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Improved drinking water quality after adding advanced oxidation for organic micropollutant removal to pretreatment of river water undergoing dune infiltration near The Hague, Netherlands

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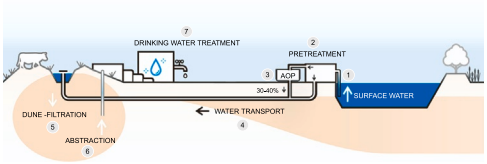
HIGHLIGHTS

- AOP decreases the number and concentration of OMP and chances of negative impact on ecology and groundwater quality.
- AOP decreased OMP concentrations in drinking water with no measurable negative effect on water quality parameters.
- MARR produces water with a highly stable chemical and microbiological composition and levels out seasonal peak fluctuations.
- There is redundancy in OMP removal by MARR and AOP, but AOP is able to remove certain OMP that MARR is not, and vice versa.

GRAPHICAL ABSTRACT



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1. Introduction

The presence and concentration of organic micropollutants (OMP) in surface water sources for drinking water production form a potential threat for water quality today and in future. OMP, such as pesticides, pharmaceutically active compounds (PhACs), endocrine disrupting compounds, X-ray contrast media and personal care products, have been found at ng/L to low μg/L concentrations in surface waters throughout the world (Kolpin et al., 2002; Jürgens et al., 2002; Stolker et al., 2004; Kasprzyk-Hordern et al., 2008; Gros et al., 2009; Houtman, 2010). PhACs and pesticides are among OMP of concern for drinking water utilities (Ray et al., 2002) because of their biological activity with possible long term effects, and sensitivity in the public media. The effect on human health is considered negligible for some OMP at low concentrations (Schriks et al., 2010), but OMP should be avoided in drinking water since the toxicity of other OMP and a mixture of them is unknown. In the Netherlands, legal standards for OMP in pre-treated river water for managed aquifer recharge and recovery (MARR) for drinking water production are set by the twelve provincial governments (IB 1993). These standards are, for most compounds, similar to national limits set for drinking water, with a maximum allowed concentration for individual pesticides of 0.1 μg/L, and a total concentration of 0.5 μg/L. This could mean that when OMP concentrations increase in surface waters in the future, extensive pre-treatment of surface water prior to MARR needs to be implemented.

Advanced oxidation processes (AOP) as pre-treatment have proven to be robust and efficient for conversion of a wide range of OMP. Pilot studies with a serial AOP of hydrogen peroxide, ozone and UV on water pretreated with rapid sand filtration (RSF) showed a high conversion of a set of OMP (Lekkerkerker-Teunissen et al., 2012). A drawback of AOP, however, may be the formation of by-products (i.e. nitrite and bromate) and transformation products, when complete mineralization is not achieved. These compounds could compromise subsequent treatment processes or the drinking water quality. Furthermore, AOP has shown to convert organic matter to smaller, oxidized and more biodegradable, assimilable organic carbon (AOC) (Huang et al., 2020; van der Kooij et al., 1989, 2015). AOC can be formed as a result of direct photolysis (UV dose $\geq$100 mJ/cm^2) of dissolved organic carbon (DOC) or through a reaction of DOC with hydroxyl radicals (Ijpelaar et al., 2010; Richardson et al., 1999; Huang et al., 2005). The organic by-products comprising AOC have been linked to increased bacterial regrowth in drinking water distribution systems (Kooij, 1992; LeChevallier et al., 1992). Biological filtration is used to remove these by-products, creating biologically stable water prior to distribution (van der Kooij et al., 1989, 2015; Huck et al., 1991; Krasner et al., 1993). Drinking water company Dunea (The Hague, The Netherlands) uses managed aquifer recharge and recovery (MARR) in the coastal dune area as one of the biological filtration steps for surface water treatment. The distribution of drinking water with a low AOC concentration in drinking water is important in the Netherlands and several other countries (e.g. Denmark, parts of Germany, Switzerland and Belgium), because water is distributed without post-disinfection in these countries. Problematic bacterial regrowth in drinking water distribution systems in these areas are prevented by the limiting amount of nutrients in the drinking water and pipe materials. The current AOC levels in drinking water produced by Dunea (3.5 – 7.5 μg/L) are below the Dutch guideline value of 10 μg C/L, which should be maintained in the future.

MARR processes are robust and cost-effective for obtaining a safe and stable water supply, and they include a wide variety of systems for different applications (Dillon et al., 2018). MARR is an engineered process in which surface or storm water is infiltrated into the aquifer through dug wells, ponds (basins), injection wells, etc., to augment groundwater and is subsequently abstracted by recovery wells (Ray et al., 2002; Bouwer, 2002). Due to the physical, chemical and biological processes involved, MARR acts as a purification step in water treatment processes (Massmann et al., 2006) Considering all the above, a combination of AOP followed by MARR could have several advantages for OMP removal, such as 1) lowering the concentration and number of OMP before MARR (resulting in low concentrations in drinking water); 2) biological removal of transformation products and by-products of AOP during MARR; 3) stimulation of the biological activity during MARR by the higher concentrations of AOC as a consequence of AOP; and thereby 4) lowering the AOC concentrations in treated water. Previous studies have indeed indicated increased levels of AOC due to ozonation that stimulated bromate degradation in nitrate- and iron reducing zones during MARR (Wang et al., 2018b; 2018c). Another reason to apply AOP before MARR is that AOP is a physical-chemical process with a short residence time, whereas MARR is a natural process with a long residence time that also levels off peak concentrations that occur when surface water is used for drinking water production.

In this study, a full scale combination of partial AOP pretreatment (30–40%) followed by MARR was tested at one of the drinking water production locations of Dunea. The experimental serial AOP was added in 2018 to treat a partial flow of water that was pretreated with rapid sand filtration. The serial AOP consisted of H_2O_2/O_3 and H_2O_2/UV. This partial AOP-treated water (30–40%) was mixed with non-AOP treated water (60–70%) before recharging the dune catchment area (see Fig. 1). Water quality parameters were monitored during different stages of the treatment process, especially aiming at a comparison between a period without AOP (2016–2017) and with AOP (2019–2020). Water quality differences between both periods were evaluated for geochemistry and (in)organic chemistry parameters, OMP presence and concentration, transformation products, biological stability and activity, toxicological effects and effects on the microbial community composition.

2. Materials and methods

2.1. Site description

The sampled locations of the treatment processes used for drinking water production are shown in Fig. 1. The RSF effluent was transported as influent for dune infiltration areas INF-M and INF-B via transport mains BAL1 and BAL2, respectively. AOP treatment was only performed on a fraction of the RSF effluent (30–40%) and was mixed with non-AOP treated RSF effluent before infiltration in dune catchment area Berkheide.

The pre-treated dune influent (INF) was transported to dune infiltration area Berkheide north of The Hague. About 25 Mm^3/a of Meuse River water was infiltrated there via 30 infiltration ponds. In this research, we have focused on one site of Berkheide within the dune infiltration of Katwijk (Fig. 2), where the water entered infiltration ponds IP-37 and IP-38 via transport mains BAL2. From here, this water was flowing northward, while infiltrating, up to IP- 25 and IP-40, which were shut off from northern supplies. Infiltrated water was abstracted via drains and abstraction wells (Fig. 2). All abstracted, raw water (RAW) was collectively mixed near the post-treatment (Fig. 1). In the study area, 4 shallow monitor wells were placed (MW's, Fig. 2, red dots), with screen depth at 1–2 m below the pond bottom. These monitor wells were equipped with loggers that measured pressure (water level), temperature and electrical conductivity.

2.2. AOP pilot installation

The applied advanced oxidation process (AOP) was a pilot scale installation developed by Dunea. It consisted of subsequently H_2O_2 addition (6 mg/l), ozonation (1.5 mg/l), and UV (0.13 kWh/m^3) of pretreated water with a flow of 2.2 m^3/h. Directly after AOP treatment, the water was treated by activated carbon filtration (Fig. 1). It was shown that residual concentrations $>$ 0.25 mg/L H_2O_2 already affected the microbial population and especially inhibited growth of anaerobic bacteria (Wang et al., 2017). Therefore, active carbon filters were operated to remove H_2O_2 to a maximum concentration of 0.25 mg/L in

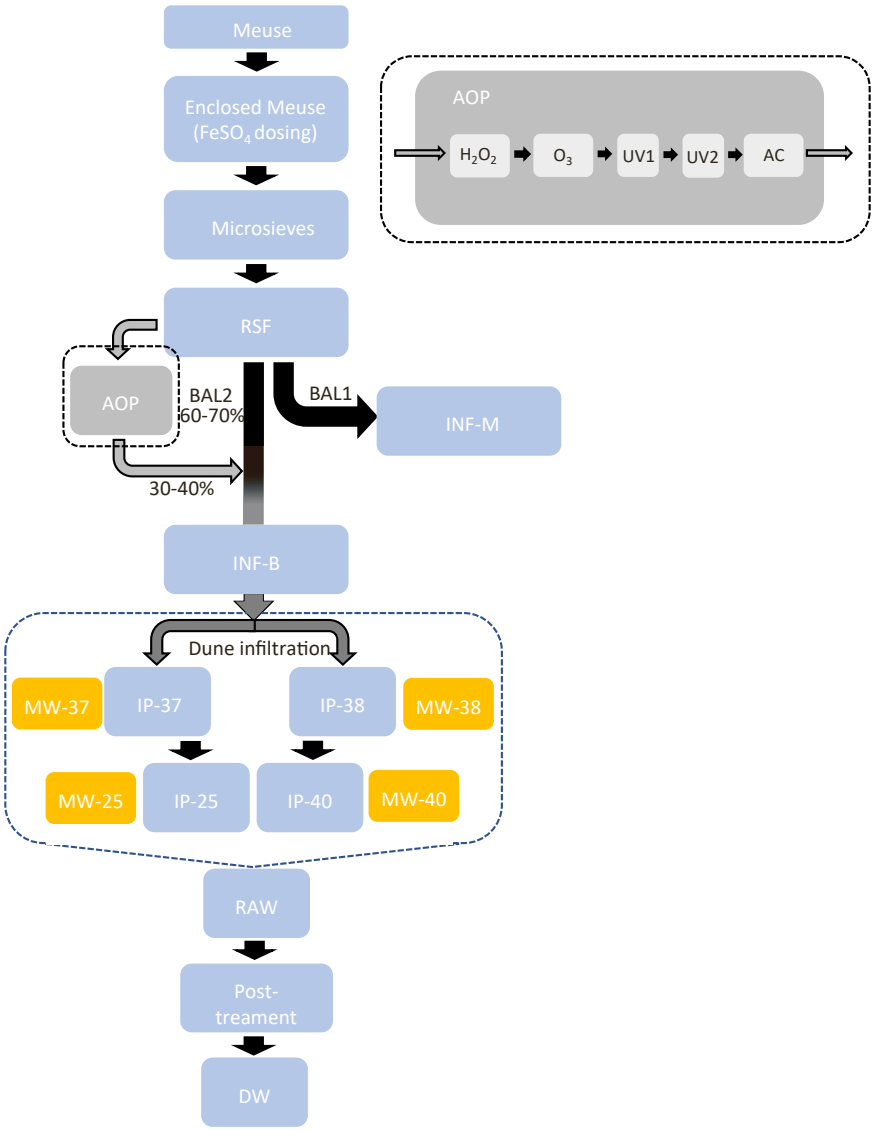

Fig. 1. Schematic of the water purification process by drinking water company Dunea with subsequent sampling points: Intake water from Enclosed Meuse (INT), Rapid sand filtration effluent (RSF), AOP effluent (AOP), influent for dune infiltration area Meijendel (sampled at end of transport pipeline); period without AOP (INF-M), Influent for dune infiltration area Berkheide (sampled at end of transport pipeline); period with AOP (INF-B), Dune infiltration with Infiltration ponds (IP) and monitoring wells (MW), collected abstracted water (RAW), and drinking water before distribution (DW). The AOP installation consisted of peroxide (6 mg/l H_2O_2), ozone (1.5 mg/l O_3), two subsequent UV reactors (0.13 kWh/m^3) and activated carbon (AC).

the effluent. The effluent after activated carbon filtration was mixed with non-AOP treated RSF effluent, which lowered the H_2O_2 concentration even more. The amount of AOP treated water that was mixed during transport (BAL2) varied during this research within 30–40% of the total infiltrated water (see Supplementary Table S1 for specific mixing at sampling points).

2.3. Resistance calculations of transport pipeline

Resistance in the transport mains was monitored indirectly using relative resistance calculations based on the pressure (P), flow (Q) and dynamic viscosity (ŋ in Pa/s). The relative resistance (¥) was calculated using:

$$¥ = P/Q^{*}ŋ^{0.237}$$

2.4. Sampling

Sampling was performed during a reference period without AOP (2016–2017) and during a period with AOP (2019–2020). Sampling locations with corresponding abbreviations are given in Fig. 1. For detailed information on sampling dates and frequency, see Supplementary Table S1. During the reference period, it was chosen to sample the end of the transport pipeline to dune infiltration site Meijendel as it was not known yet where the AOP pilot installation would be placed. It was not expected that there would be a difference in the transportation to Meijendel (INF-M) and Berkheide (INF-B), since both sampling locations contained the same pre-treated water without AOP in the reference period. Sampling of the monitor wells was performed according to the standardized norm NEN 5477/A1 (NEN, 2013). Samples were transported and stored at 5 ± 3 °C until processing. Some analytical procedures required sample preservation or pre-treatment (for more details see Supplemental Table S2).

2.5. Travel times

The travel time of Meuse River water was determined for 9 monitoring stations in the dune infiltration system: the 4 infiltration ponds (IP25, IP37, IP38 and IP40) at some distance from the dune inlet (INF), the 4 shallow monitoring wells (MW25, MW37, MW38 and MW40) near each pond monitoring station, and the raw, mixed water (RAW) as recovered from the entire dune infiltration system at Katwijk. Electrical conductivity (EC) fluctuations in the infiltration water could be used as tracer, because they overshadowed the minor changes due to e.g. precipitation reactions in the ponds and dissolution reactions in the dune

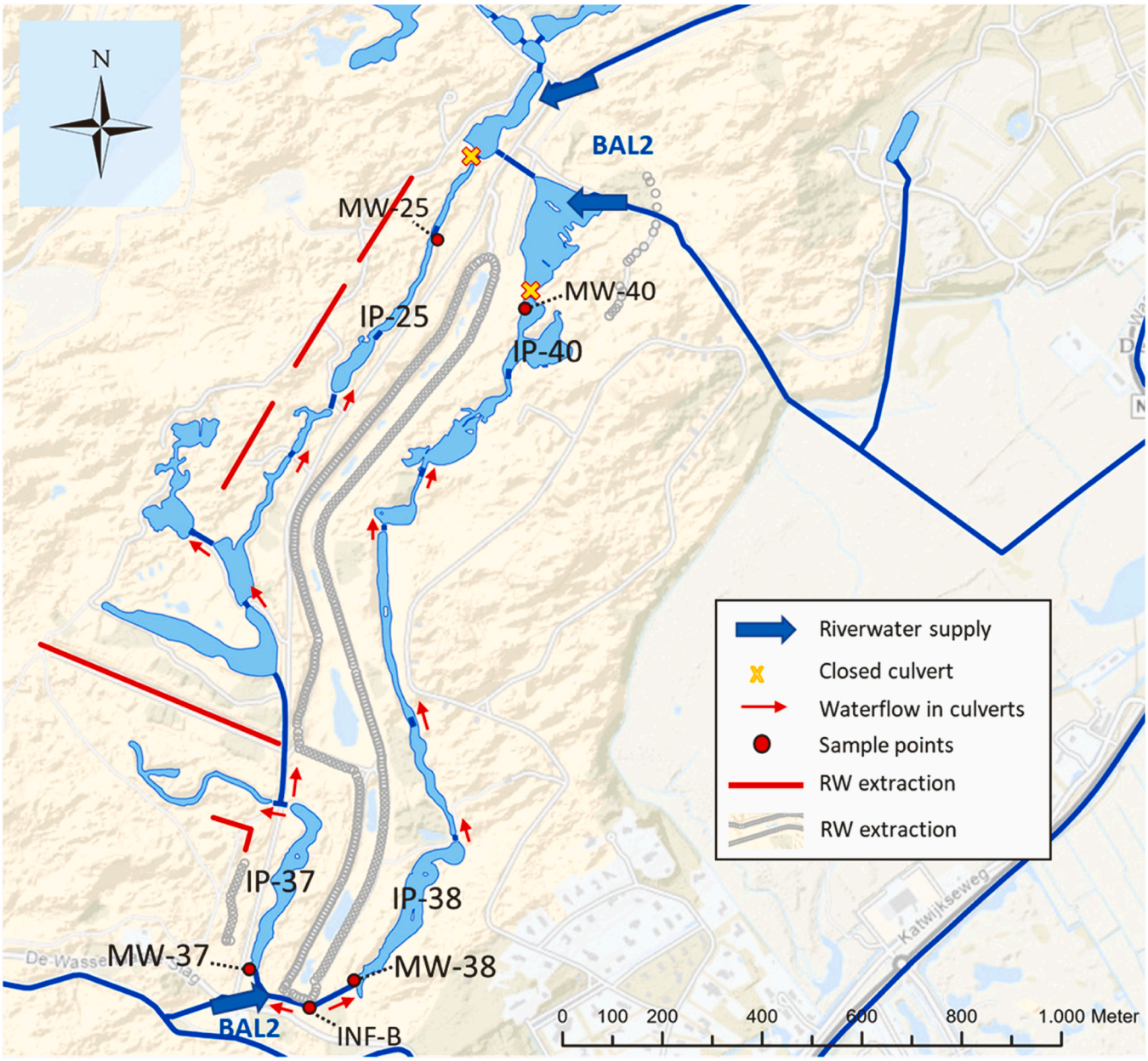

Fig. 2. The southern part of dune infiltration area Berkheide with the transport mains (BAL1 and BAL2) and entry points of river water, the investigated infiltration ponds (IP), monitor wells (MW) and local raw water (RW) recovery system.(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

sand aquifer. The time shift needed to create the best overlap for the EC signal of the inlet and 4 pond stations, and for each pond station and its nearby monitoring well was accurately measured using data from a combined EC - temperature data logger (LTC Levelogger Edge, M10/C80) with a time interval of 1 h.

The modal travel time in the upper aquifer system of the entire dune infiltration system was estimated by measuring the time shift needed for overlap of chloride and temperature fluctuations in input and output. For temperature, a retardation factor of 1.39 was calculated assuming a dune sand porosity of 41%.

The Centralized Moving Average (CMA) of the input signal was used to account for the attenuation (dampening) of EC fluctuations in the input as observed in the output. The required number of hours in the CMA is a crude dispersion indicator.

2.6. Chemical analysis

2.6.1. Analytical procedures inorganics

The main constituents of water were analyzed with conventional methods that need no further specification. Trace elements, among which arsenic and chromium, were analyzed with inductively coupled plasma mass spectrometry (ICP-MS; Thermo-Fischer) with a method equivalent to NEN-EN-ISO 17294–2. Bromide was analyzed conform NEN-EN-ISO 10304–1 using ion exchange chromatography with an ICS-1100. Bromate was analyzed using ion exchange chromatography followed by conductivity detection using a Dionex ICS-3000.

2.6.2. Analytical procedures organic micropollutants

A total number of 160 organic micropollutants (OMP) were analyzed with eight quantitative analytical methods. In the Supplemental Information, the compounds are grouped per analytical method and the limit

of quantification (LOQ) is indicated (Supplemental Table S2). Briefly, X-ray contrast media were analyzed without sample pre-treatment with a method based on a separation of the analytes by ion chromatrography (IC) and a subsequent detection by ICP-MS, as described (Sacher et al., 2005). The analysis of pharmaceuticals was performed in solid phase extracts of the water samples prepared with Oasis HLB columns eluted with MeOH that were injected into an ultra-high performance liquid chromatography (UHPLC)-triple quad MS, as described previously (Houtman et al., 2013). The analysis of sweeteners was performed in solid phase extracts of the water samples prepared with Bakerbond SDB1 cartridges at pH 3 and analyzed by LC electrospray ionization tandem MS operating in the negative ionization mode, as described in (Scheurer et al., 2009). The analysis of perfluorinated compounds was performed in solid phase extracts of the water samples prepared with C18 SPE Sep-Pak Vac 3 cm3 cartridges eluted with MeOH that were injected into a HPLC connected to a tandem MS operating in the negative ionization mode, as described in (Eschauzier et al., 2010). Samples for the analysis of benzotriazoles and pesticides were collected in sample vials of 40 ml containing 32 µl formic acid. Samples were analyzed without sample pre-treatment and were injected directly into the system. Chromatographic separation was achieved on a HSS T3, 2,1 × 100 mm 1,8 µm column and samples were analyzed by LC electrospray ionization on an UHPLC-triple quad MS operating in the positive ionization mode.

The analysis of utropine was performed using a UHPLC-triple quad MS, operated in the positive electrospray ionization mode. The water samples were filtered using a 0.20 µm regenerated cellulose filter before injecting directly into the system. The chromatographic separation was performed on a Phenomenex Kinetex HILIC column (3.0 × 150 mm, 2.6 µm).

Samples for the analysis of complexing agents were collected in 250 ml borosilicate glass bottles and acidified by the addition of 0.25 ml nitric acid 22%. Samples were filtered over a 0.45 µm spartan filter. 50 µl iron nitrate solution was added to 1 ml sample, mixed and heated at 65 ± 2 °C. Samples were injected into a LC system, whereby chromatographic separation was achieved on a ChromSep Inertsil ODS-2 C-18, 250 × 4,6 mm column. Subsequently, analysis was performed by UV detection by a diode array detector (DAD). Volatile organic compounds were analyzed using a purge and trap injector (PTI) couples to a gas chromatograph mass spectrometer (GC-MS). Samples were collected in 43 ml vials containing 0.5 ml sulfuric acid. 20 µl of internal standard was added to these vials which were subsequently placed into the autosampler of the GC-MS-PTI. After injection the volatile compounds were trapped in the purge and trap unit and after flash heating of the trap the volatile compounds were transferred into the analytic column (Restek 60 m, 0.32 mm ID df 1.8 µm (Rtx-VMS)) and subsequently detected with an MS.

Besides the target analysis of organic micropollutants, the samples were also analyzed with a targeted screening analysis. The data obtained with this method were semi-quantitative and expressed in peak areas. Peak areas of a single compound were compared between samples, giving an indication of the removal of the compound during the water treatment process. The database used for targeted screening contained around 2000 compounds. The target analysis was performed on an Impact II Quadrupole Time Of Flight (QToF) MS. Samples for the screening were collected in a 40 ml vial. Samples were filtered over a GE Healthcare 10 syringe filter lc, 0.2 µm. After filtration 1.0 ml sample and 50 µl internal standard were added. The samples were injected into the UHPLC-QTOF equipped with ESI source operating in positive and negative ionization mode.

In addition, a non-target screening (NTS) was performed for the detection of highly polar transformation products. Non-target screening was carried out using liquid chromatography – high resolution mass spectrometry (LC-HRMS) operated in the positive and negative electrospray ionization mode. For the detection of highly polar transformation products, two different chromatographic conditions, i.e. hydrophilic interaction liquid chromatography (HILIC) and mixed mode (MM) were used, as described previously (Been et al., 2021a). Samples were collected in 250 ml HDPE bottles (in triplicate). NTS data was processed with Compound Discoverer 3.1 (Thermo Fisher Scientific) for peak picking, componentization and differential analysis. The output of Compound Discoverer was a feature list, consisting of a table with accurate mass / retention time pairs (features) and their intensity reported as peak area. Features that were less than ten times higher than the maximum of the instrumental and bottle blanks, were removed. The detection of transformation products was performed by differential analysis, i.e. comparing samples after and before AOP.

2.7. Toxicity assessment using bioassays

2.7.1. CALUX bioassays

Reporter gene assays based on selective human U2-OS cell based lines were used to measure anti-androgenic (anti-AR), estrogenic (ER) and glucocorticoid (GR) activities with the anti-AR (antagonistic mode), ERα and GR CALUX (BioDetection Systems B.V., Amsterdam, the Netherlands) as described by (Houtman et al., 2018; van der Linden et al., 2008). The reference compounds were flutamide (Flt), 17β-estradiol (E2) and dexamethasone (Dex) respectively. Anti-androgenic activity was tested in the presence of dihydrotestosterone (DHT) at EC50 level. Furthermore, the p53 and Nrf2 CALUX were used to assess the transcriptional activation, the p53 pathway related to (in)directly actin genotoxins without metabolic activation of S9 liver enzymes, and the Nrf2 pathway for oxidative stress as described by (van der Linden et al., 2014). The reference compounds were actonymcin D (Act) and curcumine (Cur), respectively. Cell viability (absence of cytotoxicity) was measured with the cytotox CALUX (van der Oost et al., 2017) to check if inhibition of responses in the other CALUX assays was caused by specific receptor mediated responses or due to cytotoxicity. Tributyltin acetate (TBT) was used as a reference compound. The CALUX assays were only performed in 2019 after AOP implementation. The results of the CALUX assays were interpreted by comparing the measured responses to effect-based 'trigger values' (EBT) as proposed for the environment (Been et al., 2021b) and for drinking water (Heringa et al., 2011). For more details, see the 'Supplementary information on the toxicity assays'.

2.7.2. Ames fluctuation test

The Ames fluctuation test was performed as previously (Heringa et al., 2011), with minor modifications. *Salmonella typhymurium* strains TA98 and TA100 (Xenometrix, Switzerland) were exposed to a 100-fold concentrated water extract (n = 2) in culture medium. Water extracts were tested with and without an exogenous metabolic activation system (rat liver S9 mix), resulting in four different test conditions (TA98-S9, TA98 +S9, TA100-S9 and TA100 +S9). Procedure controls (extracts of Evian mineral water), negative controls (dimethyl sulphoxide, DMSO) and positive controls were run in parallel. Two independent experiments were performed and all experiments were carried out in triplicate cultures. Cytotoxicity was measured in parallel by measuring optical density of the bacterial culture (Heringa et al., 2011). For more details, see the Supplementary information on the toxicity assays.

2.8. Biomass Production Potential (BPP) and Assimilable Organic Carbon (AOC)

Biological stability was evaluated using a Biomass Production Potential (BPP) test and assimilable organic carbon (AOC) analyses. The BPP was determined according to (Hijnen et al., 2018). The BPP test included water sampling in AOC free, glass-stoppered Erlenmeyer flasks and incubation of samples at 25 °C for 14 days. During incubation, growth of the autochthonous microbial community in the water samples was monitored by periodic ATP analysis (van der Wielen and van der Kooij, 2010). The BPP was expressed as the maximum ATP concentration during the first seven days of incubation (BP_7, ng ATP/L) and the

cumulative ATP production from day 0–14 (BPC_{14}, d ng ATP/L).

The concentration of easily assimilable organic carbon (AOC) was carried out as described previously (van der Kooij et al., 1982).

2.9. Microbiological analysis

2.9.1. ATP measurements and total cell counts

General microbial parameters were determined by measuring the total ATP concentration and the total and membrane-intact cell counts. Determination of the ATP concentration was carried out as previously described previously (van der Wielen and van der Kooij, 2010).

Enumeration of direct total cell counts and intact cell counts was performed using flow cytometry (FCM) following the protocol described previously (Prest et al., 2013).

2.9.2. Microbial community analysis

From the collected water samples, a maximum of 1000 ml was filtered through a polycarbonate membrane filter with a 0.2 μm pore size (Track-etch membrane, Sartorius, The Netherlands). Filters were stored at − 20 °C until further DNA extraction and 16S rRNA amplicon sequencing, which was done as described previously (Vavourakis et al., 2020). Negative controls (water samples of DNase/RNase free water) and positive controls (Zymo DNA mock communities) were also added during filtration and subsequent DNA extraction.

Processing of 16S rRNA amplicon sequence data was performed using Qiime2 (Bolyen et al., 2019). Firstly, paired-end sequences were joined using vsearch. Then, sequences were quality filtered and chimeras were removed. Afterwards, denoising and amplicon sequence variants (ASVs) were determined using Deblur. Taxonomy was assigned using the q2-feature-classifier plugin and the readytowear SILVA_132_515F_806R_water-non-saline classifier (Kaehler et al., 2019; Bokulich et al., 2018) based on the SILVA reference database (Quast et al., 2012). Afterwards, alpha and beta diversity analysis was performed for first evaluation of results. Bray Curtis dissimilarity results were log transformed and plotted using PCoA and statistical testing was done using PERMANOVA pairwise comparison with 999 permutatons with a post-hoc Adonis test. Differential abundance analysis was done using ANCOM, after filtering features (minimum frequency 50 reads in minimum 4 samples) and adding pseudocounts (Mandal et al., 2015). Qiime2 output was imported into R studio using Qiime2R (Bisanz, 2018). Further analysis and visualization was done with the R software packages Ampvis2 (Andersen et al., 2018), and phyloseq (McMurdie and Holmes, 2013).

2.10. Statistical analysis

Statistical analysis of organic micropollutant concentrations over time (before and after AOP) were performed with Trendanalist (Baggelaar and Eit, 2019), software capable of performing a fully automatic trend analysis of a data series in a database. For each data series, the software used the trend test that best fitted its relevant statistical characteristics, being the kind of probability distribution (normal or non-normal) and the occurrence or absence of autocorrelation and/or seasonality. The parametric linear regression test was used for normal distributed data and the distribution free Mann–Kendall test for non-normal distributed data.

Statistical analysis of correlations between different parameters were determined using spearmann correlation tests and were performed on all collected data using the R software where only correlations > 0.4 with $p < 0.05$ were outputted. Statistical analysis of differences in parameters between periods with and without AOP or between different locations were performed using the Wilcoxon rank test ($p < 0.05$).

3. Results

3.1. Travel times

In Supplementary Fig. S1, two examples are presented of the 'signal overlap method' to determine the travel time from pond to its monitoring well and from dune inlet to raw dune output, respectively. They showed a short average travel time (t50) of 22 h and a centralized moving area of 5 h in the dune sand from pond station IP-37 to its very nearby shallow monitoring well (MW-37), and a relatively long t50 of 52 days and centralized moving area of 112 days in the whole dune infiltration system. The mixing of flow lines with diverging travel times in the system explained the high centralized moving area.

The results of all travel time (t50) measurements in the dune infiltration system, for the period without and with AOP, are summarized in Table 1. They showed a much longer travel time for the remote ponds IP-25 and IP-40 (9–13 days) than for the nearby ponds IP-37 and IP-38 (1–5 h), as expected for water flowing from inlet via the nearby to the remote ponds. Dune sand passage in the pond bank took 0.3–4.6 days for the 4 monitoring wells, of which MW-40 showed the longest t50. In the entire dune infiltration system (from inlet to output), the t50 of ~52 days consisted of on average 10 days in the ponds and 42 days in the dune sand aquifer.

The average travel time in the entire dune infiltration system was nearly equal for both periods (with and without AOP). For most infiltration ponds and shallow monitoring wells the average travel time decreased during the period with AOP, but not substantially.

3.2. Inorganic water quality changes

3.2.1. General patterns during both periods (+/- AOP)

Dune infiltration leads to important water quality changes by various processes in the infiltration ponds, during passage of the dune sand aquifer, and by mixing in the recovery system (Stuyfzand, 1989). This can also be deduced from the monitoring data collected in this study. A summary of the most important data is given in Supplementary table S3. The parameters that showed significant changes in the ponds and during dune infiltration are depicted in Fig. 3.

In the infiltration ponds close to the inlet (IP-37 and IP-38) with short retention time ('IP-short'), minor changes occurred, but further away from it (IP-25 and IP-40), with longer retention times ('IP-long'), the changes increased (Fig. 3). The main significant changes between the short and long retention time ponds consisted of: (i) a significant decrease of NO_3^- and SiO_2, possibly by uptake for biomass production by algae, diatoms and reeds, (ii) a significant increase of NH_4^+ and PO_4^{3-} possibly due to their remobilization from bottom muds which evidently exceeded their uptake; (iii), a significant increase of DOC (which was strongly correlated to TOC, UV_{254}-extinction and COD) probably due to

Table 1
Travel time to various monitoring stations during the period without AOP (2 Jan. – 26 Feb. 2018) and with AOP (3 July 2019 – 4 Dec. 2019). IP = Infiltration pond; MW = shallow monitoring well in pond bank, RAW = abstracted water.

From	to	Travel time			
		2 Jan. 2018–26 Feb. 2018		3 July 2019–4 Dec. 2019	
		hour	day	hour	day
INF-B	IP-37	3	0.13	1	0.04
INF-B	IP-38	5	0.21	4	0.17
INF-B	IP-25	228	9.5	#	#
INF-B	IP-40	*315 ##*	*13 ##*	#	#
iP.37	MW-37	22	0.9	15	0.6
iP.38	MW-38	16	0.7	8	0.3
iP.25	MW-25	7	0.3	40	1.7
iP.40	MW-40	110	4.6	100	4.2
INF-B	RAW	1200	50.0	1296	54

#: data errors ##: estimate based on various data

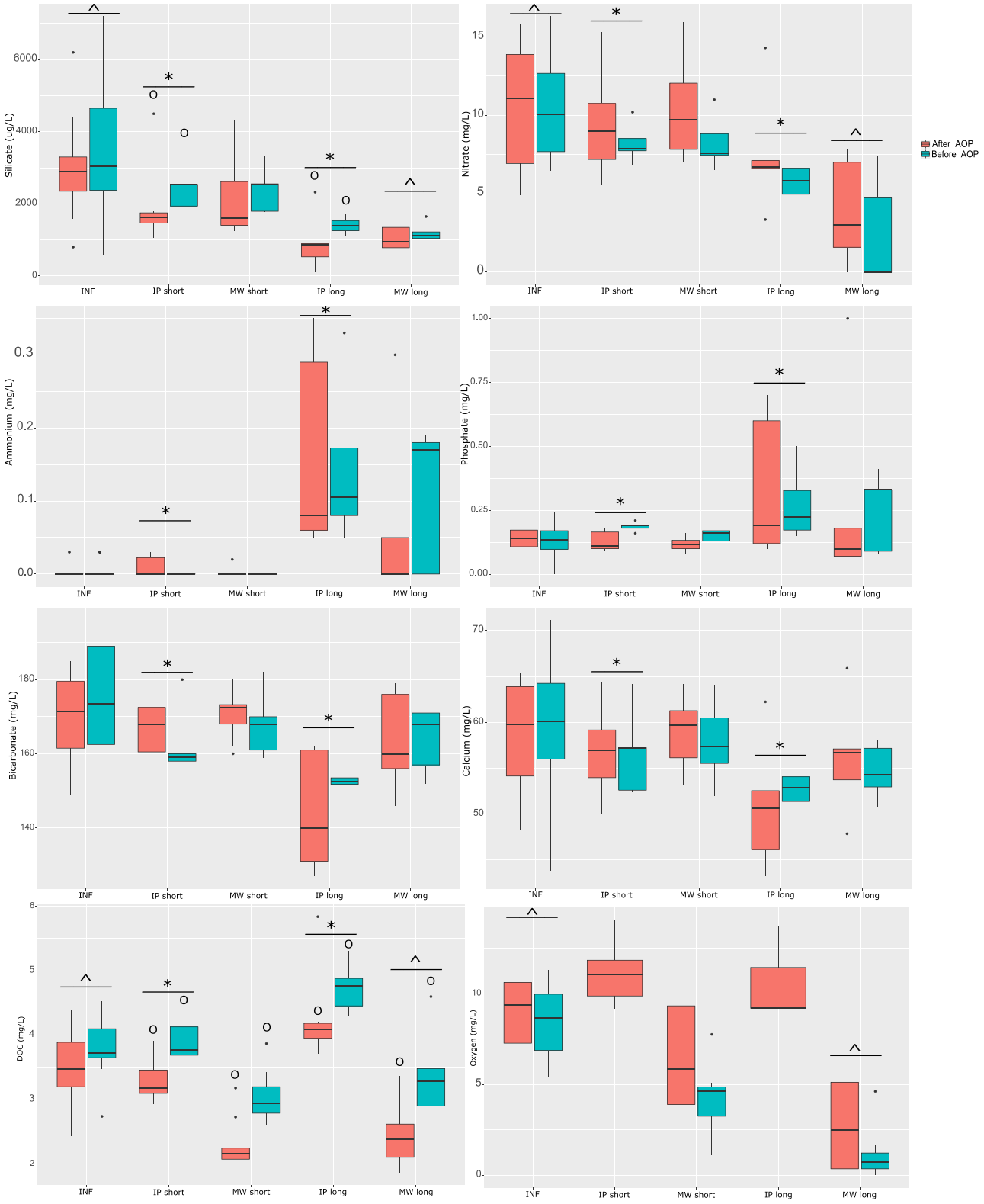

Fig. 3. Box plots showing changes in selected main constituents during transport through the MARR system. From left to right: infiltration water (INF), infiltration ponds with short (IP-short: IP-37 and IP-38 together) and long (IP-long: IP-25 and IP-40 together) detention and their monitoring wells (MW-short, MW-long) in the period with (red) and without AOP (green). Asterisks (*) show significant differences between the ponds with short and long detention time for both periods (+ and - AOP), Carets (^) show significant differences between the infiltration water and monitoring wells for both periods (+ and - AOP) together, and circles (O) show significant differences between the period with or without AOP within the different type locations. Significance tested by the Wilcoxon rank test, with $p < 0.05$.(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

intensifying primary production; and (iv) a significant decrease of Ca^{2+} and HCO_3^- due to possible biogenic hardness reduction ($CaCO_3$ precipitation by algal CO_2 uptake) (Wilcoxon rank test, $p < 0.05$).

The data also showed that 1–1.6 m of dune sand passage in 7–110 h resulted in larger quality changes than during pond detention (Fig. 3). The changes increased with larger distance (MW-25 and MW-40) to the dune inlet (INF) and with longer travel time in the dune sand (MW-40). This especially was the case for the significant decrease of O_2, NO_3^-, and DOC (and therefore TOC and COD) between infiltration water and monitoring wells of long retention ponds (MW-long) (Wilcoxon rank test, $p < 0.05$). Cu, Pb, Se and Zn also showed a decease, but these were not significant. In MW-40, the water became anoxic, probably allowing NH_4^+ and PO_4^{3-} to be mobilized from organic material in bottom muds. Anoxic water also possibly allowed Fe^{2+} and Mn^{2+} to reductively dissolve (Supplementary table S3).

The overall changes in the entire dune infiltration system (RAW) were larger than those in MW-40. This was due to a longer travel time over a longer distance (on average 40 m). Also, fluctuations in Meuse River quality were far more attenuated in RAW by mixing of flowlines with different length and flow velocity, and by the admixing of ambient dune groundwater (~10%). A substantial concentration rise of SiO_2, PO_4^{3-}, Fe, NH_4^+, As, Ti and V in the mixed raw water (RAW) as compared to the MW's occurred (Supplementary table S3). This was probably due to the dissolution of diatoms, oxidation of soil organic material, reductive dissolution of iron (hydr)oxides, and desorption. On the other hand, a substantial concentration decrease for TOC, DOC, UV-extinction, K, SO_4^{2-}, Al, Ba, Cd, Cs, Mo, Ni, Rb, Sb, Se, Sn, Ta and W was observed in RAW (Supplementary table S3), which can probably be explained by biodegradation of dissolved organic compounds, sorption and some dilution with ambient dune groundwater.

3.2.2. Effect of AOP

To determine the effect of AOP on these inorganic parameters, both periods (+/-AOP) were compared on the measured inorganic parameters and TOC/DOC (Fig. 3 and Supplementary table S3). It was observed on practically all observation points, that DOC and SiO_2 were significantly lower and O_2 and NO_3 were higher in the period with AOP. The lower PO_4^{3-} and NH_4^+ concentrations in the infiltration ponds and monitor wells also suggested that during the period with AOP, the oxidation reduction potential (deduced from the higher O_2 and NO_3^{2-} concentrations) became slightly higher. Whether this small change is due to AOP is hard to prove, because environmental conditions in the dune infiltration area varied over the years and seasons. The datasets for each period were too short to take these variations into account.

3.3. Organic micropollutants (OMP)

3.3.1. Effect of AOP

From the 164 monitored OMP, 70 compounds were detected at least once in the intake water (INT) in 2019 in concentrations above the LOQ. For 48 compounds the removal rate in AOP was calculated. These concerned industrial compounds, pharmaceuticals, X-ray compounds, sweeteners and per- and polyfluoroalkyl substances (PFAS). These compounds are listed in Supplementary table S4, where the maximum concentration in INT is shown, the removal rate by AOP, and the removal rate between INT and INF before and after implementation of AOP. Most OMP (31 compounds) were removed by AOP for more than 80% and six OMP were removed partially (50 −80%). Some compounds such as MTBE, metformin, sucralose and eight PFAS compounds were not removed by AOP.

After AOP treatment, the water was infiltrated in the dunes. At the

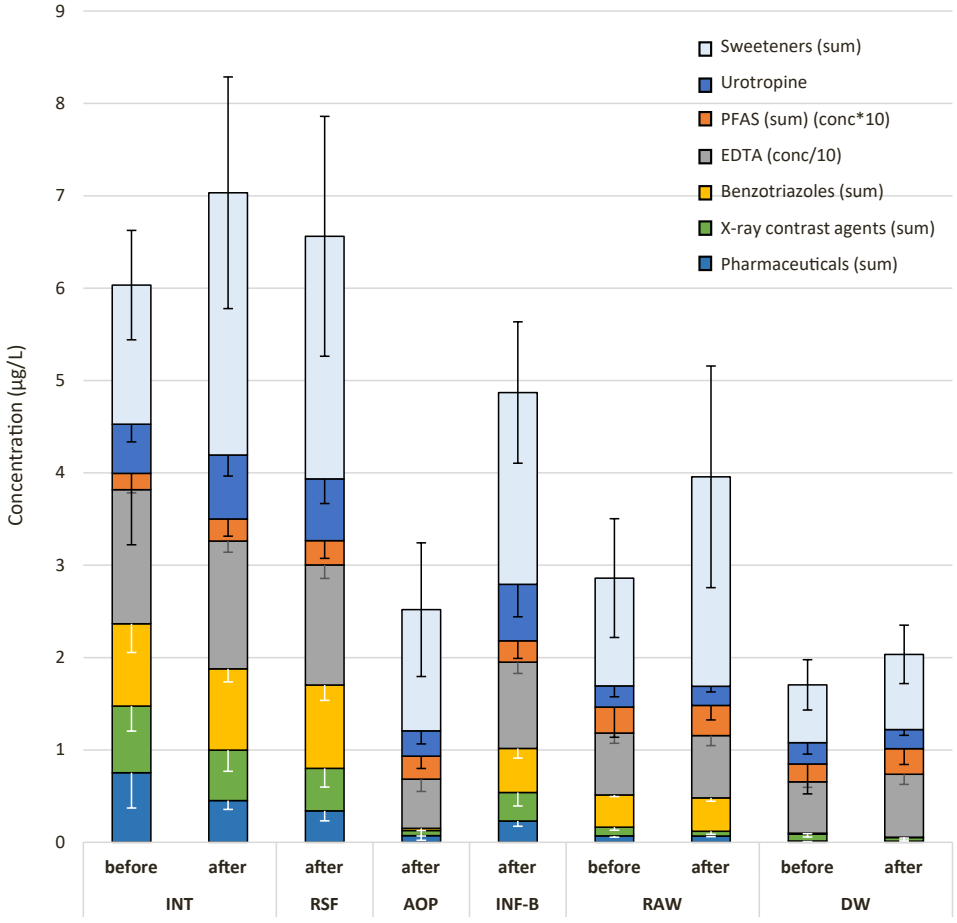

Fig. 4. Comparison of the average sum concentrations of compounds, grouped by their application, before and after the addition of AOP.

infiltration point (INF-B), the AOP effluent was diluted with untreated rapid sand filtrate in a ratio of approximately 40–60% (Fig. 1). The removal rate between INT and INF increased statistically ($p < 0.05$) for most compounds after implementation of AOP (Supplementary table S4). In Fig. 4 the sum of the average concentrations on the different sampling locations in the drinking water treatment process are clustered by the type of application. Pharmaceuticals, X-ray agents, and benzotriazoles were generally well removed. From the measured compounds, the sweeteners were the largest contributors to the sum concentration after AOP. This is due to sucralose which was detected in relative high concentrations of 0.7–2.8 μg/L after AOP. The sum concentrations in drinking water did not decrease after the implementation of AOP. In drinking water, EDTA, urotropine and PFAS compounds were detected in similar concentrations as before the implementation of AOP. The main reason for DW showing higher sum concentrations with AOP, was the increase of sweeteners in the input, which survived MARR. In addition, the raw water and drinking water also consisted of infiltrated river water with longer travel times in the MARR system and, in various cases, with higher input concentrations in the past.

From the compounds that were oxidized for more than 50%, five compounds were detected in drinking water above the LOQ. Concentrations of these compounds are given for INT, INF and DW in a five-year period between 2016 and 2020 (Supplementary Fig. S2). The concentrations of acesulfame, amidotrizoic acid, iopamidol, EDTA and urotropin fluctuated strongly in INT. After MARR, concentrations were more constant in DW. In the period of 2016–2020, the concentrations of amidotrizoic acid, iopamidol and urotropin decreased significantly in DW. In INT the concentrations did not decrease significantly. Concentrations of acesulfame and EDTA were not decreasing significantly yet, but for both compounds the concentration in DW were showing a decreasing trend.

In addition to the target analysis of selected compounds, a broader targeted screening was performed on the LC-QTOF. The database of the targeted screening contains almost 2000 compounds. The targeted screening is not a quantitative method, but the results expressed in peak area can be compared between sampling locations for a single compound. A comparison of the peak areas before and after AOP was therefore possible. In Supplementary table S5 the removal rates are shown for the 45 compounds that were detected in > 25% of INT samples, and that were not measured with a quantitative analytical method. Most compounds were removed for > 80% during AOP. Only one compound, the DNA component adenosine, was removed < 30%. Adenosine was however removed during subsequent MARR. The seven compounds that were detected at least once in drinking water were either well removed (gabapentin, N-formyl-4-aminoantipyrine, pyrimethanil, dimethomorph) or partially removed (ritalinic acid, terbutryn, melamine).

3.3.2. AOP byproducts

Bromate and bromoform are compounds that were not detected in INT. During AOP, both compounds were formed and detected in AOP effluent with concentrations up to 0.8 μg/L bromate and 0.3 μg/L bromoform (Supplementary Fig. S3). Bromoform was still detected in INF-B above the LOQ, bromate was detected below the LOQ. Both compounds were not detected anymore in RAW after MARR.

3.4. Transformation products

In order to determine if highly polar transformation products were formed with AOP treatment, LC-HRMS NTS was performed on samples without and with AOP. All features detected after AOP installation were compared (differential analysis) with features detected before AOP. No features were observed that were statistically significantly different ($p < 0.05$) in the samples after AOP (data not shown). Based on these results, no highly polar transformation products were detected after AOP.

3.5. Toxicity assessment using bioassays

Detailed results of the Ames fluctuation test are shown in the Supplementary Information on toxicity assays. The samples INT, RSF, AOP, INF-B, IP-38, MW-38 and RW showed a clear positive response in at least one sample campaign, whereas the samples IP-40, MW-40 and DW only showed negative responses.

Based on the results obtained in the current study, estrogenic activity, anti-androgenic activity and mutagenic activity were observed in intake water, but were clearly reduced, absent or below the limit of quantification (LOQ) in the drinking water. Cytotoxicity, glucocorticoid activity, direct genotoxocity (measured as an induction in the p53-enzyme) and oxidative stress were absent or below the detection limit in all samples in the current study. Anti-androgenic substances were efficiently removed by AOP (Supplementary Fig. S4). Estrogenic substances seemed to be not completely removed by AOP, whereas subsequent MARR appeared to be successful in this (Supplementary Fig. S4). The presence of mutagenic activity was variable after rapid sand filtration and AOP and plausible in one of the infiltration ponds, but in drinking water no activity of mutagenic substances was measured in the bioassays.

3.6. ATP, cell numbers, growth potential and natural organic matter

3.6.1. Through treatment

Results showed that there were fluctuations in ATP, TCC, BP_7 and BCP_{14} during water treatment. Most parameters (ATP, TCC, BP7 and BPC14) had highest values in INT and IP-25 and IP-40 as compared to all other purification steps in both periods without and with AOP taken together (Supplementary Fig. S5). These parameters strongly fluctuated between sampling dates, especially in the ponds with long retention (IP-25 and IP-40). The parameters were significantly correlated to each other, but also to pH, nutrients and organic fractions, such as nitrite, ammonium, phosphate, biopolymers, neutrals, building blocks, humic substances, and DOC (Spearmann correlations rho >0.5 and <−0.5, $p < 0.05$, Fig. 5). We also observed a strong correlation between BP_7 and BPC_{14}, which indicated that most biological active compounds were easily degradable (within 7 days) (Spearmann correlation rho 0.95, $p < 0.05$). After MARR, BP_7, BPC_{14}, ATP and cell counts drastically decreased in MW's, RAW and DW (Supplementary Fig. S5), which was correlated to a decrease in nutrients, DOC and most organic fractions. Dune infiltration therefore seemed to form a natural barrier for organic material, nutrients and microorganisms.

3.6.2. Effect of AOP

Before dune infiltration, the BPP parameters, ATP and cell counts were not significantly different after rapid sand filtration (RSF) and in the dune influent (INF-B and INF-M) between the period before and after AOP ($p > 0.05$) (Fig. 6). DOC concentrations were however significantly lower during the period with AOP in both ponds with short (IP-37 en IP-38) and long (IP-25 and IP-40) retention time together and in the resulting DW compared to the period without AOP (Wilcoxon rank test, $p < 0.05$) (Fig. 3, Supplementary Fig. S5). In IP-37 and IP-38, the BPC_{14} was also significantly lower during the period with AOP (Wilcoxon rank test, $p < 0.05$), which could have been caused by the significantly lower DOC concentrations. Since there was a strong correlation between DOC, BPP and other nutrients and organic fractions, most of these parameters were also lower (but not always statistically significant) in the period with AOP in the IP's (Supplementary Fig. S5).

In the period with AOP, the BP_7 values were significantly higher after AOP as compared to the rapid sand filtrate effluent, but decreased again when the water reached the dunes (INF-B) (Fig. 6). This decrease in BP_7 was most probably the effect of dilution by mixing with non-AOP treated RSF effluent (Fig. 1). On average 42% (v/v) AOP treated and 58% (v/v) non-AOP treated RSF effluent were mixed when these BPP measurements were performed (feb-dec 2019). The theoretical BP_7 and BPC_{14}

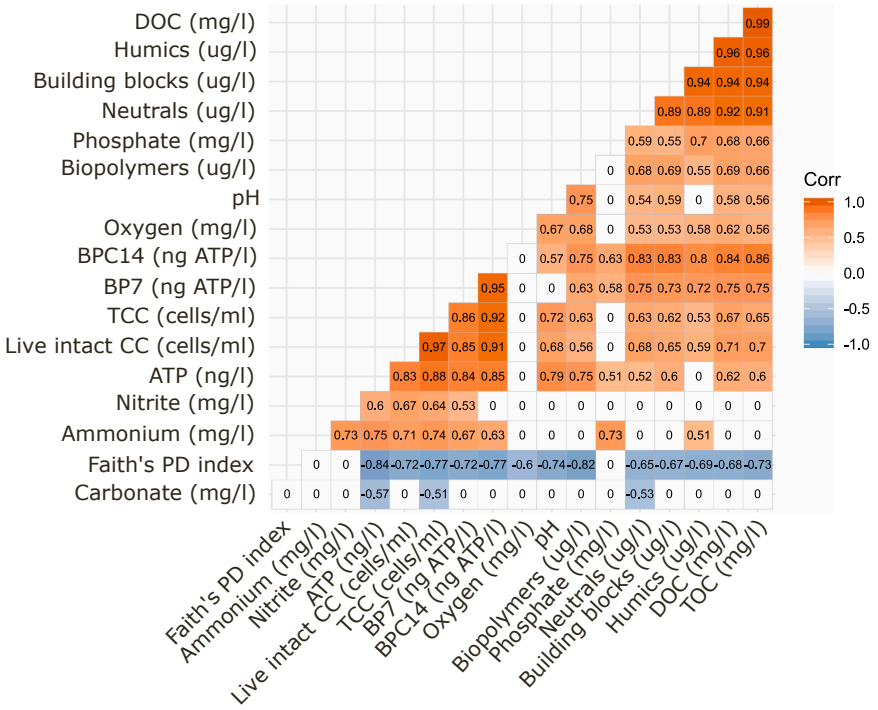

Fig. 5. Significant Spearman correlations (rho >0.5 and <−0.5) between measured parameters for all samples taken in both periods with and without introduction of AOP ($p < 0.05$). Colors represent different Spearman correlation classes (see legend).(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

values that would be achieved after mixing were calculated according to these mixing proportions (Fig. 6, T42 values). These theoretical BP_7 and BPC_{14} values (T42) were significantly higher than the values measured at INF (Wilcoxon rank test, $p < 0.05$). The measured values were therefore probably lower due to biological activity during transportation to the dunes. The flow resistance of the transport mains should increase with increasing biofilm growth, but it did not show significant changes between the two periods with and without AOP (Supplementary Fig. S6). Furthermore, intact cell counts were significantly lower in INF-B in the period with AOP than without AOP. This was probably caused by AOP, as the cell counts after AOP were dramatically lower compared to RSF (Fig. 6). The subsequent increase in intact live cell counts was also probably an effect of mixing with non-AOP treated RSF effluent.

3.7. Microbial diversity and community composition

3.7.1. Through treatment

The Faith's PD, as indicator for microbial diversity, was lowest in INT and IP's and increased significantly during and after dune infiltration (in MW's, RAW and DW) (Fig. 7 and Supplementary Fig. S7, Kruskall Wallis, $p < 0.05$). The microbial diversity was significantly and negatively correlated to biological activity parameters, DOC/TOC, organic fractions, nutrients and pH (Fig. 5) (Spearman correlation, $p < 0.05$). Indeed, these parameters were much higher before entering the dune sand, such as in the IP's, where microbial diversity was much lower. This relationship between the microbial diversity and other parameters was strongest in the ponds with long retention time (IP-25 and IP-40) as compared to IP-37 and IP-38 and INT. Ponds IP-25 and IP-40 showed a significantly lower diversity than IP-37 and IP-38 in both periods with and without AOP, with a higher concentration of organics and nutrients and higher biological production potential.

The microbial communities were also significantly different in Bray-Curtis dissimilarity before and after MARR (Fig. 7, PERMANOVA pairwise difference, $p < 0.05$). The microbial community composition of cluster B with the long detention time ponds (IP-25, IP-40, MW-25, MW-40) was highly variable and was significantly different from cluster A with shorter detention time ponds (INT, RSF, INF, IP-37, IP-38) (PERMANOVA pairwise difference, $p < 0.05$; Fig. 7). This high variation in IP-25 and IP-40 was reflected in the microbial community composition of MW-25, MW-40, which made that these were not significantly different from the communities in the ponds. For MW-40, this was also reflected in high fluctuations in the microbial diversity (Fig. 7 and Supplementary Fig. S7). This temporal variation was also observed for the biological parameters and (in)organic parameters (Supplementary Fig. S5). For IP-37 and IP-38, temporal variations were much smaller and communities of MW-37 and MW-38 were significantly different from the communities in the ponds itself (PERMANOVA pairwise difference, $p < 0.05$). The microbial community composition was also less variable over time in RAW and DW as compared to the infiltration ponds. This showed that dune infiltration produced oligotrophic drinking water with a high microbial diversity and increased microbiological stability.

3.7.2. Effect of AOP

The differences in Faith's PD between each of the IP's or the MW's were larger during the period with AOP than without AOP, and were therefore all significantly different from each other (Kruskall Wallis, $p < 0.05$, Supplementary Fig. S7). From all sample locations, only DW showed a significantly higher Faith's PD (factor 4) during the period with AOP as compared to the period without AOP (Kruskall Wallis, $p < 0.05$, Supplementary Fig. S7), which correlated to a lower amount of DOC and TOC (Fig. 5 and Supplementary Fig. S5). This was probably not an effect of AOP, as the Faith's PD was not significantly different with or without AOP treatment at INF (INF-M and INF-B). As stated previously, DOC concentrations were significantly higher in the IP's during the period without AOP. The organic material in the IP's therefore probably affected the organic material in the MW's and the resulting DW, and could explain the difference in Faith's PD as these parameters showed a strong and significant negative correlation (Fig. 5).

Microbial community compositions were not significantly different

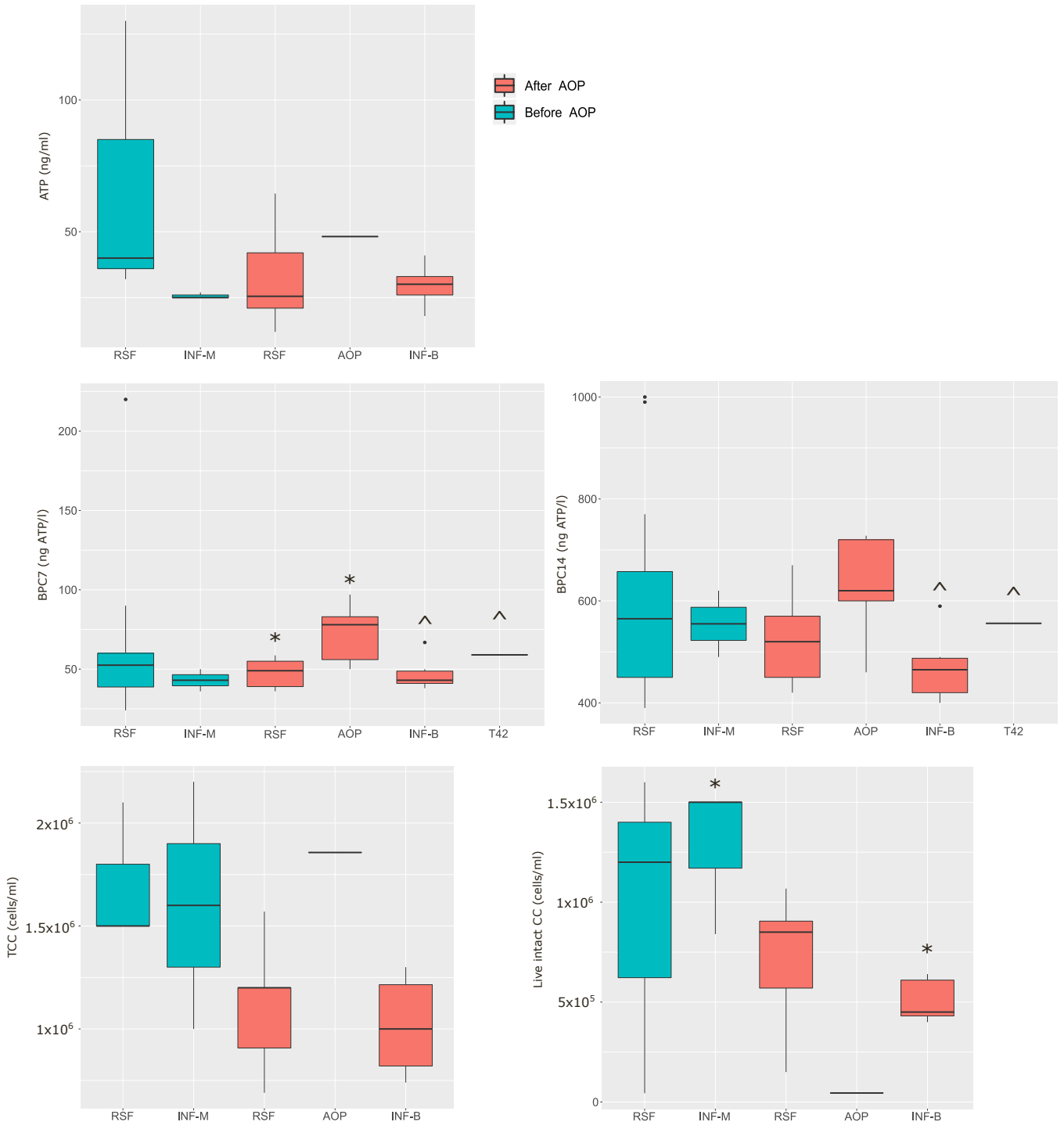

Fig. 6. Values for biological production potential (BP_7, BPC_{14}), ATP and total cell counts (TCC), live intact cell counts (CC) in the period with AOP (green) and without AOP (red). The theoretical BP_7 and BPC_{14} values that would be achieved after mixing AOP-treated with non-AOP treated RSF effluent (T42) are also shown ($BP_7 = 59$ (SD 4.7), $BPC_{14} = 556$ (SD 38.9). Standard deviations of these theoretical values were based on the relative standard deviations of the BPP analysis. These relative SDs of BP_7 (8%) and BPC_{14} (7%) were calculated as the median relative SD of all BP analysis performed. Values that were significantly different from each other are indicated with the same symbol (Wilxocon rank test, $p < 0.05$).(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

between sampling locations in the period with or without AOP (Bray Curtis distance, PERMANOVA, pairwise, $p < 0.05$). The variation in the microbial community composition was indeed only for a very small part explained by the effect of AOP (3.3%, Adonis test, $p < 0.05$) and mostly explained by temporal differences (18.6%, Adonis test, $p < 0.05$). It was expected that the higher concentrations of organic material during the period without AOP was reflected in the abundance of primary producers in the IP's at certain periods. However, higher sampling frequency and sampling at the same dates in the periods with and without AOP are needed to ascertain the significance of differences between these communities, especially with respect to the primary producers. The microbial diversity showed significant differences between both periods because Faith's PD index is very sensitive for loss of species, whereas Bray Curtis distances are less sensitive to changes in the less

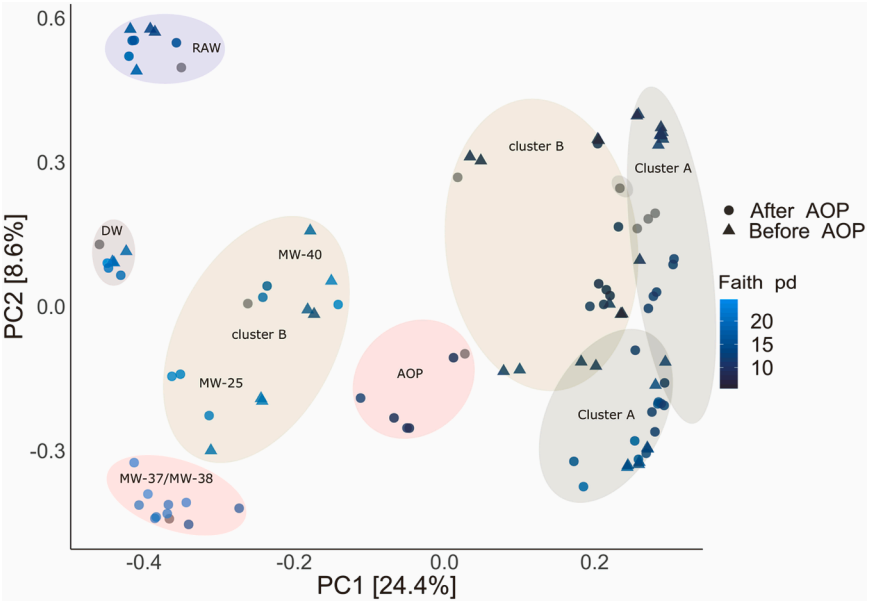

Fig. 7. Principal Coordinates Analysis (PCoA) plot based on Bray Curtis distance for all samples that were analyzed using 16S rRNA gene sequencing. Blanc samples and mock communities were excluded for this analysis. Both axes show 33% of the variation in microbial composition that could be explained by the period before (triangles) or after (circles) introduction of AOP. Sample colors represent the microbial diversity (Faith PD index). Bray Curtis distances that were significantly different are shown with clusters of different colors (PERMANOVA ($p < 0.05$)). Cluster A (INT, RSF, INF-B, INF-M, IP-37, IP-38) and cluster B (IP-25, IP-40, MW-25, MW-40) represent treatment steps before and during MARR.(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

abundant species of a community.

The microbial community of the AOP effluent was significantly different in Faith's PD (Kruskall Wallis, $p < 0.05$) and composition (Bray Curtis, PERMANOVA, $p < 0.05$) compared to all other treatment steps, but after mixing with non-AOP treated RSF effluent, INF was not significantly different anymore in microbial diversity and composition ($p < 0.05$). However, the microbial communities of IP-37 and IP-38 in the period with AOP were more similar to the microbial communities of the AOP effluent than in the period before AOP (Supplementary Fig. S8). Since these observations were not significant, this could mean that a minor part of the total microbial community was affected by AOP. It was therefore examined which amplicon sequence variants (ASVs) showed a difference in relative abundance before and after AOP, and if these ASVs proliferated after AOP, and eventually end up in DW. ASVs belonging to the genera *Gallionella*, *Bosea* and *Porphyrobacter* were indeed significantly more present in IP-37 and IP-38 during the period with AOP than without AOP, but not in IP-25 and IP-40 (ANCOM differential abundance testing, W-value >1919, Supplementary Fig. S9). These genera belonged to the relatively most abundant genera of the AOP effluent (Fig. 8). Some of these taxa were already present in the RSF effluent, but most seemed to be specifically enriched after AOP treatment, such as *Hyphomicrobium, Gallionella, Bosea, Porphyrobacter, Hydrogenophaga, Legionella, Sphingomonas* and *Afipia*. During transport and mixing with non-AOP treated water, these taxa decrease in relative abundance but they did arrive in the first IP's. As soon as the water was infiltrated, or guided to the infiltration ponds with longer detention, the effect was not visible anymore (Fig. 8). The relative abundance of these taxa fluctuated during the next dune infiltration and treatment steps, and some were also present in the drinking water, such as ASVs belonging to the *Hyphomicrobium* and *Legionella* genus. This was, however, also the case during the period without AOP, where they showed similar relative abundances and was therefore not an effect of AOP treatment.

4. Discussion

4.1. Effect of AOP on organic micropollutant oxidation and removal

Implementation of AOP during drinking water treatment clearly resulted in a high oxidation of most OMP. From the detected compounds that were either measured quantitatively or qualitatively via targeted screening, the majority was oxidized for more than 80%. OMP that were neither oxidized during AOP, nor removed during MARR were per- and polyfluoroalkyl substances (PFAS) and sucralose. These compounds are known to be very mobile and persistent during water treatment (Scheurer et al., 2009; Rahman et al., 2014). Oxidation steps with UV/H_2O_2 and ozonation can partially oxidize sucralose, probably at higher doses, but they are less efficient in oxidizing sucralose compared to the sweetener acesulfame-K (Scheurer et al., 2010; Wang et al., 2018a). PFAS are resistant to oxidation because of the strong C-F bond together with the electron withdrawing functional groups –COOH and $–SO_3H$ in the structures of perfluoroalkyl carboxylic acids and perfluoralkyl sulfonic acids, respectively (Rahman et al., 2014).

For the OMP that were partially or completely oxidized, the concentration in INF-B was reduced accordingly. Before MARR, the AOP effluent was diluted with approximately 40–60% untreated RSF effluent water. Due to the OMP concentration fluctuations in the intake water over time and the fluctuation in the exact ratio between AOP and untreated water at INF, it was not possible to determine exactly if the reduction in concentration between INT and INF was completely due to AOP. However, the OMP concentration reduction in INF in the period with AOP compared to the period without AOP was on average nearly 40% for OMP compounds that were oxidized > 80% by AOP. This means that the concentrations of those OMP in INF would become equal to the concentration in the AOP effluent if the oxidation step would treat 100% of the dune influent. MARR itself also reduced the concentration of many OMP. Some of the OMP that were poorly oxidized by AOP, such as metformin, MTBE and adenosine, were completely removed by MARR. Previous research showed poor removal of MTBE during MARR because of poor sorption characteristics (Segers and Stuyfzand, 2007), but removal highly depends on influent concentrations, residence time (especially in ponds), media sorption characteristics, water temperature and redox conditions. It was hypothesized that AOP could have a positive effect on the degradation rate of OMP during MARR due to AOC formation during AOP that results in increased biological activity after AOP. MTBE was only detected twice above the LOQ in INF-B, IP-38 and MW-38. Metformin was only detected once above the LOQ in INF-B. It was therefore not possible to investigate the hypothesis of the positive effect of AOP on OMP oxidation by MARR. However, biological activity analysis before and after introduction of AOP did give more insights into this, which is discussed in Section 4.3).

Although most OMPs were oxidized and removed during AOP and subsequent MARR, some compounds were regularly detected in drinking water. This concerned the sweetener acesulfame-K, the X-ray contrast agents amidotrizoic acid and iopamidol, and the industrial

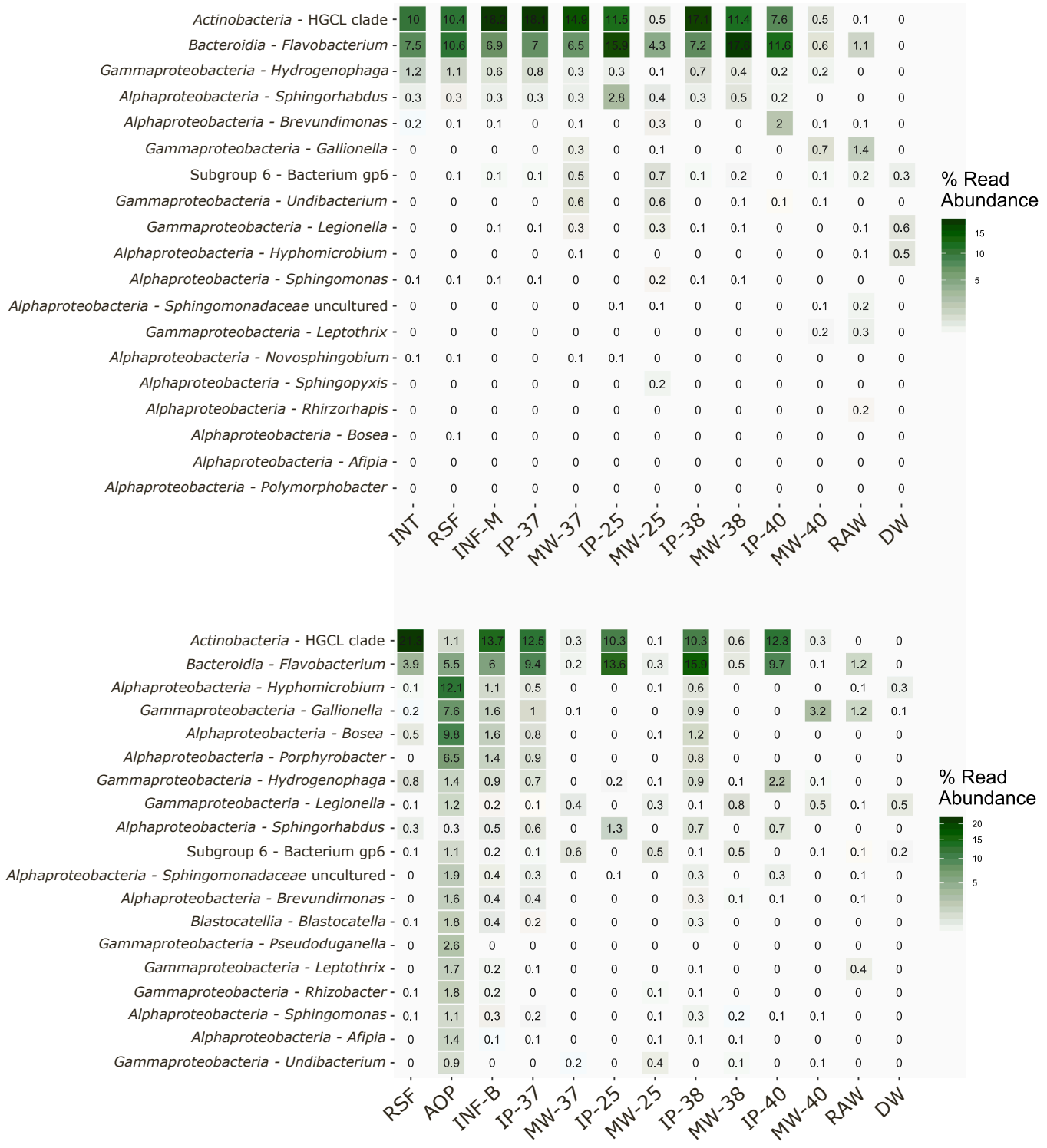

Fig. 8. Heatmap of the average relative read abundance (%) of the most abundant genera occurring in the AOP effluent and their relative abundance in other purification steps. The average relative abundance was calculated for all samples taken throughout the sampling period before (top) and after (bottom) introduction of AOP.

compounds EDTA and urotropin. The maximum concentrations in DW of 0.3 μg/L acesulfame-K, 0.07 μg/L amidotrizoic acid, 0.06 μg/L iopamidol, 13 μg/L EDTA and 0.5 μg/L urotropin in the period 2016–2020 were well below the provisional drinking water guideline values that are established by the Dutch National Institute for Public Health and the Environment, i.e. 3200 μg/L acesulfame-K, 250,000 μg/L amidotrizoic acid, 415 μg/L iopamidol, 600 μg/L EDTA, and 500 μg/L urotropin (https://rvszoeksysteem.rivm.nl/). Although the intake of these compounds via drinking water does not pose a risk for human health, it is still desirable that concentrations are lowered because drinking water utilities strive to achieve drinking water concentrations that are as low as reasonably achievable (ALARA) (van den Berg et al., 2017).

4.2. Effects of AOP on bromate and bromoform formation

Bromate and bromoform are known to be formed from bromide during AOP (Haag and Hoigne, 1983). Bromide was present in INT in concentrations between 90 and 150 μg/L. Bromide concentrations in INT were negatively correlated with the discharge of the Meuse River (Supplementary Fig. S10). On the sampling dates with higher bromide concentrations in INT, higher concentrations of bromate and bromoform were detected after AOP treatment. According to the Dutch governmental decision on infiltration based on the Soil Protection Act, water that is infiltrated should not contain more than 2 μg/L of trihalomethanes determined as the sum of bromoform, chloroform, bromodichloromethane and dibromochloromethane. The last three compounds were not detected above their LOQ of 0.03 μg/L. The concentration of bromoform in INF was well below this concentration. For bromate a 'predicted no effect concentration' (PNEC) of 11 μg/L was derived by Environment and Health Canada from the lowest acceptable toxicity value identified for a freshwater organism, i.e. 1.1 mg/L for *Hylalella azteca* (H.C.E. Environment Canada, 2010). For bromoform, a PNEC value of 13 μg/L is derived for freshwater organisms and a PNEC of 2.26 μg/kg soil dw is derived for soil organisms (E.C.A. ECHA, 2021). Based on these toxicity values, bromate and bromoform in the detected concentrations were not likely to cause a concern for the ecology in the dune filtration areas.

Health based drinking water guideline values were established for bromate and bromoform by the World Health Organization. For bromoform a drinking water guideline of 100 μg/L was derived (W.H.O. , 2005a). For bromate a concentration of 2 μg/L in drinking water was associated with an upper-bound excess lifetime cancer risk of 10^{-5}. However, based on analytical and technological feasibility, the suggested guideline value by WHO is 10 μg/L (W.H.O. , 2005b). Since bromate and bromoform were removed during MARR, and not detected in drinking water, an increased health risk via intake of drinking water was not likely.

4.3. Effects of AOP on (micro)biological growth potential and communities

AOP increased the biological production potential by introducing easily degradable compounds in the AOP effluent. These compounds decreased to similar concentrations as in the period without AOP due to mixing with non-AOP treated RSF effluent, and partly by biological degradation during transport to the MARR system. The biological degradation in the transport mains did not (yet) result in substantial biofilm formation according to flow resistance measurements. It is therefore probable that AOP did not stimulate biological degradation of OMP during MARR. This could be different if in the future when a higher proportion of AOP-treated water will be infiltrated.

Introduction of AOP did however result in lower cell numbers of the infiltrated water. This effect was cancelled out in the first infiltration ponds by primary production and other biological activity. Lastly, microbial taxa that were increased in relative abundance after AOP treatment did have a significantly higher relative abundance in the first infiltration ponds as compared to the period without AOP. These taxa decreased in relative abundance during MARR and were of similar relative abundance in the resulting drinking water between both periods, showing that AOP did not affect the microbial communities of the resulting drinking water. Whether these taxa concerned DNA of dead or live cells is not clear. However, AOP did increase AOC concentrations in the AOP effluent, which mainly includes carboxylic acids and aldehydes (Magic-Knezev et al., 2009). Bacterial isolates belonging to the same genera as found in this study (i.e. *Hydrogenophaga*, *Sphingomonas* and *Afipia*) were previously collected from activated carbon filters for water treatment and at least *Hydrogenophaga* and *Afipia* prefer carboxylic acids and/or amino acids as growth substrates (Magic-Knezev et al., 2009).

4.4. Effects of natural variations on (micro)biological growth potential and communities

Results showed that the surface waters (the intake water and infiltration ponds) showed highest values and strongest fluctuations for ATP, TCC, BP_7 and BCP_{14} in both periods without and with AOP taken together, especially the ponds with long retention times. These parameters were significantly and positively correlated to each other and to pH, nutrients and organic fractions, such as nitrite, ammonium, phosphate, biopolymers, neutrals, building blocks, humic substances, and DOC. The microbial diversity (Faith's PD index) was also significantly, but negatively correlated to the above mentioned parameters. The microbial diversity was much lower in the infiltration ponds before MARR, especially in the ponds with long retention times. The variation in the microbial community composition throughout the year was also especially observed in the infiltration ponds with longer detention times.

Since these effects were mostly observed in the ponds with long retention times, it seems to be caused by external seasonal effects (i.e. precipitation, sun hours, temperature, presence of birds or other fauna in and around the ponds). These have an effect on the availability of nutrients (nitrate, ammonium, phosphate), which determine the primary production, the pH and the concentration of organic compounds and the biological production potential (BPP) and microbial activity (ATP, cell counts). Growth of phototrophic primary producers caused a lower microbial diversity in stratified light-driven ecosystems (Bernstein et al., 2017). Longer detention times therefore could facilitate more phototrophic primary production and competitive growth due to the higher concentrations of nutrients and easily degradable compounds, resulting in lower microbial diversity.

Most of these above mentioned parameters were also lower (but not always statistically significant) in the period with AOP in the infiltration ponds, indicating that the period with AOP was a less productive period for the infiltration ponds as compared to the period without AOP. This also explained the observed, significantly lower silicate concentrations in the ponds in the period with AOP, which was probably due to a lower diatom production. A higher sampling frequency is however necessary to statistically confirm the causes for these seasonal fluctuations.

4.5. Effects of AOP on toxicity bioassays

Effects of AOP on the presence of OMP was assessed biologically using the Ames fluctuation test for mutagenicity (Heringa et al., 2011) and six CALUX reporter gene assays to cover additional toxicological mechanisms such as endocrine disruption, cytotoxicity, direct genotoxicity and oxidative stress (van der Linden et al., 2008, 2014). The results obtained in the current study provided insights in the effectivity of the water treatment process and demonstrated that AOP in combination with MARR was able to completely remove substances with biological toxicity based on the toxicological endpoints measured.

In the performed CALUX assays, indications were found for presence of estrogenic and anti-androgenic substances at the intake water as detected with the ERα and anti-AR CALUX respectively. ER and anti-AR activity in the intake water were detected at levels below the environmental EBT (van der Oost et al., 2017), with the exception of one outlier of 35 μg/L Flt-eq. In drinking water, ER and anti-AR activity levels were below the EBT derived based on human health (Been et al., 2021b).

ER activity decreased during the pretreatment with rapid sand filtration and was only detected in two out of seven samples after this step. Estrogenic activity in AOP effluent was also found in only two out of seven samples in levels around 0.1 ng/L E2-eq. The low detection frequency of ER activity before and after AOP made it difficult to estimate the impact of this treatment on the removal of estrogenic compounds. In Dutch surface waters, natural hormones estrone (E1), E2, estriol (E3), and the synthetic hormone ethinylestradiol (EE) are found to contribute to the biological response found in the ERα CALUX (Zwart et al., 2020). These compounds have a hydrophobic nature and a

relatively high sorption potential and partition to sediment (Lai et al., 2000), which explained why these were partly removed by rapid sand filtration. E1, E2, E3 and EE can be removed by AOP (Silva et al., 2012), but in this study the compounds causing the ER activity were not always removed completely by AOP.

Anti-AR responses are known to be caused by a large and diverse group of compounds. Houtman et al. performed effect directed analysis to identify compounds that are responsible for the anti-AR activity detected in INT (Houtman et al., 2021). Different pesticides were found to contribute to the activity, indicating that mixture toxicity was important for anti-AR activity at this sampling point. The removal of anti-AR activity during AOP was consistent with the efficient removal that was found for most OMPs during this treatment step.

The results of the Ames fluctuation test did not permit conclusions on the removal or neoformation of potentially mutagenic substances in some samples after rapid sand filtration and subsequent AOP. It is known that substances with mutagenic properties can be present in surface waters (Ohe et al., 2004) and the formation of potentially toxic transformation products during drinking water treatment has also been reported (Parker et al., 2017; Zoeteman et al., 1982). Others observed an increase in mutagenic activity of TA98 after UV/H_2O_2 oxidation, which was absent after granular active carbon (GAC) filtration (Heringa et al., 2011). In the present study, activated carbon filtration after AOP and subsequent MARR could have exerted a similar effect. Because the identity, potency and concentration of the potentially mutagenic substances in some of the samples were largely unknown, the risk for human health and the environment cannot be assessed.

Although the Ames fluctuation test showed mutagenic activity in some samples, none of the samples showed direct genotoxicity in the p53 CALUX assay. This can be explained by differences in test system (bacteria for the Ames fluctuation test vs. human cell line for the p53 CALUX), mechanism (heritable changes in the DNA vs. induction of a signaling cascade to prevent DNA damage) and assay-specific differences in sensitivity and specificity (Pinter et al., 2020).

Since water is a complex mixture of natural and anthropogenic substances, it is plausible that multiple substances were accountable for the observed estrogenic, anti-androgenic and mutagenic activity. Chemical analysis demonstrated that AOP and MARR were generally able to remove substances, either completely or partially, which was in line with the observed decrease in biological effects. With more information on chemical identity, it would be possible to identify (groups of) substances that are responsible for specific biological effects.

5. Conclusions

Introduction of AOP decreased the number and concentration of OMP that were introduced during MARR, which decreased the risk of negative impacts on ecology and groundwater. The many uncertainties, such as seasonal and annual fluctuations of the intake water and in the infiltration ponds, made it difficult to determine if factors were directly affected by the AOP introduction. However, AOP did increase the amount of easily biological degradable compounds, but these were diluted with non-AOP treated infiltration water and degraded during transport to the dunes, making the effects on MARR negligible. Several OMP that were not removed during AOP, were removed during MARR. The overall OMP concentrations in resulting drinking water therefore decreased after introduction of AOP, without showing a measurable negative effect on other water quality parameters. Another study in parallel on the same dune infiltration area revealed that implementation of partial AOP had no effects on the Water Framework Directive (Penders, 2014). These results showed that partial AOP treatment and MARR were complementary in OMP removal. The combination of partial AOP treatment and MARR is therefore a promising technology for lowering the amount and concentration of OMP, and for producing a stable drinking water quality without negative effects on inorganic chemistry, toxicology, biological stability, activity and microbial populations during treatment. This however needs to be reassessed when AOP treatment would be performed on 100% of the water to be infiltrated in MARR systems.

CRediT authorship contribution statement

Peer H.A. Timmers, Tineke Slootweg, Aleksandra Knezev, Astrid Reus and Pieter Stuyfzand analyzed data and wrote the manuscript, Dennis Vughs and Leo Heijnen analyzed data, Martin van de Schans, Peer H.A. Timmers and Luc Zandvliet coordinated sampling, analysis and project deliverables. Ton Knol and Jamal El Majjaoui designed the experiments and gave feedback on the manuscript, Paul van de Wielen gave feedback on the manuscript and Karin Lekkerkerker-Teunissen designed the experiments, gave feedback on the manuscript and coordinated project deliverables.

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.

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Novelty Statement

This work describes for the first time the implementation of advanced oxidation processes (AOP) combined with natural dune infiltration for organic micropollutant removal during drinking water production. The combination of (in)organic compounds, transformation products, biological activity, microbial communities, and toxicity effects that were measured to assess the effects of AOP on water quality is also a novelty.

Organic micropollutants can be toxic for ecological systems and humans. It was therefore decided to investigate pretreatment of source water with AOP and subsequent dune infiltration, so that most micropollutants and AOP byproducts do not end up in the environment or drinking water.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.128346.

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