



Analysis, occurrence and removal efficiencies of organophosphate flame retardants (OPFRs) in sludge undergoing anaerobic digestion followed by diverse thermal treatments



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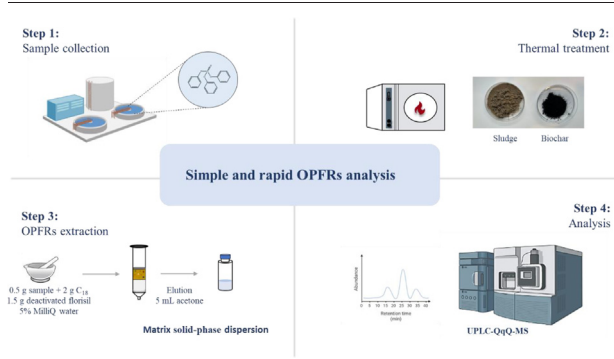
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HIGHLIGHTS

- Matrix solid-phase dispersion was optimized for the extraction of OPFRs from sludge.
- Comprehensive background contamination assessment of OPFRs was performed.
- Fate of 21 OPFRs in sludge and biochar was studied in diverse Norwegian areas.
- Removal efficiencies were assessed under different thermal treatments of sludge.
- Pyrolysis at 500 °C successfully removed OPFRs from digested sludge.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dimitra A Lambropoulou

Keywords:

Sample preparation

Sludge

Biochar

Organophosphate flame retardants (OPFRs)

Background contamination

ABSTRACT

Organophosphate flame retardants (OPFRs) are a complex group of contaminants to deal with in sewage sludge, as currently there is a lack of robust analytical methods to measure them and management strategies to remove them. To facilitate quantifications of the occurrence of OPFRs in sludge and to establish their removal efficiencies (REs%) during thermal treatments, a simple, reliable, and rapid sample preparation methodology was developed for the determination of 21 OPFRs in diverse sludge, ash and biochar matrices. Matrix-solid phase dispersion (MSPD) tailored to ultra-performance liquid chromatography (UPLC) coupled to tandem mass spectrometry (MS/MS) was applied. Under optimal conditions, 0.5 g of freeze-dried sample were dispersed in 2 g of Bondesil C₁₈, and 1.5 g of deactivated florisil were used as clean-up sorbent. The target analytes were extracted with 5 mL of acetone. The obtained extract was ready for analysis within 20 min without the need of any further treatment. The proposed methodology was assessed, providing absolute recoveries (Abs%) ranging from 50.4 to 112 % with good method repeatability (RSDs <17.9 %). Method limits of quantification ranged from 0.10 to 14.0 ng g⁻¹ dry weight (d.w.). The optimized methodology was applied to raw-, digested-, combusted and pyrolyzed sludge samples collected from different waste treatment plants located in Norway, where 16 out of 21 OPFRs were detected in digested sludge samples up to 2186 ng g⁻¹ (d.w.; sum concentration of OPFRs). Diverse thermal treatments of combustion and dry pyrolysis were assessed for the removal of OPFRs from sludge. Combustion at 300 °C reduced the concentrations of OPFRs by 98 % (in the ashes formed), whereas pyrolysis at temperatures >500 °C effectively removed the OPFRs in the produced biochar. Thermal treatments, in particularly dry pyrolysis, showed potential for achieving zero pollution management and recycling of OPFR contaminated sludge.

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1. Introduction

Organophosphate flame retardants (OPFRs) are chemical additives widely used in combustible materials to prevent fire or delay combustion processes. OPFRs are also commonly used as plastic and flame retardant additives, e.g., in furniture, upholstery, electronics, and paints (Celano et al., 2014; Woudneh et al., 2015). More than 1000 tons of flame retardants are produced every year in Europe (Pantelaki and Voutsas, 2019), rendering many OPFRs as high production volume chemicals, which warrant special attention due to their widespread use and potential environmental and human health impacts. Several reports documented their potential carcinogenic, neurotoxic and endocrine disrupting effects (Du et al., 2019). As these substances are not chemically bound to materials, they are easily released into the environment through volatilization, abrasion, or dissolution (Lai et al., 2015; Marklund et al., 2005). The main routes of entry into the environment are through usage, discharges (e.g., from wastewater treatment plants (WWTPs)) and atmospheric emissions (e.g., produced during industrial activities) (Du et al., 2019; Pang et al., 2018; Rodgers et al., 2018). Some OPFRs display limited biodegradation at the WWTPs and high accumulation in sewage sludge (Olofsson et al., 2013). Unfortunately, the primary and secondary treatments in the WWTPs are generally not sufficient to remove them from the water or sludge (Pang et al., 2018). The enormous amounts of sludge generated by WWTPs can be an environmental concern, especially if the obtained products present high OPFR concentrations. The United Nations called for responsible management of chemicals and environmental wastes such as sewage sludge, since they obtain a huge circular economy potential for the recycling of nutrients, green energy production and even as potential replacement sources of actual raw materials (Grobelak et al., 2019; Nations, 2022). Typically, sewage sludge is used as an agricultural fertilizer due to its high organic carbon, phosphorus and nitrogen content (Pang et al., 2018), but this potential reuse can become a concern due to the co-occurrence of elevated concentrations of contaminants (Pang et al., 2018).

An alternative waste handling technique for sludge is combustion or pyrolysis, which consists of heating up the sludge with the presence of oxygen (combustion) or without it (pyrolysis). The combustion process produces mainly low carbon ashes, while the pyrolysis process can result in the production of a porous carbon-rich product called biochar (Barry et al., 2019; Khan et al., 2013; Raheem et al., 2018), which can be used in other formulations, e.g., soil amendment. In addition, biochar and sewage sludge biochar are documented to improve soil quality by increasing nutrient content and water retention, soil porosity and pH, while reducing the availability of contaminants through adsorption, precipitation and redox reactions (Ahmad et al., 2014; Beesley et al., 2011; Khan et al., 2013; Lehmann and Joseph, 2015; Libra et al., 2011). Pyrolysis of sewage-sludge is studied to produce sludge-char, which due to its characteristics can be used as an agricultural fertilizer, promoting the circular economy concept in waste management (Moško et al., 2021).

The presence of OPFRs was previously reported in occupational environmental matrices, such as dust (Brandsma et al., 2013; Castro et al., 2019; Cristale et al., 2019; Peng et al., 2017; Stapleton et al., 2014; Sühning et al., 2016), air (Kerric et al., 2021; Kim et al., 2019; Vykoukalová et al., 2017; Zhou et al., 2017), water (Hao et al., 2018; Li et al., 2021; Pantelaki and Voutsas, 2022; Woudneh et al., 2015; Xu et al., 2019), drinking water (Bacaloni et al., 2007; Li et al., 2014), soil (Cristale et al., 2019; Wang et al., 2018), occupational environments (Nguyen et al., 2022), domestic environments (Diamond et al., 2021) and sewage sludge (Biel-Maeso et al., 2019; Blytt and Stang, 2018; Celano et al., 2014; Cristale et al., 2016; Kim et al., 2017; Pang et al., 2016; Thomas et al., 2014). However, the presence of OPFRs in sludge after combustion and pyrolysis has not been assessed yet.

With this background, the present study aimed to develop a simple, rapid, and reliable ultra-performance liquid chromatography electrospray ionization tandem mass spectrometry (UPLC-ESI-MS/MS) methodology tailored to matrix solid-phase dispersion (MSPD) extraction for the determination of 21 OPFRs from sewage sludge and biochar. Different MSPD

parameters, such as the dispersant, solvent and volume for elution, and type of clean-up sorbent, were assessed to obtain optimal extraction of the target analytes (TAs) and minimal matrix effects. The proposed methodology was found very suitable for diverse sludges and biochars, compared to previous methodologies. It was therefore applied for the analysis of samples obtained from various WWTPs located in different cities in Norway. To the best of our knowledge, this is the first study on the behaviour and removal efficiencies of OPFRs prior to and post diverse thermal treatments, including pyrolysis, and thus, providing relevant input for the sewage sludge recycling and circular economy.

2. Materials and methods

2.1. Chemicals and materials

Analytical standards of trimethyl phosphate (TMP, 99 %), triethyl (TEP, 99.8 %), tri-*n*-propyl (TnPP, 99 %), tri-*n*-butyl (TnBP), triisobutyl (TiBP, 99 %) and tris(4-*tert*-butylphenyl) (TTBPP) were purchased from Sigma-Aldrich (Steinheim, Germany). Tris(2-butoxyethyl) (TBOEP), tris(2-ethylhexyl) (TEHP), tris(2-chloroethyl) (TCEP), tris(1-chloro-2-propyl) (TCIPP), tris(1,3-dichloro-2-propyl) (TDCIPP), triphenyl (TPhP), tricresyl (TCrP; as a mixture of isomers), cresyl diphenyl (CDP), 2-ethylhexyl diphenyl (EHDP), and 2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl) (V6) were acquired in neat form from Chiron AS (Trondheim, Norway). Individual stock solutions (100–1000 $\mu\text{g mL}^{-1}$) of those were prepared in methanol. Analytical standards (50 $\mu\text{g mL}^{-1}$ in methanol) of tetraphenylresorcinol bis(diphenyl phosphate) (RDP), bisphenol A bis(diphenyl phosphate) (BPA-BDPP), hydroxyethyl phosphate (BBOEHP; metabolite of TBOEP), and bis(2-butoxyethyl) hydroxyl-2-butoxyethyl phosphate (3OH-TBOEP; metabolite of TBOEP) were purchased from Chiron AS (Trondheim, Norway). The analytical standard (50 $\mu\text{g mL}^{-1}$ in isooctane) of isodecyl diphenyl phosphate (IDPhP), and the isotopically labelled internal standards (ISs) of TEP- d_{15} (99 %), TnPP- d_{27} (99 %), TCEP- d_{12} (98 %) and TDCIPP- d_{15} (99 %) were also purchased from Chiron AS (Trondheim, Norway). TPhP- d_{15} (98 %) and BBOEHP- d_4 (neat) were supplied by Sigma-Aldrich (Oslo, Norway) and Toronto Research Chemicals (Toronto, Canada), respectively. Chemical structures of the TAs, CAS number, molecular weight, $\log K_{ow}$ values and their flash and boiling points are compiled in Table S1.

Florisil (60–100 mesh) and C_{18} -bonded silica (40 μm) were purchased from Agilent Technologies (Santa Clara, CA, USA). Supelclean PSA SPE Bulk Packing (ethylenediamine-*N*-propyl-bonded silica), MSPD empty polypropylene syringes (12 mL volume) and 20 μm polyethylene frits were purchased from Merck (Darmstadt, Germany).

LC-MS grade methanol (MeOH), acetone, acetonitrile (ACN), 2-propanol (IPA), ethyl acetate (AcOEt) and dichloromethane (DCM) were purchased from VWR Chemicals (Trondheim, Norway). Formic acid (FA, >96 %) was acquired from Sigma Aldrich (Oslo, Norway). Water was purified with a Milli-Q grade water purification system (Q-option, Elga Labwater, Veolia Water Systems LTD, U.K.).

2.2. Sample collection and handling

Grab sludge samples were collected between January 2021 and February 2022 from four WWTPs and one sewage treatment plant (STP) that serve populations between 85,000 and 600,000 inhabitants across Norway. Details about the different treatments applied in each facility are summarized in Table 1. Raw sludge samples were collected in amber glass jars, while digested sludge was collected in sterile polypropylene bags. Once in the laboratory, samples were frozen at $-20\text{ }^{\circ}\text{C}$ in aluminium foil containers for 12 h and freeze dried ($-21\text{ }^{\circ}\text{C}$, 6 mbar). Dried samples were homogenised in a mortar and kept at $4\text{ }^{\circ}\text{C}$ until analysis. A pooled sludge sample was prepared by mixing 7 different samples, in equal amounts, for sample preparation optimization and method performance validation.

Table 1
Information about the WWTPs and STP in Norway.

WWTP code	Treatment description	Population equivalents (PE)	Samples and sampling periods
WWTP1	Primary treatment (anaerobic digestion*)	170,000	Raw sludge (1 sample per day, n = 3 days) Digested sludge (1 sample per day, n = 3 days) 2 sampling campaigns (May and August 2021)
WWTP2	Primary treatment (anaerobic digestion)	120,000	Raw sludge (1 sample per day, n = 3 days) Digested sludge (1 sample per day, n = 3 days) 2 sampling campaigns (June and September 2021)
WWTP3	Primary and secondary treatment (anaerobic digestion combined with hygienization with lime#)	600,000	Pre-digested sludge (1 sample per day, n = 3 days) Lime stabilized sludge (1 sample per day, n = 3 days) 1 sampling campaign (January 2021)
WWTP4	Primary treatment (dewatering)	85,000	Digested sludge (1 sample per day, n = 2 days) 1 sampling campaign (June 2021)
STP1	Secondary treatment (CAMBI* thermal hydrolysis process (THP) combined with anaerobic digestion)	–	Raw sludge (1 sample, n = 1 day) THP sample (1 sample, n = 1 day) THP/Digested sludge (1 sample, n = 1 day) 1 sampling campaign (January 2021)
Combustion	Combustion	–	1 sampling campaign (May 2021) from WWTP1
Pyrolysis	Dry pyrolysis**	–	1 sampling campaign (February 2022) from WWTP3, WWTP4 and STP1

*Anaerobic digestion: The organic waste is biologically degraded into biogas and other energy-rich organic compounds in the absence of oxygen (Hanum et al., 2019).

#Hygienization with lime: Sludge is stabilized by the addition of CaO.

*#CAMBI thermal hydrolysis process (THP): Organic waste is submitted to high temperature and pressure.

**Dry pyrolysis: Organic wastes are pyrolyzed in the absence of oxygen to produce syngas, oil and biochar.

Combustion tests were performed with freeze dried digested sludge samples at a laboratory scale in a combustion oven (Carbolite® model AAF 11/7) at two different temperatures (100 and 300 °C). The samples were weighed prior to and post combustion. For pyrolysis the digested sludge was stored cold (4 °C) until drying (generally within weeks or months after the collection date). Drying was performed in batches of 2 m³ of sewage sludge (5–10 % moisture) in a paddle dryer (1.5 × 5 m) operating at 102–110 °C, built by Scanship AS (Tønsberg, Norway). Water was removed at a rate of 300 L hour⁻¹ by a superheated steam, supplied from a heat exchanger into a heating jacket fitted around the drier. Dried samples were then pelletized (length 40 mm, radius 8 mm) before pyrolysis.

The pyrolysis thermal treatment of sludge generates three sub-products: syngas, pyrolysis oil and biochar (Fig. S1). Syngas, also known as synthesis gas, is a mixture of molecules containing H₂, CH₄, CO, CO₂, H₂O, N, and other hydrocarbons and condensable compounds; when it condensates, pyrolysis oil is obtained, while the biochar is the solid product obtained from the pyrolysis (Ethia, 2022; Libra et al., 2011). Herein, only the biochar fraction was analysed. Pyrolysis was carried out in a medium scale unit (2–10 kg h⁻¹), the Biogreen© pyrolysis unit (ETIA, France), which was installed by VOW ASA (Lysaker, Norway) for running pyrolysis experiments. The pyrolyzer contained an electrically heated reactor (up to 800 °C), a condenser unit for syngas (≈ 10 °C) with a collection tray for the pyrolysis oil, and a combustion chamber (700–900 °C) for the remaining syngas. The samples were produced at different temperatures (500–800 °C). The biochar produced during a 2-h period of stable conditions at a given pyrolysis temperature (~4–10 kg produced in total) was subsampled (100 g) using random grab sampling, and thereafter stored in glass jars (200 mL) for further analysis. Due to logistical challenges regarding access to the pyrolyzer, the number of temperatures in which the biochar was produced varied for the different sludge samples.

2.3. Sample preparation

The extraction of OPFRs was carried out by MSPD, using C₁₈-bonded silica as dispersant (Casado et al., 2015; Castro et al., 2018; Celano et al., 2014). Extraction conditions were optimized with the indicated pooled sample, and the samples were fortified with TAs at 60 ng g⁻¹ dry weight (d.w). Under optimal conditions, 0.5 g of dried sample, fortified with 20 ng g⁻¹ of ISS, were dispersed in 2 g of Bondesil C₁₈ in an agate mortar with the aid of a pestle. The obtained blend was loaded into a MSPD

cartridge containing (from bottom to top) a polyethylene frit and 1.5 g of florisil deactivated with 5 % (w/w) Milli-Q water. The blend was compacted with a second frit placed on top. The TAs were eluted with 5 mL of acetone. The obtained extract was analysed by UPLC-MS/MS.

2.4. Instrumental analysis

The OPFRs were determined by UPLC-MS/MS with a Xevo TQ-S triple quadrupole mass spectrometer (that contains a Z spray ESI source) connected to an Acquity UPLC I-Class system, both acquired from Waters (Milford, MA, U.S.). Chromatographic separation was performed in a Kinetex C₁₈ column (30 × 2.1 mm, 1.3 μm) serially connected to a C₁₈ security guard (2 × 2.1 mm i.d.), both supplied by Phenomenex (Torrance, CA, U.S.). Milli-Q grade water (A) and ACN (B), both containing 0.1 % v/v formic acid, comprised the mobile phase, and were maintained at a constant flow rate of 400 μL min⁻¹. The UPLC column and precolumn were kept at 40 °C. The mobile phase gradient was step-programmed as follows: 0–1 min, 25 % B; 2.5–3.5 min, 100 % B; and 4–5 min, 25 % B, ensuring the chromatographic separation of the TAs (Fig. S2). The injection volume was 2 μL.

The analytes were ionized under positive ionization mode (ESI+). Nitrogen was used as drying gas at the ionization source (350 °C at 1000 L hour⁻¹). The ESI-MS/MS parameters were optimized by direct infusion of methanolic standards for each individual chemical; two MRM (Multiple Reaction Monitoring) transitions per chemical were optimized. The most intense one (higher S/N ratio) was considered as the quantification transition (Q1) and the second in intensity was considered as the confirmation transition (Q2). Both transitions were monitored with a scan time window of 60 s around the retention time of the analyte. The dwell time per transition was adjusted to obtain 12 points per peak assuming an average baseline peak width of 4 s. Capillary voltage, collision energies and source offset voltage were also optimized. Optimal values were achieved when the capillary voltage was maintained at +2.8 kV, the cone voltage at 50 V, and the source offset voltage at 80 V.

2.5. Method development

The extraction efficiency of the MSPD protocol was assessed through the study of absolute recoveries (Abs%) and relative recoveries (Rel%) for each TA in a pooled sludge matrix fortified at two different concentrations (5 and 50 ng g⁻¹ d.w.), and 20 ng g⁻¹ d.w. of ISS. The Abs% for each TA at

a specific fortification concentration was calculated from the response (area of quantification MRM peak) of the TA in the pre-extraction matrix matched spiked standard solution divided by the response of the analyte in the post-extraction matrix matched spiked standard solution and multiplied by 100. The Rel% (to IS) for each TA at a specific fortification concentration was calculated from the ratio of the analyte response to the IS response in the pre-extraction matrix matched spiked standard solution divided by the same ratio in the post-extraction matrix matched spiked standard solution, and multiplied by 100 (Arvaniti et al., 2014). The fortification concentrations (5 and 50 ng g⁻¹) of the TAs were selected accordingly due to the occurrence of endogenous concentrations in the pooled sample. The matrix effect (ME%) for each TA was estimated as the ratio between the slope of its matrix matched (sludge matrix) post-extraction calibration curve and the slope of its calibration curve prepared in solvent, multiplied by 100. The closer the values to 100 %, the lower the effect of the matrix during ionization, while values below and above 100 % indicated signal suppression and enhancement, respectively (Castro et al., 2022; Raposo and Barceló, 2021). Quantification of the TAs was accomplished based on the internal standard method and matrix-matched calibration standards (Asimakopoulos et al., 2016).

The linear range for every TA was assessed by the injection of an 11-point standard solvent calibration curve ranging from 0.02 to 150 ng mL⁻¹. Within this range, the obtained calibration curves fitted a linear model with correlation coefficients (R²) > 0.99 (Table S2). Instrumental repeatability and reproducibility (n = 3 days) were assessed with n = 6 replicates of 60 ng mL⁻¹ standard solvent solution; and the obtained results showed RSDs < 12 and 24 %, respectively. The instrumental limit of quantification (iLOQ) was defined for each TA as the concentration of the lowest calibration standard concentration providing a signal-to-noise (S/N) ratio ~ 10 or alternatively 10 times the standard deviation of the instrumental blanks if the TA was detected in them (Castro et al., 2020); the obtained iLOQs ranged from 0.02 and 2.00 ng mL⁻¹ (Table S2). The method limits of quantification of the complete methodology (mLOQs) were estimated accordingly as the iLOQs by using pre-extraction spiked pooled samples (with a nominal dried sample mass of ~0.5 g). For those TAs present in the procedural blanks, their mLOQs were calculated by multiplying by 10 the standard deviation of the signal response (area) of the TA in the procedural blanks (n = 3). The mLOQs ranged from 0.10 (for V6) to 14.0 ng g⁻¹ d.w. for (TTBPP) (Table S3).

2.6. Data analysis

UPLC-MS/MS data was acquired with the MassLynx v4.1 software, while quantification processing was carried out with TargetLynx; both softwares supplied by Waters (Milford, U.S.). Excel (Microsoft 365) was used for data analysis and general descriptive statistics. Data analysis did not include censored data [non-detects (n.d.) and concentrations < mLOQ]. For each TA the concentrations ≥ mLOQ were considered as detected with acceptable certainty (and presented by the detection frequency %; DF%). Concentrations were reported as ng g⁻¹ (d.w.).

2.7. Removal efficiency

The removal efficiencies (REs%) of OPFRs were calculated following the Eq. (1) proposed by Chen et al. (2018) and used for biochar yields by Moško et al. (2021).

$$RE (\%) = \frac{C1 - C2 * Sludge Yield}{C1} \times 100 \quad (1)$$

C1 and C2 are the concentrations in ng g⁻¹ d.w. of each TA in the sludge before and after the treatment, respectively. Sludge yield during the treatment was also considered, defined as the ratio of the dry weight mass after treatment divided by the dry weight mass before treatment. Herein “sludge yields” were considered for anaerobic digestion, combustion, and dry pyrolysis. The values for anaerobic digestion were provided for each

WWTP, and those for combustion and dry pyrolysis were determined by weighting the samples before and after the thermal treatment (Table S4). The RE% represents a mass change, by normalizing the C2 as if the mass of the sludge was unchanged. Positive RE (%) values indicate the removal percentage, with 100 % indicating the complete removal of the compound during the treatment, while negative RE values (presented here in bold) represent formation. It should be noted that sample heterogeneity may affect RE values, so this was compensated by: a) performing the correction with sludge yields presented above, and b) establishing a detection cut-off value. The cut-off value was established when C2-C1 < 2mLOQ, and then considering RE as 0 %. Values for “sludge yield” in Eq. (1) are presented in Table S4.

2.8. Quality assurance and quality control (QA/QC)

Contamination is an important issue for the analysis of OPFRs, due to the high concentration of these contaminants in the background blanks. To eliminate any potential contamination during sample preparation, the laboratory working benches were cleaned with acetone and covered with aluminium foil prior to sample preparation (see Section 3.2). Mortars and pestles of agata were consecutively rinsed with water, methanol, and acetone prior to use. Furthermore, one procedural blank per batch of seven samples was analysed. The signals in the blanks were subtracted from the sample as it could be assumed to be contamination valid for all samples.

Solvent blanks and solvent standards (10 ng mL⁻¹) were incorporated in the sample sequence after every 15 consecutive samples to check for potential sample carryover and instrumental drift in response, respectively. A solution of MeOH:IPA:ACN:Milli-Q (1:1:1:1 v/v) was used as washing solution to avoid carryover issues; the injection needle was washed with this solution 5 s before and after each injection.

3. Results and discussion

3.1. Optimization of the sample extraction protocol

Different parameters were assessed to select the optimal combination of MSPD dispersants, sorbents, and extraction solvents, which maximized the yield of the extraction process, while minimizing the matrix effects.

3.1.1. Selection of elution solvent

The sample preparation protocol for the extraction of OPFRs from mussel samples reported by Castro et al. (2020) was tested with minor modifications. Briefly, ~0.5 g of pooled freeze-dried sludge (fortified with 60 ng g⁻¹ d.w. of the mixture of the TAs) were dispersed in 2 g of Bondesil C₁₈. The obtained blend was placed into a MSPD cartridge which contained 1.5 g of florasil and was compacted with a polyethylene frit. Then, the extraction efficiencies of three different solvents were tested. The TAs were either eluted with 10 mL of DCM, 10 mL of acetone or 10 mL of AcOEt (Fig. 1). The obtained extracts were concentrated to near dryness and reconstituted in 1 mL of MeOH:Milli-Q water (1:1 v/v). It is noteworthy that the experiments were performed in triplicates (n = 3).

DCM failed in the extraction of medium to polar compounds, logK_{ow} < 3 (Table S1), and moreover it provided very low extraction efficiencies for TCIPP, TPhP, and CDP compared to those obtained with acetone. In addition, DCM produced high RSDs for most of the studied TAs. Particularly high RSDs were obtained for compounds with higher logK_{ow} (logK_{ow} > 6), which was the case for TCrP, IDPhP, TTBPP and RDP. AcOEt performed similar to DCM, producing extraction efficiencies < 20 % for TMP, TPhP, CDP, BBOEHP, TCrP, 3OH-TBOEP, TTBPP, RDP, V6 and BPA-BDPP, but presenting lower RSDs than DCM (< 35 %). Acetone was the solvent that performed best, recovering 15 out of 21 TAs with Abs% > 40 % and RSDs < 23 %. Since this solvent provided the best results and visually cleaner extracts than the others, it was selected for further optimization of the protocol.

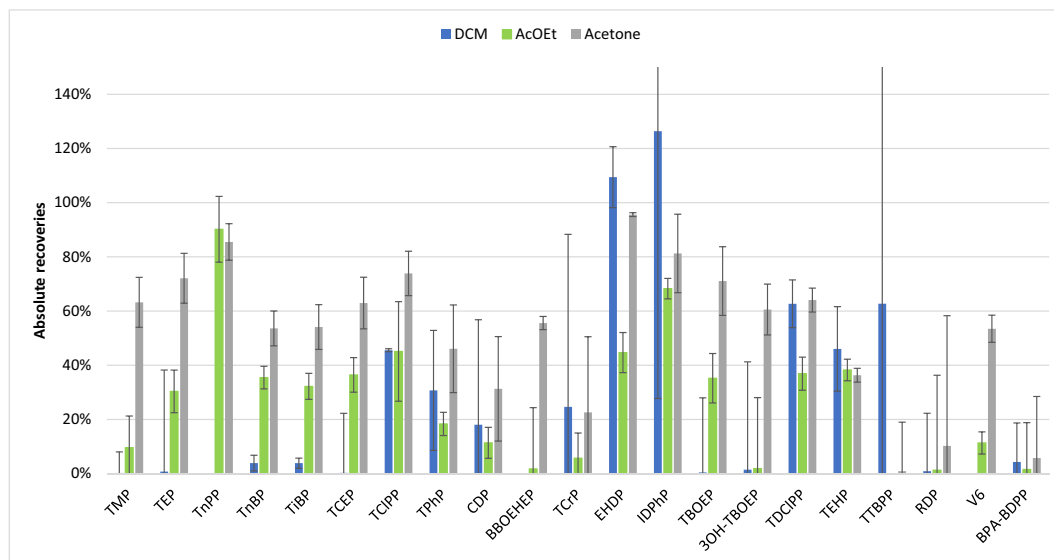


Fig. 1. Absolute recoveries (Abs%) and RSDs% obtained during the elution of sludge samples (fortification concentration of 60 ng g^{-1} d.w. of the TAs) with different solvents ($n = 3$).

3.1.2. Selection of clean-up sorbent

Two different clean-up sorbents were tested, PSA and florisil. PSA did not perform well since it strongly retained the chemicals during clean-up. In contrast, florisil provided better results, and therefore, it was selected as sorbent for further optimization; the findings in this study were in agreement with those previously reported (Castro et al., 2020). Activation and deactivation of florisil is a commonly studied technique for clean-up and extraction purposes (Villaverde-de-Sáa et al., 2013). Therefore, florisil was activated overnight in an oven at 120°C , followed by controlled deactivation with different percentages of Milli-Q water: 0, 5 and 10 % (w/w) (Fig. 2). Florisil deactivated with 5 % (w/w) of Milli-Q water presented optimal Abs (%) ranging from 62.8 to 128 % and RSDs < 13 % ($n = 3$) (Fig. 2), and therefore, was selected as the clean-up sorbent.

3.1.3. Selection of elution solvent volume

The volume of solvent required to achieve complete elution of the TAs was also assessed. Triplicate extractions were performed following the protocol described above (see Section 3.1. Selection of clean-up sorbent). Two consecutive fractions of 5 mL of acetone were collected and analysed separately (Fig. S3). The obtained results demonstrated that 5 mL are sufficient

to completely recover all TAs. Thus, 5 mL of acetone were selected as the final volume for elution.

3.2. Sources of background contamination

The main challenge during the analysis of OPFRs is the background contamination. Several authors described background contamination issues during analysis (Brandtsma et al., 2013; Castro et al., 2020; Liang et al., 2015), reporting high concentration for those in indoor air and dust that can contaminate the materials for sample preparation, while TCIPP and TnBP contamination is documented to derive from various analytical instrumentations (Brandtsma et al., 2013).

Herein, the chromatographic system was thoroughly cleaned with IPA, while the ESI cone and source chamber were washed according to the vendor instructions prior assessing instrumental contamination (Waters, 2014). Non-injection tests (only the solvent chromatographic gradient passes through the pre-column and the chromatographic column, while no injection is performed) were carried out, and 11 out of 21 TAs (TEHP, TDCIPP, TBOEP, EHDP, CDP, TPhP, TCIPP, TnBP, TiBP, RDP and BPA-BDPP) were detected in concentrations ranging from 0.02 to 26.5 ng

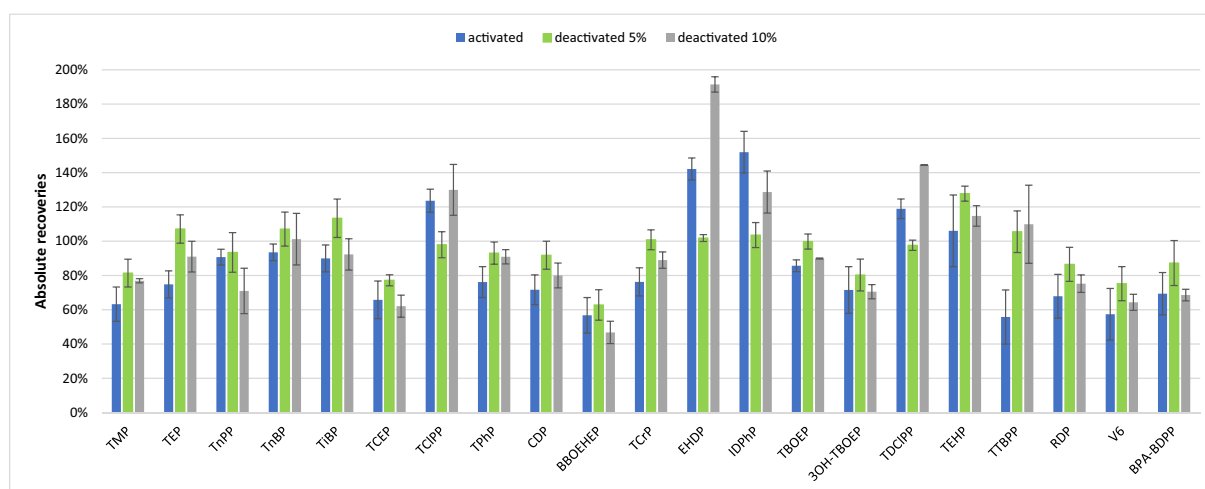


Fig. 2. Absolute recoveries (%) obtained using different percentages of water for the deactivation of florisil. Extraction conditions: 0.5 g of dried sample spiked with 60 ng g^{-1} , 2 g of C_{18} as dispersant and 1.5 g of florisil. Analytes were eluted with 5 mL of acetone.

mL^{-1} (Table S5). In view of the obtained results, a brand-new guard column and chromatographic column were installed, and instrumental contamination of the same TAs was observed, but in lower concentrations; one to three-times lower (0.02 to 12.7 ng mL^{-1}) (Table S5). To pinpoint the source of contamination, by-pass tests (mobile phase passed through the system, without a column) were carried out. As a result, clean chromatograms were obtained, indicating that the chromatographic column itself provided signals in the procedural blanks. In Fig. 3 the obtained results prior to and post cleaning with IPA are presented.

3.2.1. Procedural blanks

Procedural blanks ($n=2$) were analysed after cleaning the instrument and using the new chromatographic column. Under those conditions, the obtained concentrations remained stable between 0.04 (BPA-BDPP) and 17.1 ng mL^{-1} (TCIPP), depending on the TA, demonstrating that the

contamination of OPFRs was also derived from the sample preparation itself in addition to the instrumental source (Table S5).

Several authors documented this issue in OPFRs determination; however, many studies have not directly acknowledged it. Brandsma et al. developed an international interlaboratory scheme on OPFRs in dust, fish oil and sediments (Brandsma et al., 2013), where blank contamination was assessed by each laboratory, reporting contamination of TnBP, TiBP, TCEP, TDCIPP, TBOEP, TPhP, EHDP, TEHP, TCIPP and TCrP at different concentrations (Table 2). In the case of sediment samples, mean concentrations of procedural samples were reported ranging from 0.20 (TCrP) to 19.0 ng g^{-1} (TiBP) (Brandsma et al., 2013). It was evident though that each laboratory presented different procedural blank contamination profiles, due to the different materials used in each case. Castro et al. (2020) assessed the occurrence of this chemical class in mussel samples using MSPD as the extraction technique. In that case, authors reported the

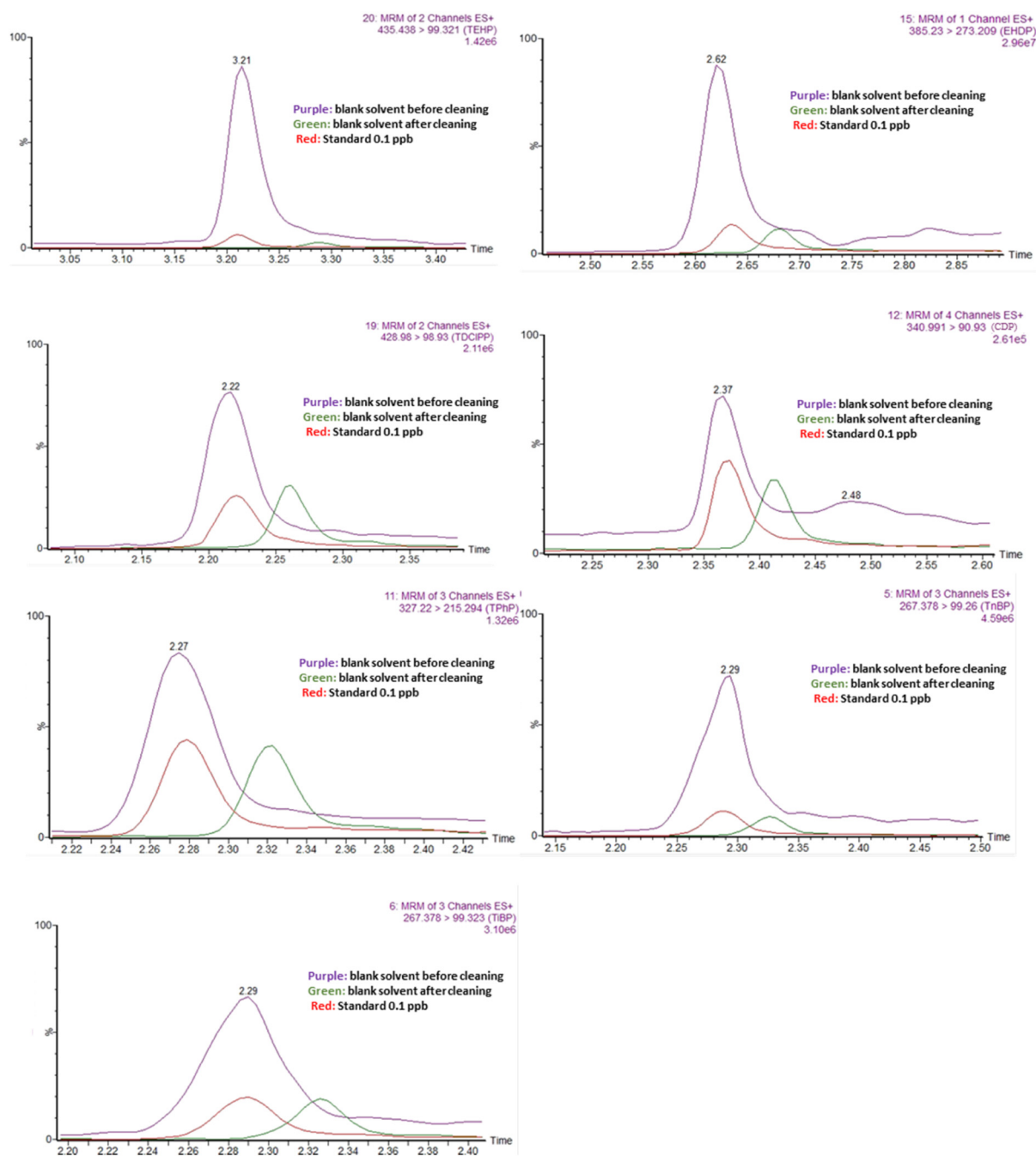


Fig. 3. Chromatograms of the blank contamination obtained during the analysis of an instrumental blank before and after cleaning the instrument.

Table 2
Mean blank concentrations of OPFRs during analysis reported in literature.

Matrix	Number of TAs	Sample preparation	Units*	TnBP	TiBP	TEP	TnPP	TCEP	TCIPP	TDCIPP	TPhP	EHDP	TBOEP	TEHP	CDP	TCrP	RDP	BPA-BDPP	Reference
Sediment	10	Ultrasonication, ASE [#] , Soxhlet	ng g ⁻¹	3.00	19.0	NA	NA	4.70	13.0	3.50	1.80	2.90	8.60	1.90	NA	0.20	NA	NA	(Brandsma et al., 2013)
House dust	10	Ultrasonication, ASE, Soxhlet	ng g ⁻¹	36.0	262	NA	NA	45.0	75.0	51.0	15.0	21.0	1.40	19.0	NA	3.80	NA	NA	(Brandsma et al., 2013)
Fish oil	10	LLE [#] , ASE, None	ng g ⁻¹	7.90	11.4	NA	NA	11.0	41.0	9.40	4.80	4.70	54.0	11.0	NA	4.50	NA	NA	(Brandsma et al., 2013)
Mussels	18	MSPD (n = 3)	ng mL ⁻¹	1.00	2.00	NA	NA	n.d.	3.00	n.d.	n.d.	0.50	0.50	n.d.	NA	n.d.	n.d.	NA	(Castro et al., 2020)
Sewage sludge compost	5	ASE (n = 3)	ng mL ⁻¹	2.95	NA	NA	NA	n.d.	3.90	NA	9.38	NA	2.00	NA	NA	NA	NA	NA	(Pang et al., 2017)
Water and sediments	18	LLE, Soxhlet (n = 15)	ng L ⁻¹	n.d.	NA	n.d.	n.d.	9.20	9.80	n.d.	n.d.	n.d.	15.8	n.d.	NA	NA	NA	NA	(Lee et al., 2018)
Soil	12	Ultrasonication	ng g ⁻¹	1.00	1.44	0.15	0.01	0.90	2.80	n.d.	0.46	0.22	1.1	0.18	NA	n.d.	NA	NA	(Ji et al., 2019)
Soil and dust	12	Ultrasonication (n = 6)	ng g ⁻¹	< 1.40	7.00	< 1.40	n.d.	6.20	4.20	< 1.40	n.d.	< 1.40	n.d.	n.d.	NA	NA	NA	NA	(Wang et al., 2018)
Sewage sludge	6	Ultrasonication (n = 4)	ng L ⁻¹	n.d.	NA	NA	NA	24.8	12.4	24.7	< LOD	NA	n.d.	NA	NA	NA	NA	NA	(Pang et al., 2016)
Sewage sludge	21	MSPD (n = 2)	ng mL ⁻¹	1.59	1.48	n.d.	n.d.	n.d.	17.1	8.16	1.21	13.9	1.61	0.25	0.50	n.d.	0.11	0.04	Current study

NA, not analysed; n.d., non-detected; *Units for the reagent blanks; #Accelerated solvent extraction; ##Liquid-liquid extraction.

presence of TCIPP, TBOEP, TiBP, TnBP and EHDP in procedural blanks in concentrations ranging from 1.00 (TnBP) to 3.00 ng mL⁻¹ (TCIPP) (Table 2). Wang et al. (2018) analysed 12 OPFRs in soils and dust from a multi-waste recycling site in China. Background analysis showed no contamination during sample collection, but procedural blanks demonstrated contamination of TiBP, TCEP, and TCIPP at mean amounts of 7.00, 6.20 and 4.20 ng, respectively (Table 2), while TEP, TnBP, TDCIPP and EHDP were found in amounts <1.40 ng (Wang et al., 2018). Hao et al. (2018) determined 12 OPFRs in surface water and wastewater by direct injection analysis in LC-MS; their approach avoided any contamination derived from sample preparation, but the chromatographic peaks of TCIPP, TDCIPP, EHDP, TPhP and TBOEP were observed during the injection of Milli-Q water. Pang et al. (2017) reported similar low concentrations of TnBP and TBOEP in procedural blanks to those found in the study herein (Table 2). Overall, TnBP, TiBP, TCIPP and TBOEP were the most common TAs determined as background contamination (Table 2). Documented sources of contamination are plastic materials (Brandsma et al., 2013; Pang et al., 2016), cellulose filters used during pressurized liquid extraction (PLE) (Quintana et al., 2007), teflon-layered silicone septum (Rodríguez et al., 2006), and analytical instrumentations (Brandsma et al., 2013; Celano et al., 2014). To reduce contamination, laboratory materials must be free of OPFRs. Pre-heated and cleaned glass-materials are recommended (Pantelaki and Voutsas, 2019). In a few studies, a C₁₈ column was installed prior to the injection valve of the auto-sampler to retain the TAs leaching out of the LC system (including the mobile phase) and delay their elution time window to avoid interference with the concentrations of the TAs in the actual analysed sample (Brandsma et al., 2013; Celano et al., 2014; Hao et al., 2018).

3.3. Method performance

Obtained Abs% ranged from 50.4 to 112 % with RSDs <17.9 % (Table S3). Celano et al. (2014) developed an analytical methodology for the analysis of 8 OPFRs based on MSPD as the extraction technique, and similar recoveries ranging from 70 to 117 % with RSDs <13 % were reported. Rel (%) ranged from 57.6 to 122 % with RSDs <19.7 % (Table S3).

Regarding matrix effects (MEs%), some of the TAs showed signal suppression during the ionization in ESI (Table S3), presenting MEs% < 70 %, including EHDP (23.6 %), IDPhP (18.6 %), TEHP (6.62 %), TTBP (6.34 %) and BPA-BDPP (35.2 %). TnBP and TCIPP demonstrated ionization enhancement with values of ME of 175 and 183 %, respectively. The remaining TAs did not demonstrate any significant matrix effects since the MEs% ranged between 70 and 140 % (Table S3). This multiresidue method herein determines OPFRs in sludge samples with low mLOQs (0.1–14 ng g⁻¹ d.w., 21 TAs). For comparison, previous studies reported mLOQs ranging from 0.05 to 10 ng g⁻¹ d.w. (14 TAs) (Kim et al., 2017), from 0.2 to 5.1 ng g⁻¹ d.w. (10 TAs) (Marklund et al., 2005), and from 2 to 50 ng g⁻¹ d.w. (8 TAs) (Celano et al., 2014).

4. Analysis of digested sludge samples

The proposed analytical methodology was applied in digested sludge and the obtained concentrations are presented in Table 3. It is noteworthy that the presented concentrations from WWTP1 and WWTP2 are the median concentrations of two sampling campaigns (Table 1). Sixteen out of 21 TAs were detected in the studied samples. Ten of those presented DF % > 40 %: TnBP, TiBP, TBOEP and BPA-BDPP (DF 100 %); CDP and TEHP (DF 80 %); TEP, TCrP (DF 60 %); and TPhP and RDP (DF 40 %). The OPFRs detected with DF 20 % were: TCEP, TCIPP, BBOEHP, IDPhP, 3OH-TBOEP and V6. TnPP, EHDP, TDCIPP, TTBP were found below mLOQ, and TMP was not detected in any sample, which can be attributed to its high polarity (logK_{ow} = 0.6, Table S1), indicating its tendency to remain in the aqueous phase matrices during the treatment in the WWTPs. Obtained median concentrations ranged from 0.64 to 396 ng g⁻¹ d.w. (Table 3). TCIPP was the TA determined at the highest concentration (396 ng g⁻¹ d.w.), followed by TEHP (170 ng g⁻¹ d.w.), TBOEP (133 ng

Table 3Concentrations (ng g⁻¹, dry weight) in digested sludge samples collected from facilities located in Norway (n = 18 samples).

Analyte	Concentration (ng g ⁻¹)						DF (%) [#]
	WWTP1*	WWTP2*	WWTP3	WWTP4	STP1	Median	
TMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
TEP	14.1	22.9	15.8	n.d.	n.d.	15.8	60
TnPP	<mLOQ	n.d.	n.d.	n.d.	n.d.	<mLOQ	0
TnBP	33.7	25.2	19.4	30.4	28.3	28.3	100
TiBP	20.3	14.6	12.5	18.0	12.3	14.6	100
TCEP	16.5	n.d.	n.d.	n.d.	n.d.	16.5	20
TCIPP	n.d.	396	n.d.	n.d.	n.d.	396	20
TPhP	45.2	53.6	n.d.	<mLOQ	n.d.	49.4	40
CDP	1495	87.9	n.d.	12.7	5.04	50.3	80
BBOEHEP	n.d.	n.d.	n.d.	38.4	n.d.	38.4	20
TCrP	95.4	61.2	n.d.	22.4	n.d.	61.2	60
EHDP	n.d.	<mLOQ	n.d.	n.d.	n.d.	<mLOQ	0
IDPhP	78.3	n.d.	n.d.	n.d.	n.d.	78.3	20
TBOEP	124	133	140	189	80.8	133	100
3OH-TBOEP	n.d.	n.d.	n.d.	11.3	n.d.	11.3	20
TDCIPP	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	0
TEHP	217	175	126	166	n.d.	170	80
TTBPP	<mLOQ	<mLOQ	n.d.	n.d.	n.d.	<mLOQ	0
RDP	7.87	5.61	<mLOQ	n.d.	<mLOQ	6.74	40
V6	n.d.	0.64	n.d.	n.d.	n.d.	0.64	20
BPA-BDPP	37.8	24.7	2.76	0.81	2.53	2.76	100
ΣOPFRs	2186	1000	317	489	129	489	-

n.d., non-detected; DF, detection frequency.

*Median values of the two sampling campaigns.

#For each TA the concentrations ≥ mLOQ were considered as detected with acceptable certainty (and presented by the DF% herein).

g⁻¹ d.w.) and TCrP (61.2 ng g⁻¹ d.w.). TBOEP was detected in all the samples, contributing 27 % to the total median concentration of the sum of OPFRs in the sludge samples (Fig. S4). This contaminant is commonly used as plasticizer in rubber and as an additive in floor waxes and polishes (Pantelaki and Voutsas, 2019), and presents two characteristic transformation products/metabolites (3OH-TBOEP and BBOEHEP). According to the World Health Organization (WHO), TBOEP is rapidly biodegraded by organisms in environmental media (Esch et al., 2000). 3OH-TBOEP and BBOEHEP were detected solely in one of the facilities (WWTP4). Concentrations of 11.3 and 38.4 ng g⁻¹ d.w. were determined for 3OH-TBOEP and BBOEHEP (Table 3), respectively, which pointed out that BBOEHEP was the predominant transformation product during the biodegradation process, presenting concentrations 3 times higher than those for 3OH-TBOEP. CDP represents 10 % of the total OPFRs median concentration (Fig. S4), being particularly high in WWTP1 (1495 ng g⁻¹ d.w., Table 3), which treats urban and industrial sludge. It is noteworthy that the main application of CDP is its use as additive in PVC and ABS plastic, food packaging, paint, coatings and rubbers (Kubwabo et al., 2021). Regarding chlorinated OPFRs (TCIPP, TCEP and TDCIPP), TDCIPP was not quantified in the studied samples, while TCIPP and TCEP were determined with DF % of 20 %. However, chlorinated OPFRs contribute ~80 % to the ΣOPFRs concentration (Fig. S4), which is attributed to their extensive use and production (Pantelaki and Voutsas, 2019). The concentrations of ΣOPFRs in the different WWTPs ranged from 129 to 2186 ng g⁻¹ d.w. (Table 3 and Fig. S4), with the highest concentration detected in WWTP1, which is closest in proximity to industrialized areas, which is known to be the main source of exposure to these chemicals (Pang et al., 2018). The above concentrations agree with those reported in literature. Celano et al. (2014) reported TBOEP and TCIPP concentrations ranging from 810 to 909 and from 700 to 1184 ng g⁻¹ d.w. in primary sludge, respectively, and from 213 to 1786, and from 396 to 780 ng g⁻¹ d.w. in biological sludge from Spain, respectively. Marklund et al. (2005) measured concentrations of TBOEP and TCIPP ranging from 480 to 1900, and from 610 to 1900 ng g⁻¹ d.w. in digested sludge, respectively, collected from Sweden in 2003. Concentrations of TBOEP, TDCIPP and TCIPP were also reported in USA, presenting the highest concentrations of TBOEP (7290 ng g⁻¹, d.w.), TDCIPP (783 ng g⁻¹, d.w.) and TCIPP (411 ng g⁻¹, d.w.) (Kim et al., 2017). Pantelaki and Voutsas (2022) also detected TBOEP in dewatered sludge

collected from WWTPs in Thessaloniki (Greece) in concentrations ranging from 357 to 8960 ng g⁻¹ d.w., while TCIPP was found ranging from 326 to 1147 ng g⁻¹, d.w.. In Norway, OPFRs have been monitored in sewage sludge samples for more than a decade. According to Thomas et al., TBOEP was predominant in sludge samples (collected in 2010), with median concentrations of 3660, 2580, and 246 ng g⁻¹ (d.w.) for TBOEP, TCIPP and TDCIPP, respectively (Thomas et al., 2011). The lower concentrations reported herein can be attributed to the decrease in the use of chlorinated OPFRs since 2010 (Blytt and Stang, 2018).

5. Removal of OPFRs during the waste treatment

5.1. Anaerobic digestion

Anaerobic digestion is a common treatment applied in WWTPs in Norway due to the environmental and economic benefits of biogas production. During the treatment, anaerobic bacteria decompose organic matter into CH₄, CO₂, H₂O and H₂S and other combustible byproducts that can be further used for power generation (Hanum et al., 2019). WWTP1 and WWTP2 consist of a primary treatment in which the raw sludge is submitted for pasteurization at 70 °C for 30 min, followed by anaerobic digestion at 30 °C for a minimum of 15 days. Concentrations of raw and digested sludge in WWTP1 and WWTP2 are presented as the median concentrations of the two sampling campaigns (Table 4), alongside with their removal efficiencies (REs%) calculated using Eq. (1) in Section 2.7. Based on the results, anaerobic digestion can contribute towards the degradation of OPFRs, providing REs % ranging from 9 (WWTP1) to 81 % (WWTP2) for the ΣOPFRs concentrations. In addition, two of the studied compounds, TCEP and CDP, presented negative values, indicating actual formation during the treatment, potentially derived from the removal of other OPFRs. This is supported by the findings of Yu et al. (2022), where they presented the biodegradation pathway for TCrP under aerobic conditions, which was further transformed into CDP. In addition, Pang et al. (2018) presented negative removal efficiencies for TCEP under aerobic and anaerobic treatments, indicating higher concentrations after the treatment.

The WWTP3 combines anaerobic digestion with a stabilization and hygienization step (addition of lime). Sludge was hygienized through the addition of 39 % CaO (w/w). This step facilitates the mobility and/or

Table 4
Concentrations (ng g^{-1} , dry weight) of OPFRs in raw and digested sludge collected from the different facilities in Norway. Removal efficiencies (RE%) are presented (n = number of samples analysed).

Analyte	WWTP1 ng g^{-1} d.w.			WWTP2 ng g^{-1} d.w.			WWTP3 ng g^{-1} d.w.			STP1 ng g^{-1} d.w.				
	Raw Sludge	Digested n=6	RE (%)	Raw Sludge	Digested n=6	RE (%)	Pre-digestion n=3	Lime stabilized n=3	RE (%)	Raw Sludge n=1	THP n=1	THP/Digested n=1	THP RE (%)	THP/Digested RE (%)
TMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TEP	10.6	4.80	0	12.3	7.78	0	11.8	21.9	-46	35.1	34.9	n.d.	0	100
TnPP	<mLOQ	<mLOQ	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TnBP	28.2	11.4	59	22.8	8.57	62	22.5	27.0	0	18.1	13.9	11.3	0	0
TtBP	16.8	6.90	59	11.3	4.98	56	13.7	17.3	0	10.7	6.68	4.91	37	54
TCEP	n.d.	5.62	Formation**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TCIPP	n.d.	n.d.	n.d.	799	135	83	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TPhP	79.9	15.4	81	134	18.2	86	13.0	n.d.	100	24.3	32.6	n.d.	0	100
CDP	82.7	508	-84	91.9	29.9	67	22.4	n.d.	100	29.6	44.8	2.02	-34	93
BBOEHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.
TCpP	57.3	32.4	43	56.3	20.8	63	31.0	n.d.	100	33.4	28.2	n.d.	16	100
EHP	n.d.	n.d.	n.d.	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
IDPhP	53.9	26.6	51	46.4	n.d.	100	54.1	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.
TBOEP	113	42.3	63	122	45.1	63	294	194	34	70.2	107	32.3	-35	54
3OH-TBOEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TDCIPP	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ
TEHP	319	73.9	77	425	59.4	86	299	176	41	880	171	n.d.	81	100
TtBPP	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RDP	27.0	2.68	90	7.60	1.91	75	6.46	<mLOQ	100	2.81	0.88	<mLOQ	69	100
V6	1.13	n.d.	100	0.87	0.22	75	0.26	n.d.	100	1.20	0.44	n.d.	63	100
BPA-BDPP	23.0	12.8	44	17.2	8.38	51	14.6	3.83	74	14.2	14.7	1.0	0	93
Σ OPFRs	813	743	9	1747	340	81	805	440	45	1120	455	51.6	59	95

n.d., non-detected.

*Median values of the two sampling campaigns.

*** Formation is reported when the concentration in the raw sludge is n.d.

transformation of OPFRs (Su et al., 2016), providing REs% of 45 %. TBOEP and TEHP were found predominant in pre-digested sludge, presenting concentrations of 294 and 299 ng g⁻¹ d.w. The results demonstrated that the treatment in WWTP3 facilitates the transformation of 34 and 41 % of the concentration of TBOEP and TEHP, respectively. On the contrary, no RE (0 %) was obtained for TnBP and TiBP, while TEP showed negative values (-46 %), indicating its formation during the treatment (assuming no sampling heterogeneities). When CaO is added to dewatered sludge, the pH and temperature of the sludge increases, while evaporation of the water remaining in the sludge is occurring alongside the hydrolysis of the organic compounds present in the sludge (Su et al., 2016). According to Su et al. (2016), high pH (>13) favours the transformation of organophosphate triesters (three ester bonds) into diesters (two ester bonds). TEP, TPP, TBP and TEHP displayed high stability across the pH range (between 7 and 13 over a period of 35 days).

STP1 treats sludge from different WWTPs along with different types of organic waste residues, such as food and by-products derived from food production, garden wastes and others (Table 1). The sludges combined with those other wastes are submitted into a CAMBI thermal hydrolysis process (THP), where they are gradually heated up to 160 °C. The obtained product is then combined with food waste slurry (food waste residues preliminary treated) into a buffer tank at 60 °C and submitted into anaerobic digestion for 12–14 days. Obtained results suggest that the CAMBI process successfully removed the ΣOPFRs concentrations by 59 %, while the combination of CAMBI and anaerobic digestion increased the removal percentage up to 95 % (Table 4). It is noteworthy that herein grab-samples were used for the removal efficiencies calculations, and future studies should consider the use of composite samples.

5.2. Combustion assessment of OPFRs in digested sludge

Digested sludge samples from WWTP1 were combusted at 100 and 300 °C, as this treatment plant presented the highest ΣOPFRs concentrations. The ΣOPFRs concentrations decreased by 4 % at 100 °C (sludge yield: 2.60 %), reaching up to 98 % (sludge yield: 13.3 %) when the temperature increased up to 300 °C (Table S6; note: the flash point of these flame-retardant chemicals is >100 °C- as shown in Table S1).

Table 5

Concentrations (ng g⁻¹, dry weight) of OPFRs in pyrolyzed samples at different temperatures. Removal efficiencies (REs%) for the lowest temperature are presented (n = 1 sample per temperature).

Analyte	WWTP3 ng g ⁻¹ d.w.			WWTP4 ng g ⁻¹ d.w.				STP1 ng g ⁻¹ d.w.						
	Lime stabilized	Pyrolysed 500 °C	RE (%) 500 °C	Digested	Pyrolysed 600 °C	Pyrolysed 700 °C	Pyrolysed 800 °C	RE (%) 600 °C	Digested	Pyrolysed 500 °C	Pyrolysed 600 °C	Pyrolysed 750 °C	Pyrolysed 800 °C	RE (%) 500 °C
TMP	n.d.	n.d.	n.d.	n.d.	n.d.	36.5	14.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TEP	21.9	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.
TnPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TnBP	27.0	n.d.	100	30.4	2.21	<mLOQ	<mLOQ	93	11.3	n.d.	n.d.	n.d.	n.d.	100
TiBP	17.3	n.d.	100	18.0	<mLOQ	n.d.	n.d.	100	4.91	n.d.	n.d.	n.d.	n.d.	100
TCEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TCIPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TPhP	n.d.	n.d.	n.d.	<mLOQ	n.d.	<mLOQ	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CDP	n.d.	n.d.	n.d.	12.7	<mLOQ	n.d.	3.05	100	2.02	n.d.	n.d.	<mLOQ	n.d.	100
BBOEHP	n.d.	n.d.	n.d.	38.4	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TCrP	n.d.	n.d.	n.d.	22.4	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EHDP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
IDPhP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TBOEP	194	n.d.	100	189	n.d.	n.d.	0.96	100	32.3	n.d.	4.81	n.d.	n.d.	100
3OH-TBOEP	n.d.	n.d.	n.d.	11.3	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TDCIPP	<mLOQ	n.d.	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.
TEHP	176	n.d.	100	166	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TTBPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RDP	<mLOQ	n.d.	<mLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	<mLOQ	n.d.	<mLOQ	n.d.	n.d.	<mLOQ
V6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BPA-BDPP	3.83	n.d.	100	0.81	n.d.	n.d.	n.d.	100	1.01	n.d.	n.d.	n.d.	n.d.	100
ΣOPFRs	440	0.00	100	489	2.21	36.5	18.1	99.5	51.6	0.00	4.81	0.00	0.00	100

n.d., non-detected.

5.3. Pyrolysis of digested sludge

The samples were subjected to pyrolysis at different temperatures (500, 600, 700, 750 and 800 °C), with a constant residence time of 20 min for the samples from WWTP3 and STP1, and 40 min for the samples from WWTP4. It must be highlighted that the pyrolysis experiments were carried out on digested sludge from the 3 facilities that maintained distinctly different sludge treatments (WWTP3, WWTP4, and STP1; Table 1). The ΣOPFRs concentrations in the digested sludge and biochar are presented in Table 5. According to the results, pyrolysis was deemed enough to reduce the ΣOPFRs concentrations <10 % (Fig. 4).

The REs% demonstrated that pyrolysis was able to reduce >99 % of the ΣOPFRs at 500 °C. In WWTP3 and STP1, none of the studied OPFRs were detected in the biochar, providing a complete removal percentage at the lowest temperature (500 °C). As mentioned before, the treatment applied in STP1, CAMBI, which is a mild thermal treatment, combined with anaerobic digestion was already able to remove up to 95 % of the ΣOPFRs (Table 4), which denotes that the ΣOPFRs concentrations were already low. As for WWTP4, REs >99 % were obtained at 600 °C. However, it is noteworthy that in some cases at higher temperatures, some of the OPFRs were present at trace concentrations that were difficult to account for and were attributed to impurities or sample heterogeneities (e.g., TMP in WWTP4 at 700 °C and 800 °C, Fig. S5, Table 5; and TBOEP in STP1 at 600 °C, Table 5). In literature, numerous studies documented the same trend for other chemicals such as pharmaceuticals and personal care products (PPCPs), polychlorinated biphenyls (PCBs) and poly- and perfluoroalkyl substances (PFAS), whose REs (%) shifted close to 100 % at 500 °C (Alinezhad et al., 2022; Buss, 2021; Buss et al., 2020; Moško et al., 2021; Ross et al., 2016).

To summarize, based on the obtained results, pyrolysis of sewage sludge at 500 °C could be considered as an alternative for the treatment of sludge, since it successfully reduces the concentrations of ΣOPFRs by up to 99 %. However, future research on the mass balance and the environmental risks of emission into syngas or condensate are required.

6. Conclusions

The MSPD constituted a simple, rapid, and highly versatile sample preparation technique for the selective extraction of OPFRs from complex solid

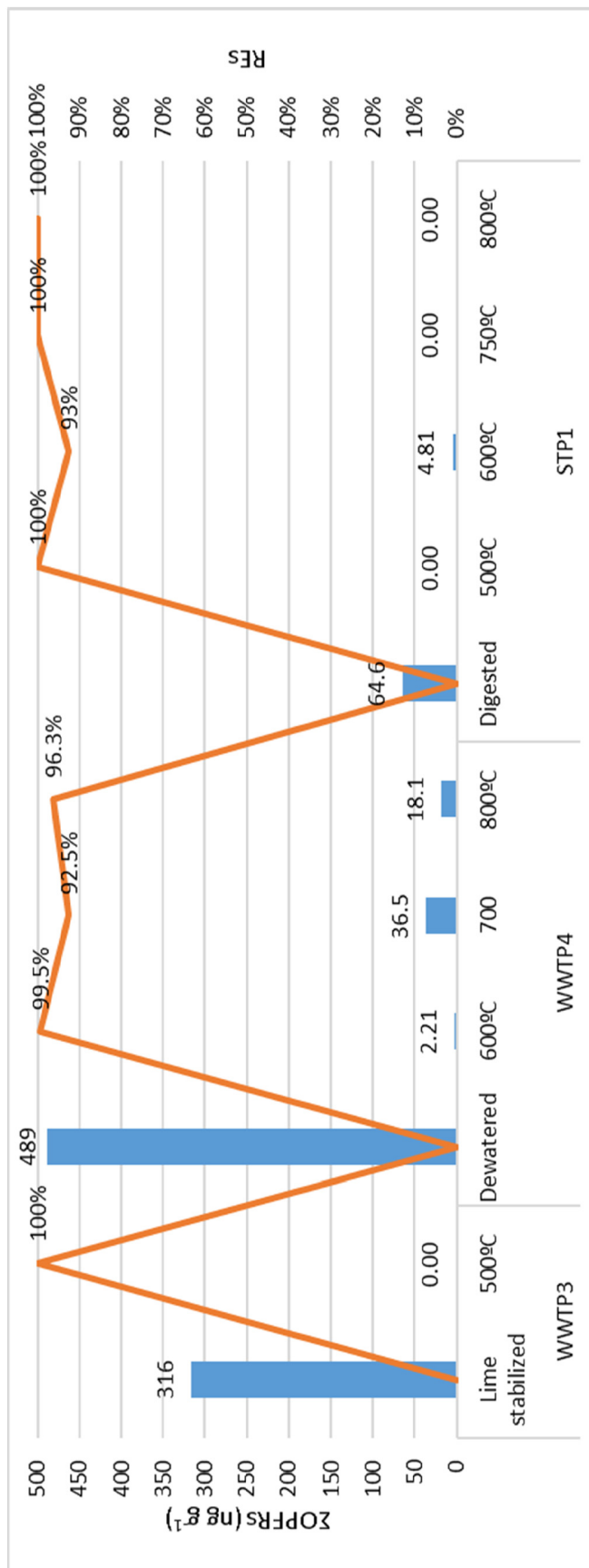


Fig. 4. OPFR concentrations of digested sludge and the obtained biochars at different temperatures (n = 1 sample per temperature).

environmental matrices, combining extraction and clean-up in a single step and overcoming the use of high solvent volume, while producing sample extracts ready for analysis in <20 min. The analysis of actual samples demonstrated the presence of OPFRs in digested sludge samples collected from these WWTPs in Norway, where different sludge treatments were applied. High concentrations of TBOEP and TEHP were determined, displaying median concentrations of 133 (DF 100 %) and 170 ng g⁻¹ d.w. (DF 80 %), respectively (Table 1). High concentrations of TCIPP were also measured in WWTP2, reaching up to 396 ng g⁻¹ d.w.. The effect of different treatments on WWTPs, as well as the alternative thermal treatments such as combustion and pyrolysis were studied for the removal of OPFRs in the sludge. It was concluded that anaerobic digestion is not an effective treatment for the removal of these chemicals, with the exception of treatment with the CAMBI process. Nonetheless, combustion and pyrolysis were found promising towards the removal of OPFRs, regardless of the sludge treatment conditions. Pyrolysis at 500 °C was considered the best approach since a removal of >99 % of ΣOPFRs concentration was achieved, while offering specific environmental advantages over combustion, such as carbon and nutrients recycling in applications as fuel for metal smelting or soil fertilizer (Barry et al., 2019).

Overall, the data presented herein points out to the necessity of assessing systematically the presence not only of OPFRs, but also of other contaminants of emerging concern, to fully comprehend their mass balance in the WWTPs, and to evaluate the potential risks associated with the re-introduction of those into the terrestrial environment during the application of sludge as agricultural fertilizer. The methods developed herein will be incorporated in investigations towards sustainably managing OPFRs in sewage sludge and complex matrices during management and recycling processes and optimization.

CRedit authorship contribution statement

Gabriela Castro: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing-original draft. **Erlend Sørmo:** Conceptualization, Methodology, Resources, Writing – reviewing & editing. **Guanhua Yu:** Formal analysis, Investigation, Visualization. **Shannen T. L. Sait:** Methodology, Investigation, Resources, Software, Writing - Review & Editing. **Susana V. Gonzalez:** Methodology, Resources, Software, Writing - Review & Editing. **Hans Peter H. Arp:** Conceptualization, Methodology, Formal analysis, Project administration, Supervision, Validation, Funding acquisition, Writing – reviewing & editing. **Alexandros G. Asimakopoulos:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - review & editing.

Data availability

Data will be made available on request.

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.

Acknowledgements

This study was financially supported by the Norwegian Research Council through the SLUDGEFFECT project (project number 302371) and VOW project (project number 299070). The authors also thank the waste facilities for the help during the sampling campaigns and the pyrolysis experiments. Analysis was carried out in the EnviroChemistry Lab at NTNU. The graphical abstract was created in Biorender.com.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.161856>.

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