively or negatively affected by temperature. Moreover, the following section shows that biodegradability and its temperature dependence do not strongly correlate with any of the physicochemical properties of the OMPs. Consequently, unlike in the case of adsorption (HLB value), no physicochemical property was found to predict the temperature-dependent biodegradation of OMPs. These conclusions were drawn based on data from the CAS at WWTP Nette, which was operated within the same temperature range as the pilot plant GAC filters. While the effects of adsorption and biodegradation cannot be evaluated separately in the pilot-scale GAC filters, the CAS demonstrates a predominantly biodegrading removal process.

With the help of Arrhenius plots, the relationship between k_{bio} and temperature in the CAS of the WWTP Nette was used to determine E_a. The results show that the OMPs with the highest removal exhibit the smallest fluctuations in the 95 % confidence interval of E_a. Overall, the mean removal in CAS exceeded a value greater than 35 % (moderate removal) for only three substances: metoprolol (55 %), 1H-benotriazole (53 %) and diclofenac (47 %). Fig. 5 shows the influence of temperature on the removal of these three OMPs in the full-scale CAS of the WWTP Nette. The influence of temperature on the removal of the remaining OMPs examined in the CAS, as well as the determined E_a values can be found in the SI (Chapter 4).

The E_a values determined for 1H-benzotriazole, diclofenac and metoprolol (11, 37, and 62 kJ/mol) for the CAS of the WWTP Nette are all below the value of 69 kJ/mol assumed in Chen et al. (2020) for heterotrophic microorganisms in wastewater treatment. Consequently, the OMP removal rate constants show a slightly weaker decrease at falling temperatures than assumed by Chen et al. (2020) for substrate degradation in municipal WWTPs. In Koch et al. (2000) a temperature dependence factor of 0.07 1/ °C was determined for the degradation kinetics of Swiss municipal wastewater. This corresponds to an E_a of around 50 kJ/mol and is thus between the values determined in this study for diclofenac and metoprolol. The temperature dependence of the degradation kinetics of OMPs that show a higher removal (1H-benzotriazole, diclofenac, and metoprolol) in CAS is therefore at a comparable level to that of general carbon compounds in municipal wastewater. This indicates that the co-metabolic degradation of these OMPs is affected by temperature changes to a similar extent as the degradation of organic substrates. For OMPs that show lower removal in the CAS, other influencing factors such as overall pollutant loading, precipitation, solar radiation or the concentration of mixed liquor suspended solids (MLSS) may offset the influence of temperature (Hai et al., 2011; Sui et al., 2016). In addition to biodegradation, it is most likely sorption to the activated sludge that determines the removal of certain OMPs in CAS (Liwarska-Bizukojc et al., 2018).

No strong correlation with the physicochemical properties of the OMPs was found, either for biodegradability or for its temperature dependence. Overall, this is not an unexpected result, as OMPs undergo different biotransformation pathways in CAS. Rather, correlations with physicochemical parameters are expected to be found in clusters of OMPs that undergo the same type of enzyme-catalysed biotransformation (Wang et al., 2020). Moreover, in addition to biodegradation, other removal processes contribute to OMP removal in CAS. Depending on the physicochemical properties, a different removal process dominates, and thus different substance properties determine the overall removal.

3.5. *Adapted microbial community in GAC filters may enhance biodegradation of individual OMPs*

In addition to the temperature-dependent conversion and growth rates (examined in Chapter 3.4), it is the microbial composition that affects the co-metabolic biodegradation of OMPs (Meynet et al., 2024). Thus, additional biodegradation experiments were conducted to

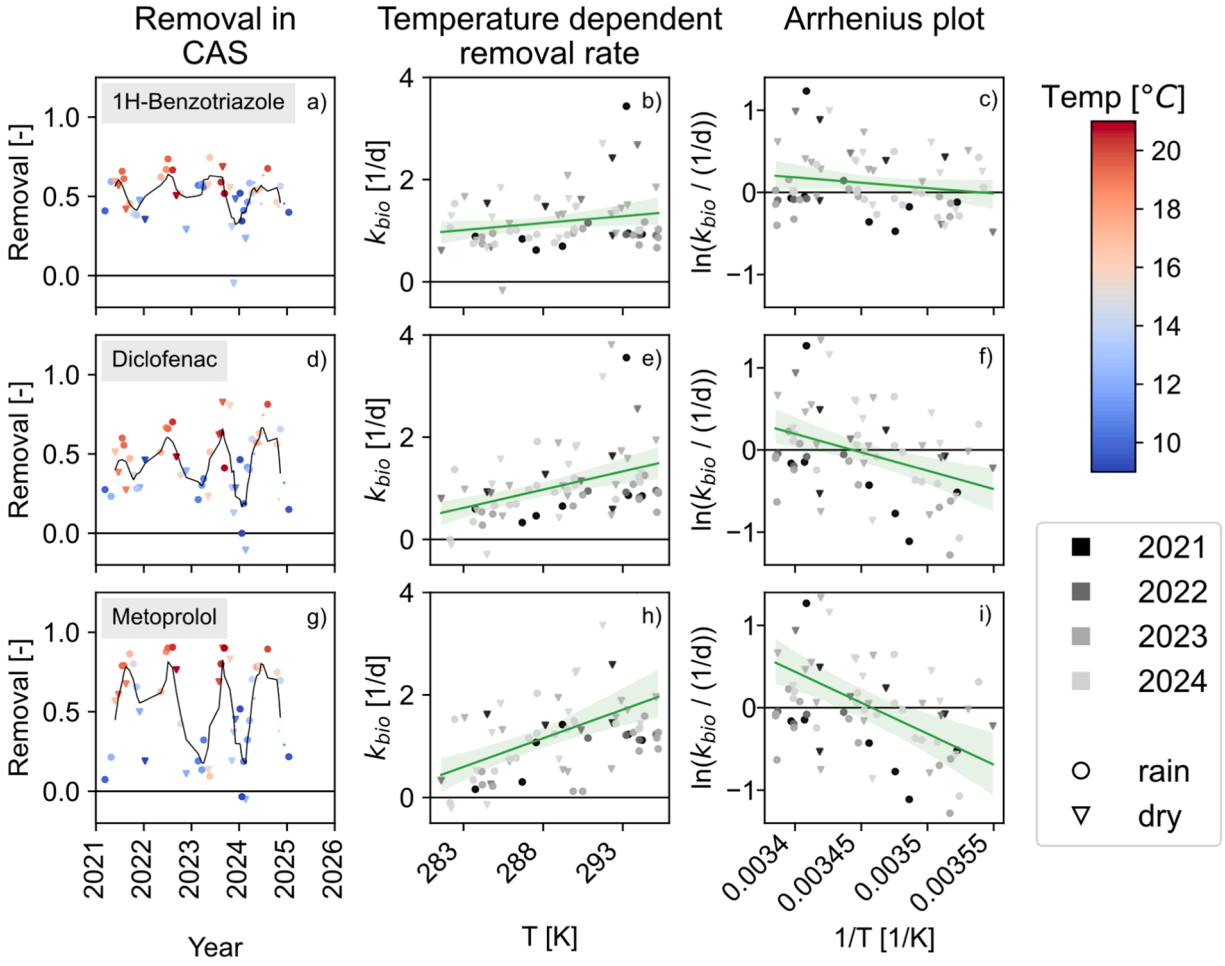


Fig. 5. Influence of temperature on the removal of 1-H-benzotriazole (a-c), diclofenac (d-f) and metoprolol (g-i) in the CAS of the WWTP Nette. Subfigures a), d) and g) show the moving average of 5 alongside the data points (color coded for temperature). Subfigures b), c), e), f), h) and i) show a linear regression line (green solid line) with a 95% confidence interval (green shaded area) alongside the data points (greyscale coding for year of operation).

investigate the difference in OMP biodegradation between CAS sludge and GAC filter backwash sludge. For these experiments, microorganisms from GAC filter backwash sludge and from the activated sludge of the WWTP Nette were used as inoculum. The results of the biodegradation experiments show improved degradation behaviour of individual OMPs in the backwash sludge of the GAC filters compared to the CAS sludge. Since the inoculum was the only difference in the individual degradation experiments, these were further investigated by 16S rRNA sequencing to explore the improved biodegradation in the GAC sludges. The results from the 16S rRNA sequencing show that microbial communities in the two GAC filter backwash sludges differed decisively from the activated sludge of the WWTP Nette. Fig. 6 shows the comparison of OMP removal with activated sludge from the CAS of the WWTP Nette and backwash sludge from the two examined GAC filters. Moreover, the relative abundance at phylum level for the CAS sludge and the two GAC backwash sludges is displayed. The relative abundance at genus level is shown in the SI (Figure 17).

The sludge from GAC filter A and GAC filter B both exhibit a higher proportion of Proteobacteria (52 % and 50 % of relative abundance) than the CAS sludge from the WWTP Nette (34 %) at phylum level. While Bacteriodota account for the third largest proportion in the CAS of the WWTP Nette with 15 % of the relative abundance, this phylum occurs decisively less frequent in GAC filters A and B, with 2 % and 3 % respectively. Actinobacteria, which make up the second largest proportion in the CAS of the WWTP Nette (19 %), are significantly less prevalent in the GAC filters (7 % and 5 %). Moreover, Firmicutes (5 % in CAS) were no longer found in GAC filter sludge. However, other phyla such as Chloroflexi or Cyanobacteria account for a higher proportion of the relative abundance in the GAC filters than in the CAS. In addition to the percentage increase in Proteobacteria of 18 % and 16 % respectively compared to the CAS, it is Planctomycetota that increase by 15 % and 13 % respectively of the relative abundance in GAC filter A and B. In the CAS sludge Planctomycetota accounted for <1%. The fact that Proteobacteria make up the largest proportion of the microbial community in CAS and in GAC filters is consistent with values reported in literature (Meynet et al., 2024; Sauter et al., 2023; Shi et al., 2024). Bacteriodota and Acidobacteria were the second and third most common phyla in GAC filters in the study by Sauter et al. (2023).

These differences in microbial composition can be attributed to the altered environmental conditions in the GAC filters compared to the CAS. Due to the separately operated UF, the inflow to the GAC filters is saturated with oxygen (9.4 ± 1.0). Furthermore, carbon-limited conditions prevail in the effluent of the CAS/in the influent to the pilot plant (Graß et al., 2025). The study by Hübner et al. (2021) found that oligotrophic conditions promote the establishment of alternative metabolic pathways and thus favour the biodegradation of especially slowly-degrading substances. Such improved biodegradability in the backwash sludge of the pilot GAC filter compared to the sludge from the CAS of the WWTP Nette was observed particularly for the OMPs clarithromycin, diclofenac and amisulpride (additional removal of 31 %, 82 % respectively > 100 %). Amisulpride was already described in Fundneider et al. (2021b) as being readily degradable in biologically

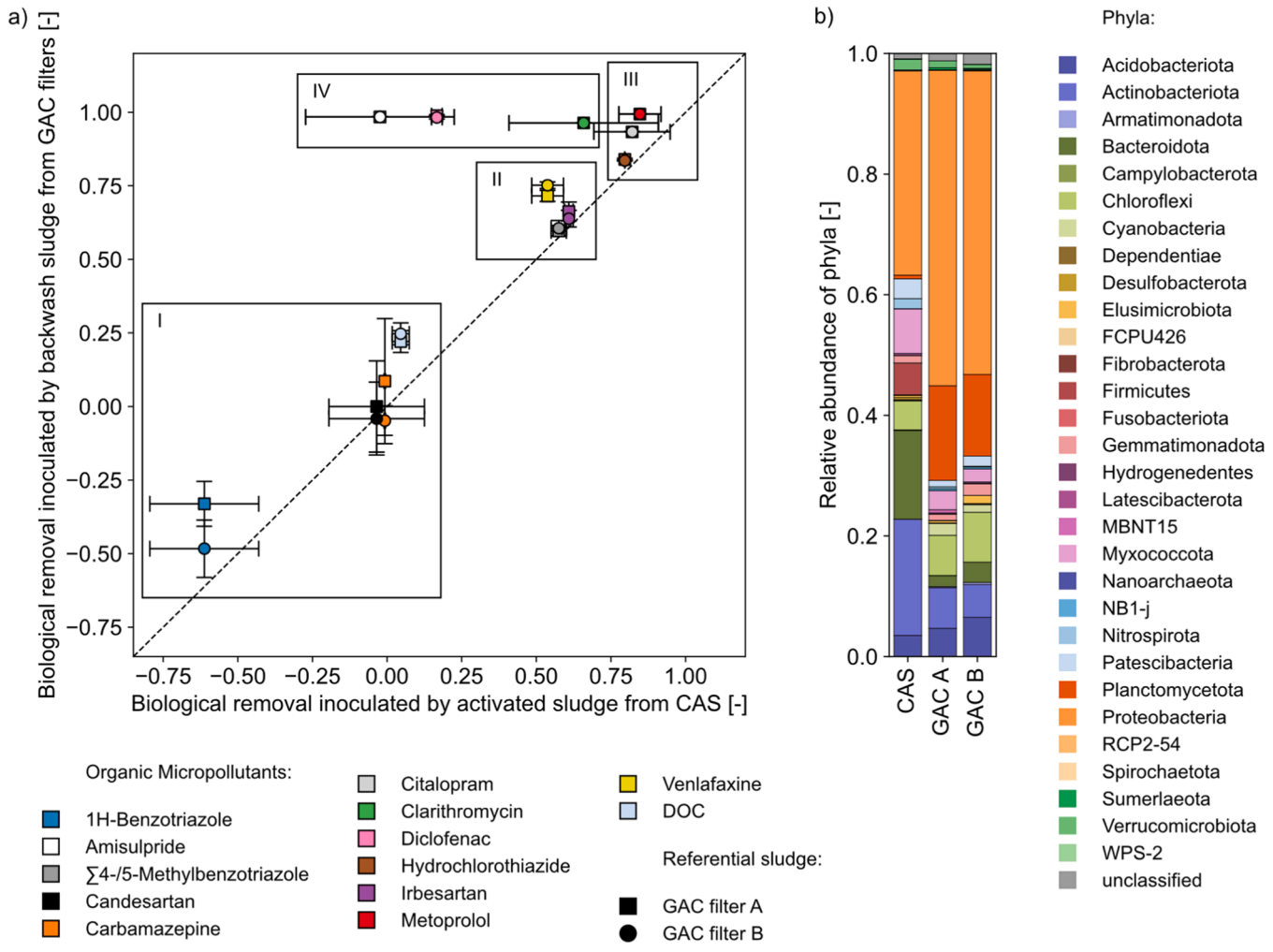


Fig. 6. a) Comparison of OMP removal in biodegradation tests using activated sludge (x-axis) and backwash sludge from GAC filter A and B (y-axis) and b) relative abundances at phylum level for the CAS sludge of the WWTP Nette and backwash sludge of GAC filter A and B of the pilot plant.

active GAC filters but it exhibits low degradation rates in CAS (Bollmann et al., 2016). The improved biodegradability of diclofenac in biofilm systems compared to activated sludge flocs was observed in Falås et al. (2013), who compared biofilms on carrier materials with CAS sludge. Furthermore, high degradability of diclofenac in biologically active GAC filters was reported by Fundneider et al. (2021b). Consequently, this study and findings from the literature show that the adapted environmental conditions in GAC filters improve the degradation of individual OMPs compared to CAS. Whether the favouring of alternative metabolic pathways is due to the changed oxygen and nutrient conditions or to the changed growth form of the microorganisms (sessile vs. suspended) needs further investigation. 6.

However, based on the results in Fig. 6, the OMPs examined can be clustered into four groups:

- group I contains the OMPs that are biologically persistent in both CAS and GAC filter backwash sludge (1H-benzotriazole, candesartan, and carbamazepine),
- group II contains OMPs that exhibit moderate bioavailability in both CAS and GAC filter backwash sludge (∑4-/5-methylbenzotriazole, irbesartan and venlafaxine),
- group III contains OMPs that exhibit high bioavailability for both CAS and GAC filter backwash sludge (citalopram, hydrochlorothiazide and metoprolol) and.
- group IV contains OMPs that exhibit decisively better bioavailability in GAC filter backwash than in CAS sludge (clarithromycin, diclofenac and amisulpride).

The four OMPs that exhibited exothermic behaviour in the adsorption tests (1H-benzotriazole, ∑4-/5-methylbenzotriazole, diclofenac and hydrochlorothiazide) differ decisively in their biodegradation behaviour. While 1H-benzotriazole and ∑4-/5-methylbenzotriazole exhibit low to moderate biodegradability (groups I and II), hydrochlorothiazide and diclofenac are readily degraded in GAC filter backwash sludge (groups III and IV). Of the endothermically adsorbing OMPs, it is primarily carbamazepine, irbesartan and venlafaxine (groups I and II) that are poorly to moderately biodegradable in GAC sludge. Metoprolol and clarithromycin (groups III and IV) thus display good biodegradability in GAC filter backwash sludge. The two OMPs (1H-benzotriazole and clarithromycin) compared in Chapter 3.1 exhibit contrasting properties in terms of both temperature-dependent adsorption behaviour and biodegradation behaviour. While 1H-bezotriazole adsorbs most exothermically and has very poor bioavailability, clarithromycin adsorbs most endothermically and has high bioavailability, especially in GAC filter backwash sludge.

Alongside metoprolol, diclofenac and 1H-benzotriazole are among the OMPs that were most effectively removed in the large-scale WWTP Nette (see Section 3.4). However, in the biodegradation tests (laboratory tests) shown in Fig. 6, 1H-benzotriazole and diclofenac were poorly degraded by CAS sludge. In the laboratory experiments, the VSS was kept as low as possible (0.03 g/L) to minimise the influence of sorption effects on OMP removal. Consequently, the difference between the results of the laboratory tests and the degradation in the large-scale CAS indicates increased removal in the CAS of the WWTP Nette due to sorption to the sludge. In their study, Carballa et al. (2005) investigated the sorption behaviour of several OMPs on sludge in primary treatment and classified diclofenac as highly adsorbable due to its hydrophobic properties. Moreover, in their study on physicochemical properties that determine the degradation behaviour of OMPs in CAS, Wang et al. (2020) found that, in the clusters of benzotriazole and diclofenac the activated sludge-water distribution coefficient (k_d) influences the degradation behaviour even at $k_d < 500$ L/kg. Consequently, sorption processes appear to influence OMP removal in CAS even at low k_d values in specific OMP clusters (Wang et al., 2020). Metoprolol, on the other hand, showed good degradability by CAS sludge in laboratory experiments and had the highest E_a in the CAS of the WWTP Nette. Both aspects indicate that metoprolol in the full-scale CAS is also predominantly removed by biodegradation processes. In summary, this examination shows that an adapted microbial community in the GAC filters has a positive effect on the degradation of OMPs. For endothermically adsorbing OMPs, good biodegradability can additionally have a beneficial effect on removal performance at high temperatures. For exothermically adsorbing OMPs, good biodegradability can counteract the decrease in adsorption at high temperatures. Moreover, further investigation is needed to determine to what extent OMP conversion rates from the CAS can be applied to GAC filters. In addition to the adapted microbial community, sorption processes on sludge flocs respectively the biofilm are expected to play a decisive role.

3.6. *Exothermic adsorbing OMPs exhibit the most pronounced temperature-dependent removal behaviour in the pilot-scale GAC filters*

The conducted classification of OMPs in the laboratory experiments reflects in their temperature-dependent behaviour in the pilot-scale GAC filters. Overall, it is the exothermic adsorbing OMPs (1H-benzotriazole, ∑4-/5-methylbenzotriazole, hydrochlorothiazide and diclofenac) that react most strongly to temperature changes in the pilot-scale GAC filters. However, unlike 1H-benzotriazole and ∑4-/5-methylbenzotriazole, the exothermic adsorption of hydrochlorothiazide and diclofenac is outweighed by increased biodegradation at higher temperatures. Thus, 1H-benzotriazole and ∑4-/5-methylbenzotriazole are the only two OMPs that exhibit increasing effluent concentrations at increasing temperatures. For hydrochlorothiazide and diclofenac, higher concentrations were measured at lower temperatures. This is particularly evident in the topmost filter layer. However, the positive temperature effect on the concentrations of hydrochlorothiazide and diclofenac decreases continuously across the filter bed depth. The temperature effect on endothermically adsorbing OMPs is lower than for diclofenac and hydrochlorothiazide. The declining OMP concentrations at higher temperatures, especially in the uppermost filter layers, indicate increased biological degradation. This is consistent with Fundneider et al. (2021b) and Hallé et al. (2015), who observed decreasing biomass with increasing filter bed depth. Fig. 7 shows, as an example, the regression lines between concentration and temperature for 1H-benzotriazole at different sampling points (SP1 to 4) of GAC filter A and for different years. As demonstrated for 1H-benzotriazole (left-hand side of Fig. 7), regression curves relating concentration to temperature were also examined for all other OMPs. The corresponding slopes of the regression curves at various bed heights are shown on the right-hand side of Fig. 7.

The concentrations on different filter bed depths of all OMPs examined are shown in the SI (Chapter 7). Over the years examined, the majority of OMPs show no overall upward or downward trend in effluent concentrations of the biologically active GAC filters. Thus, apart from temperature-related fluctuations, the concentrations remain at a constant level, when the GAC filter is biologically active. Exceptions to this are ∑4-/5-methylbenzotriazole, candesartan and carbamazepine, which show an overall upward trend in addition to seasonal fluctuations. These three OMPs belong to the poorly to moderate biodegradable OMPs (group I and II) identified in this study. The only OMP that shows an overall downward trend in effluent concentrations is diclofenac, which showed significantly improved degradation in GAC filter backwash sludge compared to CAS sludge (group IV). Additionally to the individual OMPs, an analysis of the average removal of all OMPs examined is shown in the SI (Figure 27). The progression curve for the average OMP removal demonstrates a largely consistent removal level, with corresponding seasonal fluctuations. Consequently, the average OMP removal begins to decline for the first time after slightly <10,000 BV and then stabilizes at a constant level whilst the GAC filters remain biologically active. Contrary to what would be expected from pure biofilters, the GAC filters examined exhibit reduced removal rates and higher effluent concentrations at higher temperatures. Thus, the exothermically adsorbing and poorly biodegradable OMPs (1H-

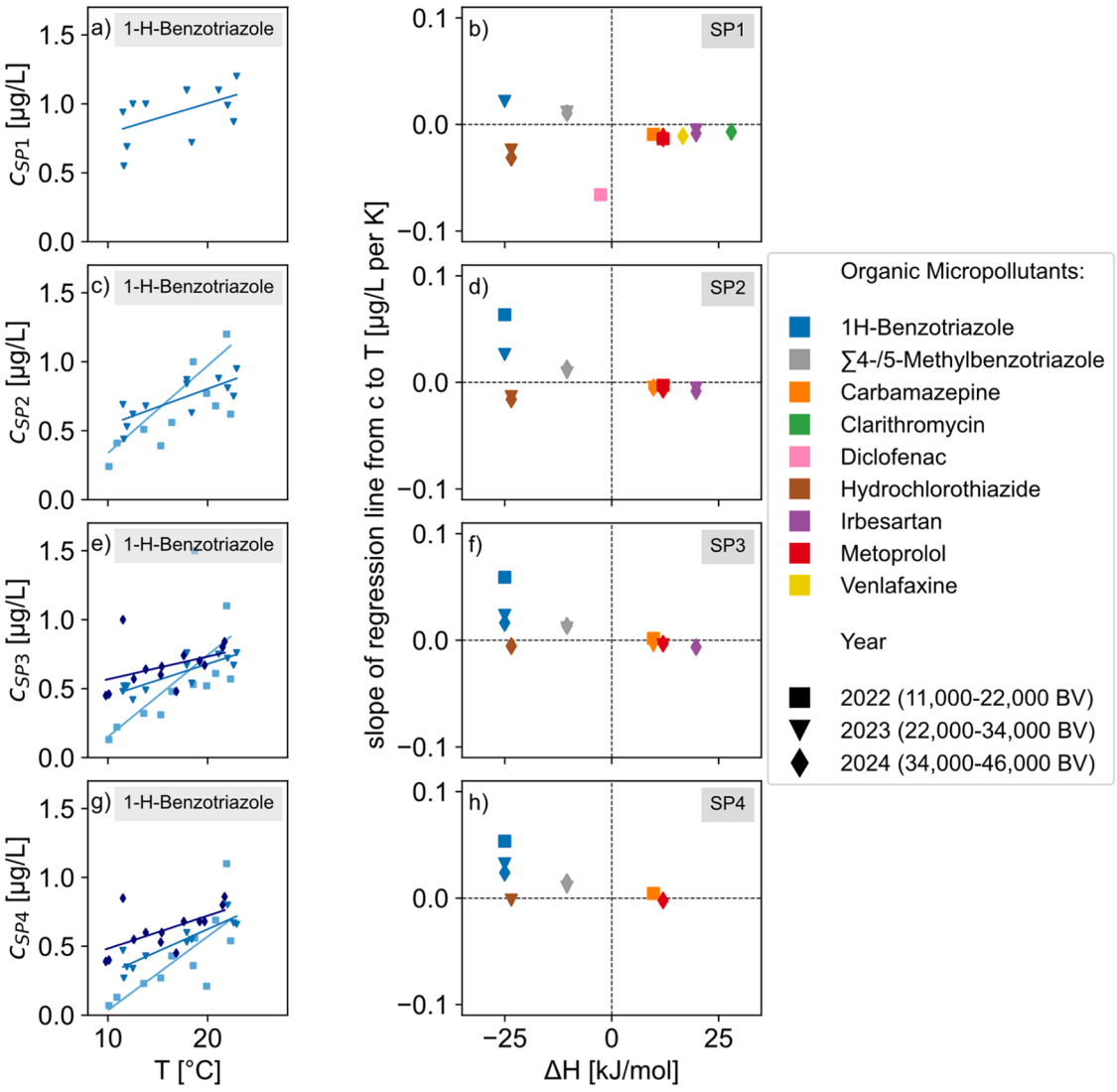


Fig. 7. On the left-hand side (a, c, e, g) is the correlation between 1H-benzotriazole concentrations and temperature at different sampling points and in different years. On the right-hand side (b, d, f, h) are the slopes calculated for further OMP concentrations over temperature (determined in the same way as shown for 1H-benzotriazole) above ΔH. Only data from years and sampling points whose regression line had an $R^2 > 10$ % and at least 50 % of the values > LOQ were used for the analysis.

benzotriazole and ∑4-/5-methylbenzotriazole) dominate the seasonal fluctuations in the pilot-scale GAC filter performance.

In addition to the data for GAC filter A shown in Fig. 7, the same assessment was carried out for GAC filter B and can be found in the SI (Chapter 6). The temperature-dependent behaviour of the OMPs in GAC filter A largely corresponds to the results from GAC filter B. The temperature-dependent behaviour of the OMPs examined is therefore not decisively impacted by the increased backwash frequency applied to GAC filter B. When comparing the average removal of all OMPs examined, no significant difference was observed between the weekly (Filter B) and the two-to-three-weekly (Filter A) backwash frequency (two-tailed paired *t*-test, P = 0.32>0.05). In line with this, Graß et al. (2025) found that DOC removal was limited by the bioavailable fraction of DOC in the influent to the GAC filters. Consequently, it appears that it is not primarily backwashing but rather the bioavailable substrate in the influent that has a limiting effect on biological activity in the GAC filters. This could also explain why Emelko et al. (2006) were unable to detect a significant temperature effect on TOC removal in their biofilters. However, this study and Hallé et al. (2015) show that, unlike DOC/TOC, OMP degradation in biologically active filters certainly is affected by temperature. Extending beyond the findings of Hallé et al. (2015), this study demonstrates that temperature affects not only the biological but also the adsorptive removal of OMPs in GAC filters. However, the extent to which higher temperatures lead to increased biological activity in GAC filters, despite influent substrate limitations, requires further investigation.

4. Conclusions

The results of this study show that annual temperature fluctuations influence both the biological and adsorptive degradation of OMPs in biologically active GAC filters. Furthermore, the HLB value was identified as the main predictor for the temperature-dependent adsorption behaviour of the OMPs investigated. The detailed conclusions are:

- In addition to their affinity for forming hydrogen bonds, it is the temperature-dependent dissociation shift that determines the temperature-dependent adsorption behaviour of individual OMPs. The influence of the temperature-dependent dissociation shift is detectable for 1H-benzotriazole, both in lab batch adsorption and in pilot GAC filters.

- An adapted microbial community showed decisively improved biodegradation of OMPs in GAC filter backwash sludge compared to CAS sludge, especially for diclofenac, clarithromycin and amisulpride.
- In addition to diclofenac, clarithromycin and amisulpride, citalopram, hydrochlorothiazide and metoprolol exhibited high bioavailability for both CAS sludge and backwash sludge from GAC filters.
- Overall, it is the exothermic adsorbing OMPs (1H-benzotriazole, ∑4-/5-methylbenzotriazole, hydrochlorothiazide and diclofenac) that react most strongly to temperature changes in the pilot-scale GAC filters. However, unlike 1H-benzotriazole and ∑4-/5-methylbenzotriazole (poor to moderate biodegradability), the exothermic adsorption of hydrochlorothiazide and diclofenac is outweighed by increased biodegradation at higher temperatures.
- Unlike for 1H-benzotriazole and ∑4-/5-methylbenzotriazole, which exhibit constant exothermic behaviour, the temperature-related concentration fluctuations of biodegradable OMPs decrease with increasing filter bed depth. Thus, mainly exothermically adsorbing and poorly biodegradable OMPs cause temperature-dependent fluctuations in the pilot GAC filter effluent.

CRediT authorship contribution statement

Larissa Graß: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Daniel Hillebrandt:** Data curation, Resources. **Julian Firk:** Data curation, Resources. **Laurence Palmowski:** Funding acquisition, Project administration, Supervision, Writing – review & editing. **Benedikt M. Aumeier:** Conceptualization, Methodology, Visualization, Writing – review & editing. **Thomas Wintgens:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Niersverband (Viersen, Germany), the Federal Ministry of Education and Research (BMBF) and the Ministry of Culture and Science of the German State of North Rhine-Westphalia (MKW) under the “Excellence Strategy of the Federal Government and the Länder” (EXU-JPI).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2026.126506.

Data availability

Data will be made available on request.

References

Aumeier, B.M., 2020. The hydrothermal solution for decentralized drinking water purification. AVT.CVT - Chem. Process Eng. 6, 1–180. https://doi.org/10.18154/RWTH-2020-09122. Aachen.

Aumeier, B.M., Augustin, A., Thones, M., Sablotny, J., Wintgens, T., Wessling, M., 2022. Linking the effect of temperature on adsorption from aqueous solution with solute dissociation. J. Hazard. Mater. 429, 128291. https://doi.org/10.1016/j.jhazmat.2022.128291.

Basu, O.D., Dhawan, S., Black, K., 2016. Applications of biofiltration in drinking water treatment – a review. J. Chem. Technol. Biotechnol. 91 (3), 585–595. https://doi.org/10.1002/jctb.4860.

Bollmann, A.F., Seitz, W., Prasse, C., Lucke, T., Schulz, W., Ternes, T., 2016. Occurrence and fate of amisulpride, sulpiride, and lamotrigine in municipal wastewater treatment plants with biological treatment and ozonation. J. Hazard. Mater. 320, 204–215. https://doi.org/10.1016/j.jhazmat.2016.08.022.

Carballa, M., Omil, F., Lema, J.M., 2005. Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment. Water. Res. 39 (19), 4790–4796. https://doi.org/10.1016/j.watres.2005.09.018.

Chandler, D., 2005. Interfaces and the driving force of hydrophobic assembly. Nature 437 (7059), 640–647. https://doi.org/10.1038/nature04162.

ChemAxon, 2024. Chemicalize Database. Retrieved June 2024, from. https://chemicalize.com/.

Chen, G.-H., van Loosdrecht, M.C., Ekama, G.A. and Brdjanovic, D. (2020) Biological Wastewater Treatment: Principles, Modelling and Design, IWA Publishing, London. http://iwaponline.com/ebooks/book/791/Biological-Wastewater-Treatment-Principles, ISBN: 9781789060362.

Cirja, M., Ivashechkin, P., Schäffer, A., Corvini, P.F.X., 2008. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). Rev. Environ. Sci. Bio/Technol. 7 (1), 61–78. https://doi.org/10.1007/s11157-007-9121-8.

Çeçen, F., Aktas, Ö., 2011. Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. John Wiley & Sons, Weinheim. ISBN: 978-3-527-33014-0.

Emelko, M.B., Huck, P.M., Coffey, B.M., Smith, E.F., 2006. Effects of Media, backwash, and temperature on full-scale biological filtration. J. AWWA 98 (12), 61–73. https://doi.org/10.1002/j.1551-8833.2006.tb07824.x.

European Parliament and Council of the European Union, 2024. Directive (EU) 2024/3019 of the European Parliament and of the Council of 27 November 2024 concerning urban wastewater treatment (recast). Off. J. Eur. Union L 2024/3019. http://data.europa.eu/eli/dir/2024/3019/o.

Falås, P., Longrée, P., la Cour Jansen, J., Siegrist, H., Hollender, J., Joss, A., 2013. Micropollutant removal by attached and suspended growth in a hybrid biofilm-activated sludge process. Water Res. 47 (13), 4498–4506. https://doi.org/10.1016/j.watres.2013.05.010.

Fontecha-Cámara, M.A., López-Ramón, M.V., Álvarez-Merino, M.A., Moreno-Castilla, C., 2006. About the endothermic nature of the adsorption of the herbicide diuron from aqueous solutions on activated carbon fiber. Carbon. N. Y. 44 (11), 2335–2338. https://doi.org/10.1016/j.carbon.2006.05.031.

Fundneider, T. (2020) Filtration und Aktivkohleadsorption zur weitergehenden Aufbereitung von kommunalem Abwasser – Phosphor -und Spurenstoffentfernung – (Filtration and activated carbon 39 filtration for advanced treatment of municipal wastewater – phosphorus and micropollutants removal) vol. 259. Verein zur Förderung des Instituts IWAR der Technischen Universitöt Darmstadt e. V, Darmstadt. isbn: 978-3-940897-60-2, doi:10.25534/tuprints-00012020.

Fundneider, T., Acevedo Alonso, V., Abbt-Braun, G., Wick, A., Albrecht, D., Lackner, S., 2021a. Empty bed contact time: the key for micropollutant removal in activated carbon filters. Water. Res. 191, 116765. https://doi.org/10.1016/j.watres.2020.116765.

Fundneider, T., Acevedo Alonso, V., Wick, A., Albrecht, D., Lackner, S., 2021b. Implications of biological activated carbon filters for micropollutant removal in wastewater treatment. Water. Res. 189, 116588. https://doi.org/10.1016/j.watres.2020.116588.

Graß, L., Hillebrandt, D., Firk, J., Palmowski, L., Wintgens, T., 2025. Origin of dissolved organic matter in wastewater treatment plant effluents and its removal in biologically active granular activated carbon filters. J. Water. Process. Eng. 77, 108585. https://doi.org/10.1016/j.jwpe.2025.108585.

Hai, F.I., Tessmer, K., Nguyen, L.N., Kang, J., Price, W.E., Nghiem, L.D., 2011. Removal of micropollutants by membrane bioreactor under temperature variation. J. Memb. Sci. 383 (1–2), 144–151. https://doi.org/10.1016/j.memsci.2011.08.047.

Hallé, C., Huck, P.M., Peldszus, S., 2015. Emerging contaminant removal by biofiltration: temperature, concentration, and EBCT impacts. J. AWWA 107 (7), E364–E379. https://doi.org/10.5942/jawwa.2015.107.0086.

Hübner, U., Wolff, D., Achermann, S., Drewes, J.E., Wick, A., Fenner, K., 2021. Analyzing (Initial) biotransformation reactions as an organizing principle for unraveling the extent of trace organic chemical biotransformation in biofiltration systems. ACS. ES. T. Water. 1 (8), 1921–1931. https://doi.org/10.1021/acsestwater.1c00145.

Hess, A., Morgenroth, E., 2021. Biological activated carbon filter for greywater post-treatment: long-term TOC removal with adsorption and biodegradation. Water. Res. X. 13, 100113. https://doi.org/10.1016/j.wroa.2021.100113.

Heusch, R., 1970. Eine experimentelle methode zur bestimmung des HLB-Wertes von Tensiden - (An experimental method for determining the HLB value of surfactants). Kolloid-Z. Z. Polym. 236 (1), 31–38.

Huck, P.M., Sozanski, M.M., 2008. Biological filtration for membrane pre-treatment and other applications: towards the development of a practically-oriented performance parameter. J. Water Supply: Res. Technol.-Aqua 57 (4), 203–224. https://doi.org/10.2166/aqua.2008.010.

Husain, A., Azim, M.S., Mitra, M., Bhasin, P., 2011. A review on candesartan: pharmacological and pharmaceutical profile. J. Appl. Pharm. Sci. 01 (10), 12–17.

Kim, S., Chen, J., Cheng, T., Gindulyte, A., He, J., He, S., Li, Q., Shoemaker, B.A., Thiessen, P.A., Yu, B., Zaslavsky, L., Zhang, J., Bolton, E.E., 2025. PubChem 2025 update. Nucleic. Acids. Res. 53 (D1), D1516–D1525. https://doi.org/10.1093/nar/gkae1059.

Koch, G., Kühni, M., Gujer, W., Siegrist, H., 2000. Calibration and validation of activated sludge model No. 3 for swiss municipal wastewater. Wat. Res. 34 (14), 3580–3590.

Larasati, A., De Cata, D., Mazzeo, L., van Veelen, H.P.J., Ma, S., Piemonte, V., Gagliano, M.C., 2026. Modelling and pilot-scale testing of aged biological activated carbon filters predict the optimal contact time for micropollutant removal from WWTP effluents. Chem. Eng. J. 529, 172663. https://doi.org/10.1016/j.cej.2026.172663.

Liao, X., Chen, C., Zhang, J., Dai, Y., Zhang, X., Xie, S., 2015. Operational performance, biomass and microbial community structure: impacts of backwashing on drinking water biofilter. Environ. Sci. Pollut. Res. Int. 22 (1), 546–554. https://doi.org/10.1007/s11356-014-3393-7.

Liwarska-Bizukojc, E., Galamon, M., Bernat, P., 2018. Kinetics of biological removal of the selected micropollutants and their effect on activated sludge biomass. Water. Air. Soil. Pollut. 229 (11), 356. https://doi.org/10.1007/s11270-018-4015-7.

Masson, S., Vaulot, C., Reinert, L., Guittonneau, S., Gadiou, R., Duclaux, L., 2017. Thermodynamic study of seven micropollutants adsorption onto an activated carbon cloth: van't Hoff method, calorimetry, and COSMO-RS simulations. Environ. Sci. Pollut. Res. Int. 24 (11), 10005–10017. https://doi.org/10.1007/s11356-016-7614-0.

Meynet, P., Davenport, R.J., Fenner, K., 2020. Understanding the dependence of micropollutant biotransformation rates on short-term temperature shifts. Environ. Sci. Technol. 54 (19), 12214–12225. https://doi.org/10.1021/acs.est.0c04017.

Meynet, P., Joss, A., Davenport, R.J., Fenner, K., 2024. Impact of long-term temperature shifts on activated sludge microbiome dynamics and micropollutant removal. Water. Res. 258, 121790. https://doi.org/10.1016/j.watres.2024.121790.

Nam, S.W., Choi, D.J., Kim, S.K., Her, N., Zoh, K.D., 2014. Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. J. Hazard. Mater. 270, 144–152. https://doi.org/10.1016/j.jhazmat.2014.01.037.

Ngo, H.H., Cheng, D., Guo, W., Pandey, A., Lee, D.-J., Deng, L., 2020. Biotransformation of organic micro-pollutants in biological wastewater. Curr. Dev. Biotechnol. Bioeng. 185–204.

Parniske, J., Froemelt, A., Morck, T., 2026. Modelling competitive adsorption of organic micropollutants onto granular activated carbon in fixed-bed adsorbers for advanced wastewater treatment. Water. Res. 288 (Pt A), 124631. https://doi.org/10.1016/j.watres.2025.124631.

Perrin, D.D., Dempsey, B., Serjeant, E.P., 1981. pKa Prediction for Organic Acids and Bases. Springer Netherlands, Dordrecht, ISBN 9789400958852. http://link.springer.com/10.1007/978-94-009-5883-8.

Price, P.B., T, S., 2004. Temperature dependence of metabolic rates for microbial growth, maintenance, and survival. Natl. Acad. Sci. USA 101 (13), 4631–4636. https://doi.org/10.1073/pnas.0400522101.

Sauter, D., Steuer, A., Wasmund, K., Hausmann, B., Szewzyk, U., Sperlich, A., Gnirss, R., Cooper, M., Wintgens, T., 2023. Microbial communities and processes in biofilters for post-treatment of ozonated wastewater treatment plant effluent. Sci. Total. Environ. 856 (Pt 2), 159265. https://doi.org/10.1016/j.scitotenv.2022.159265.

Sbardella, L., Comas, J., Fenu, A., Rodriguez-Roda, I., Weemaes, M., 2018. Advanced biological activated carbon filter for removing pharmaceutically active compounds from treated wastewater. Sci. Total. Environ. 636, 519–529. https://doi.org/10.1016/j.scitotenv.2018.04.214.

Shi, S., Wang, F., Hu, Y., Zhou, J., Zhang, H., He, C., 2024. Effects of running time on biological activated carbon filters: water purification performance and microbial community evolution. Environ. Sci. Pollut. Res. Int. 31 (14), 21509–21523. https://doi.org/10.1007/s11356-024-32421-y.

Simpson, D.R., 2008. Biofilm processes in biologically active carbon water purification. Water. Res. 42 (12), 2839–2848. https://doi.org/10.1016/j.watres.2008.02.025.

Sui, Q., Yan, P., Cao, X., Lu, S., Zhao, W., Chen, M., 2016. Biodegradation of bezafibrate by the activated sludge under aerobic condition: effect of initial concentration, temperature and pH. Emerg. Contam. 2 (4), 173–177. https://doi.org/10.1016/j.emcon.2016.09.001.

Tarigan, M., Raji, S., Al-Fatesh, H., Czermak, P., Ebrahimi, M., 2025. The occurrence of micropollutants in the aquatic environment and technologies for their removal. Processes 13 (3), 843. https://doi.org/10.3390/pr13030843.

Thuptimdang, P., Siripattanakul-Ratpukdi, S., Ratpukdi, T., Youngwilai, A., Khan, E., 2021. Biofiltration for treatment of recent emerging contaminants in water: current and future perspectives. Water Environ. Res. 93 (7), 972–992. https://doi.org/10.1002/wer.1493.

Wang, Y., Fenner, K., Helbling, D.E., 2020. Clustering micropollutants based on initial biotransformations for improved prediction of micropollutant removal during conventional activated sludge treatment. Environ. Sci.: Water Res. Technol. 6 (3), 554–565. https://doi.org/10.1039/c9ew00838a.