Research

Structural diversity of organic contaminants in sewage sludge: a comparison of sewage fingerprints from Germany and China

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Abstract

Sewage sludge is formed during wastewater treatment and in recent years, the amount of sewage sludge increased rapidly all over the world. This sewage sludge is attractive for usage in agriculture as an inexpensive nitrogen and phosphorus fertilizer. However, there is only very limited knowledge about the spectrum of organic pollutants that might occur in sewage sludge and is probably posing a threat to the environment. We therefore conducted GC–MS based non-target screening analyses in order to identify a wide spectrum of organic contaminants in sludge samples from several wastewater treatment plants and to figure out corresponding finger-prints of pollution. The plants are located in Germany and China and have various capacities ranging from 35,000 to 1.1 million population equivalents. The special focus was to reveal information on the structural variety of individual organic compounds in sludge samples from the two countries. Several emerging pollutants including some fragrances, pharmaceutical educts, vitaminoids, technical additives were identified accompanied by compounds of biogenic origin. Some of these compounds have rarely been reported as constituents of sewage sludge to date and, consequently, are relevant candidates for more specific assessments including the ecotoxicological long-term effects. Based on the results of this study, it seems mandatory to establish non-target screening analyses on a regularly base as a tool for a comprehensive identification of the variety of anthropogenic organic constituents. Following, such contaminant spectrum can act as basis for further environmental risk assessments as well as to provide individual fingerprints for evaluation of impacts on ecosystems.

Keywords Sewage sludge · Structural variety or organic pollutants · GC/MS · Non-target screening · Pollutant pattern · Anthropogenic organic contaminants

1 Introduction

Sewage sludge is a major waste product of wastewater treatment of both industrial and municipal wastewater. Municipal wastewater treatment plants (WWTP) receive effluents from numerous sources such as households, industrial complexes, hospitals, surface runoff [1]. The amount of sewage sludge has increased in the past rapidly all over the world [2]. Noteworthy, sewage sludge is widely used as inexpensive nitrogen and phosphorus fertilizer in agriculture [3] and soil conditioning material. Sludge may contain a wide spectrum of organic pollutants (e.g. pharmaceuticals,

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[4, 5]) representing fingerprints of the corresponding sewage water contamination. However, till the 1980s, there was little information available regarding the structural diversity of anthropogenic organic contaminants collected and eliminated in WWTPs [6]. In recent years, the occurrence of organic contaminants in wastewaters and sewage sludge of industrialized countries, including Europe, North America and Australia, have been widely investigated and well documented [2, 7–10].

Numerous organic pollutants accumulate in sewage sludge because of their lipophilicity and the incomplete degradation during the wastewater treatment [11]. The concentration levels of organic contaminants in sewage sludge can vary from $\mu\text{g kg}^{-1}$ to mg kg^{-1} levels [7, 12, 13]. Information about the variety and pattern of organic contaminants occurring in sewage sludge samples is the first crucial step (see also [14, 15]), before the persistence and the ecotoxicological impacts of the identified compounds can be assessed in further studies.

As an example, recent studies reported the occurrence of traces of pharmaceuticals, including antibiotics, even in treated sewage sludge [2, 16]. As the result of inappropriate usage, overdose, uncontrolled disposal and lack of regulations for numerous pharmaceuticals, the risk of uncontrolled exposure is probably higher in developing economies. China for example is an emerging country that has both a high production and an intensive consumption of pharmaceuticals—approximately 1.9 million tons in 2009 [17]. However, only a few studies have been reported about the emissions of pharmaceutical from Chinese WWTPs [16, 18–23]. Most of the studies focused exclusively on the aqueous phase and, consequently, contamination of sewage sludge were rarely examined, probably the effect of the challenging efforts required for the analysis of the complex matrix [5, 7].

Noteworthy, all studies related to organic pollution in sewage sludge focused solely on selected treatment plants in individual countries, many of them considering only preselected contaminants. To our best knowledge, a more systematic comparison of emission pattern or fingerprints as the result of different national characteristics of consumption and application of technical products has not been reported so far.

Therefore, non-target screening analyses of lipophilic organic pollutants in sewage sludge samples from Germany and China were conducted for this study. The special focus was a comparison of the structural diversity of sewage sludge constituents in the samples from the two countries and the characterization of corresponding fingerprints. Moreover, selected contaminants were quantified to provide a more detailed view on the concentration levels of organic constituents in sewage sludge samples. This will provide baseline data for future assessments of the environmental impacts of sewage sludge usage e.g. in agriculture. Further on, this study will represent a preliminary approach on pattern comparison of sewage derived pollutants.

2 Experimental

2.1 Chemicals and reagents, quality assurance

In order to prevent sample contamination by artefacts, only glass, metal and teflon materials were used. All materials were cleaned ultrasonically and were rinsed with pure acetone and *n*-hexane prior to usage. Organic solvents and chemicals used for sample processing were purchased from Merck, Germany. The solvents were distilled over a 0.5 m packed column (reflux ratio $\sim 1:25$) and their purity was tested by gas-chromatographic (GC) analyses. For quality assurance, procedural blank analyses in the same way as the analyses of the sewage sludge samples (as described in Sect. 2.3) were performed to identify and quantify background concentrations. The blank analyses revealed no contamination by the reported compounds. Recovery rates of selected substance classes by accelerated solvent extraction of particulate matter were reported to range between 85 and 110%. The corresponding relative standard deviations range between 0.5 and 5% [24, 25].

2.2 Samples

Sewage sludge samples were taken in urban wastewater treatment plants (WWTP) of varying capacities in Germany and China (Table 1). All WWTPs are operating with mechanical and biological treatment sections, at which sewage samples for this study were taken from the biological treatment facilities. German sewage sludge samples were taken from two WWTP in Bavaria (WWTP A and B) and two WWTP in North-Rhine-Westphalia (NRW) (WWTP C and D). The Chinese sewage sludge samples were taken from two WWTP (WWTP E and F) located in Haikou, the capital of Hainan Province. The

samples from Germany (~ 500 g) were obtained by a ladle and placed into several 250 mL glass vessels with Teflon-lined screw caps. All samples were stored in the dark at a temperature of 4 °C until sample preparation. Sewage sludge samples from China (~ 100 g) were obtained by a ladle and placed into aluminum cans and then dried at 70 °C for 48 h prior to shipping to Germany under cooled conditions.

2.3 Extraction

Prior to extraction, the German samples were dried at 70 °C for 48 h. Accelerated solvent extraction (ASE) was applied to ~ 10 g of dry sample material. The sample material was extracted sequentially with 30 mL acetone, 30 mL acetone/*n*-hexane 1:1 (v/v) and 30 mL *n*-hexane. During each extraction step, the cell was held at a temperature of 100 °C for five minutes for a static extraction under a pressure of 10.35 MPa. After each extraction step, the extracts were collected and combined. The raw sample extract was concentrated to ~ 5 mL by rotary evaporation at ambient temperature and then dried over anhydrous sodium sulfate (Na₂SO₄). After further concentration to ~ 0.5 mL, activated copper powder was added and the sample was treated ultrasonically for 15 min in order to remove elemental sulfur. The sample extracts were fractionated into six fractions using a micro glass column packed with ~ 2 g of anhydrous silica gel as stationary phase which was activated with *n*-pentane previously. As eluents, mixtures of *n*-pentane, dichloromethane and methanol were used, according to [26]. Fractions one to five were spiked with 50 µL surrogate standard solution containing d₁₀-benzophenone (19.8 ng µL⁻¹). Acidic compounds in fraction six were derivatised with a methanolic diazomethane solution and spiked with 200 µL surrogate standard solution. Fractions one to five were concentrated to 50 µL and the 6th fractions were concentrated to 200 µL at ambient temperature. The general preparation scheme is displayed in Fig. 1.

2.4 GC/MS analyses

GC/MS analyses were performed on a Trace MS mass spectrometer (Thermo Fisher Scientific, USA) linked to a MegaSeries 5160 gas chromatograph (Carlo Erba HRGC 5160 Mega Series, Italy) equipped with a ZB-Multi Residue-2 capillary column (30 m × 0.25 mm I.D. × 0.25 µm film) (Phenomenex, Germany). Chromatographic conditions were as follows: 1 µL sample was injected at 270 °C (injector temperature) at a splitless mode and the helium carrier flow rate was 1.03 mL min⁻¹. The oven temperature started at 60 °C (3 min) and was heated up with the heating rate 5 °C min⁻¹ to 300 °C (20 min). The GC/MS transferline was kept on a temperature of 270 °C. The mass spectrometer was operated in full-scan electron impact ionization mode (EI⁺, 70 eV) with a source temperature of 200 °C, scanning from 35 to 700 amu at a rate of 2.5 scans s⁻¹.

Identification of contaminants is based at first by comparison of gas chromatographic and mass spectral properties (using the software Excalibur[®], MassLib[®] and) with mass spectral data bases (Wiley 7th Ed, NIST14) and published information. In particular, retention order of structural isomers (e.g. PAHs with the same molecular weight) as well as retention pattern of technical mixtures such as DIPNs or LABs have been checked with published gas chromatographic data. The screening was performed as a thorough peak-to-peak investigation independent of peak abundances.

For an unambiguous identification the substances were verified by comparison of gas chromatographic and mass spectral properties with authentic reference material (according to [27]). If reference material was not available, the identification was verified by supplementary information such as in-depth evaluation of mass spectral fragmentation, reasonable evaluation of occurrence due to its technical applications and comparison with structurally highly similar compounds (e.g. homologues or substitution isomers of halogenated substances).

Table 1 Characteristics of the municipal wastewater treatment plants (WWTP) of varying capacities in Germany (WWTP A–D) and China (WWTP E–F) that were sampled for this study

WWTP	Capacity [PE]	Annual flow [m ³ y ⁻¹]	Type	Receiving water average flow [m ³ s ⁻¹]
WWTP A	1,000,000	180,000,000	Municipal and industrial	175
WWTP B	35,000	4,000,000	Municipal	2.0
WWTP C	500,000	25,000,000	Municipal	1.4
WWTP D	300,000	20,000,000	Municipal and industrial	22.2
WWTP E	1,130,000	180,500,000	Municipal	n.a
WWTP F	1,130,000	180,500,000	Municipal	n.a

n.a. data were not available, PE population equivalents

Fig. 1 Analytical procedure used for GC/MS-based non-target-screening analyses of sewage sludge samples

Quantification was based on integration of characteristic ion chromatograms (Table S1) and an external four-point-calibration using reference substances. If reference material was commercially not available, response factors of structurally similar substances were used for quantification (Table S1). The surrogate standard was used for the correction of sample and injection volume inaccuracies. All compounds identified and quantified were checked for possible laboratory contamination by blanks.

3 Results and discussion

The subsequent discussion will focus on the structurally most interesting and—with respect to potential environmental impacts—the most important anthropogenic contaminants detected in the sewage sludge samples from Germany and China. Characteristics of the various WWTP are given in Table 1. However, the focus of this study is not to

document the individual state of pollution of each WWTP, but to display the variety of organic constituents depending on location and characteristics of the different WWTP for characterizing fingerprints. Generally, two groups of compounds have been differentiated: (1) common organic pollutants that were frequently described as constituents of wastewaters and sewage sludge in previous studies, and (2) emerging organic pollutants which have to date not been reported as contaminants in this matrix.

The applied GC/MS non-target screening analyses allowed for the identification of a wide range of organic compounds. In total, 74 compounds were identified, which are listed in Table 2 and Table S3 of the supplementary material. This reflects the high structural diversity of organic contaminants in sewage sludge.

Among the identified compounds, 42 compounds with an elaborated specificity in terms of application or marker properties were selected for fingerprinting and for quantification as listed in Table 2. They were classified into groups according to their application or origin. The other identified organic compounds were grouped in chemical substance classes and listed in Table S3. Finally, information about water and ash content of the sewage sludge samples are shown in Table S2.

3.1 Common organic pollutants

Several common pollutants that were frequently described as constituents of wastewaters and sewage sludge in previous studies were identified (examples see Fig. 2). The polycyclic musk fragrance HHCB was detected in three sewage sludge samples with concentrations ranging from 5 to 28 mg kg⁻¹ dw (No. 1, Table 2). Due to its persistence and quantitatively major use as fragrance in household products, HHCB occurs ubiquitously in surface waters which receive municipal sewage discharges and HHCB was defined as typical wastewater and sewage sludge constituent (e.g. [27–31]. The HHCB concentrations reported here are more than eight times lower than the values from [31], but comparable to those of [32]. Our results mirror the high usage rate of this synthetic fragrance in Germany and China to date. At present, HHCB has not been the subject of specific regulatory activity in the European Union [33].

The provitamin vitamin E acetate (No. 8) was detected in three of the six sewage sludge samples, with a maximum concentration of 320 mg kg⁻¹ (Table 2). The compound has been suggested as a marker for the occurrence of municipal wastes into the environment [34]. It is applied in a large variety of consumer products and can be distinguished from biogenic vitamin E, which occurs only as the free alcohol.

Further well-known constituents of the sewage sludge samples were linear alkylbenzenes (LABs). C₁₀–C₁₄ LABs were detected in all sludge samples from Germany and China (Nos. 10–14, Table 2). LABs are residues from the synthetic production of linear alkylbenzene sulfonates (LAS) [34]. LABs are in contrast to the sulfonated derivatives poorly degradable and are therefore suitable anthropogenic marker for the entry of urban wastewaters into aquatic systems. Total LABs concentrations as determined in this study (5–55 mg kg⁻¹, Table 2) are comparable to those of other studies conducted with sewage sludge [35, 36]. The I/E ratio (ratio of internal to external isomers) is indicative for the extent of the LABs degradation [37]. The higher the I/E ratio, the higher the biodegradation, due to the higher degradation rate of the external isomers. In the investigated sludge samples, the I/E ratios ranged from 0.7 to 2.5 (Table 3) suggesting only a low to moderate biodegradation of LABs in the studied treatment plants. Also these values are comparable to other studies dealing with sewage sludge or suspended solids in wastewaters [36, 38].

Organophosphorus compounds are also frequently reported as sewage sludge constituents (e.g. [41–43]). Since they are used dominantly as flame retardants or plasticizers in a large number of consumer products (e.g. [44]) but also as additives in lubricating oils and hydraulic fluids with technical application [42]. Noteworthy, the chlorinated organophosphorus compounds, for example TCPP (tris (2-chloro-*iso*-propyl) phosphate), are mainly used as flame retardants, the compounds without chlorine atoms such as triphenyl phosphate (TPP) are mainly used as plasticizers. The predicted partition behavior of TCPP in WWTP has been estimated to be 97.9% to water, 2.1% adsorbed to sewage sludge, 0% to air with 0% degradation [45] (ECHA 2008b). The concentrations of all three organophosphorous compounds determined in our study (Nos. 17–19, Table 2) are higher than those previously reported in sewage sludge samples from European sewage treatment plants (as compiled in [15, 46]).

Polycyclic aromatic compounds (PACs) were identified in all sludge samples (Nos. 20–36, Table 2). It was reported that several PACs have toxic, mutagenic and/or carcinogenic properties. This substance class has a strong tendency to bioaccumulate and poses a threat to ecosystems and to human health [47]. Due to the multiple sources of PACs, they may enter WWTP along different pathways, such as polluted rainwater, street runoff, municipal sewage and industrial effluents. PACs accumulate because of their lipophilic character primarily in sewage sludge. The most abundant compounds in the

Table 2 Quantified compounds in sewage sludge samples from six municipal wastewater treatment plants (WWTP) located in Germany (WWTP A–D) and China (WWTP E–F). All concentrations are given in mg kg⁻¹ dry weight

No.	Compound	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F
(Synthetic) fragrances							
1	Galaxolid, HHCB		28	10			5
2	Methyl-2-phenylacetate ^a	7				46	0.4
3	4-tert-Butylcyclohexanol ^b	2					
4	Phenylpropanoic acid ^{a,f}	20			270		
Pharmaceutical educts							
5	4-Aminoacetophenone ^c	0.3					
6	2,3-Dimethylnaphthalene-1,4-dione ^d			0.1			
Vitaminoids and metabolites							
7	Menadione		1				
8	α-Tocopherol acetate, vitamin E acetate		13		320		0.4
9	Phitiocol		46	36	204	586	
Surfactant residues and technical additives							
10	C ₁₀ -Linear alkylbenzenes (LABs)	8	1	2	1		5
11	C ₁₁ -LABs	15	7	4	6	1	9
12	C ₁₂ -LABs	15	5	4	7	2	8
13	C ₁₃ -LABs	16	5	4	5	2	5
14	C ₁₄ -LABs	1	1				
	LABs total concentration	55	19	13	20	5	27
15	Di-iso-propylnaphthalenes, DIPN	2	7	1	18		
16	Isocyanatocyclohexane ^e			7			
Plasticizers and flame retardants							
17	Tris(2-chloro-iso-propyl) phosphate, TCP		70		19		
18	Triphenyl phosphate, TPP		14				
19	Triethyl phosphate, TEP		269		39		
Polycyclic aromatic compounds (PACs)							
20	Naphthalene	0.04	0.02				
21	Acenaphthene	0.04	0.02	0.01			
22	Fluorene		0.06	0.01	0.06		
23	Phenanthrene	0.6	0.4	0.1	0.3	0.07	0.5
24	Anthracene	0.1	0.05	0.02	0.04		
25	Fluoranthene	0.5	0.4	0.1	0.3	0.1	0.6
26	Pyrene	0.5	0.4	0.1	0.2	0.1	0.6
27	Benzo[a]anthracene	0.05		0.02	0.1	0.07	0.3
28	Chrysene	0.06		0.02	0.2	0.2	0.6
29	Benzo[b]fluoranthene				0.3	0.1	0.03

Table 2 (continued)

No.	Compound	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F
30	Benzo[k]fluoranthene				0.02		
31	Benzo[a]pyrene				0.1	0.6	0.05
32	Indeno[1,2,3-cd]pyrene				0.1		
33	Dibenzo[a, h]anthracene						
34	Benzo[g, h, i]perylene						
35	C ₁ -Anthracenes /phenanthrenes				0.2		1.0
36	C ₁ -Fluoranthenes/pyrenes				0.1	0.1	0.9
Biogenic origin							
37	Dehydroabietin		19				9
38	Tetrahydroretene		12				
Fecal steroids							
39	Coprostanol	3100	650	1100	2000	550	650
40	Cholesterol	7200			370	710	500
41	Coprostanone		870	270			
42	Cholestanol		36	7	810	120	290

The chemical names of the compounds are given in Table S1 of the supplementary material

^a-eRF value was determined with structurally related compound

^f was identified in its methylated form due to the derivatization

Fig. 2 Molecular structures of selected quantified compounds. Full chemical names are given in Table 2. References for log K_{OW} and BCF values: **a**: [51], **b**: [52]

Common organic pollutants

HHCb, Galaxolid

α -Tocopherolacetate

TEP

TCP

TCP

Emerging organic pollutants

Methyl-2-phenylacetate

4-*tert*-Butylcyclohexanol
log K_{OW} 3.1; BCF 47.8

3-Phenylpropionic acid

4-Aminoacetophenone
log K_{OW} 0.8; BCF 3.0

Phtiolol

Menadione
log K_{OW} 2.2; BCF 1.4

2,3-Dimethylnaphthalene-1,4-dione

Isocyanatocyclohexane
log K_{OW} 3.1; BCF 45

Dehydroabietin

Tetrahydroretene
log K_{OW} 7.0; BCF 4.8

sewage sludge samples from Germany and China were low-molecular weight PACs (Table 2). Overall, the concentration levels were lower than those reported by Stevens et al. [33] from the UK. Total PACs concentrations in our sample set were far below 6 mg kg⁻¹ dry weight, the limit for sludge use in agriculture in the European Union [48]. Indicative ratios according to [39] were determined in order to assess the dominant emission sources of the detected PACs (Table 3). The calculated ratios suggest a pyrogenic formation or mixed pyrogenic and petrogenic sources of the PACs.

Several steroids were detected in the majority of sewage sludge samples from Germany and China (Nos. 39–42, Table 2; Table S3). Only the steroids known as markers for fecal pollution (Takada and Eganhouse 1998) were quantified for this study (Nos. 39–42, Table 2). Coprostanol was reported to make up a proportion of 24–89% of the total steroid content in human feces (e.g. [37]). This steroid occurred in concentrations ranging from 550 to 3100 mg kg⁻¹ dw in the sewage sludge samples (Table 2). This is a similar concentration range as determined in digested sewage sludge samples from four French municipal sewage treatment plants [49]. Fecal steroid ratios were calculated and compared to the human fecal contamination thresholds as reviewed for environmental and sludge samples by [40] (see Table 3). All determined ratios were in accordance with the thresholds so far considered as indicative for fecal contamination. These high coprostanol/cholestanol ratios are in line with the results of [50].

Table 3 Calculated compound ratios in sewage sludge samples from WWTP A–F for the characterization of the compound degradation rate (LABs, according to [37]) or the characterization of the compound sources (PACs and fecal steroids, according to [39, 40], respectively)

	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F	
Linear alkylbenzenes (LABs)							
I/E ratio C ₁₂ homologues	0.7	1.3	1.2	1.0	2.5	1.1	
Polycyclic aromatic compounds (PACs)							Pyrogenic or petrogenic source
(1) An/178	0.1	0.1	0.2	0.1	n.a	n.a	> 0.1 Pyrogenic
(2) Fl/(Fl + Py)	0.5	0.5	0.5	0.6	0.5	0.5	> 0.5 Pyrogenic
(3) BaA/228	0.5	n.a	0.5	0.3	0.3	0.2	> 0.35 Pyrogenic 0.2–0.35 Mixed sources
Fecal steroids							Fecal contamination threshold
Coprostanol/(cholestanol + cholesterol)	0.4	n.a	n.a	1.7	0.7	0.8	> 0.2
Coprostanol/cholestanol	n.a	18	157	2.5	4.6	2.2	> 0.5
Coprostanol/(coprostanol + cholestanol)	n.a	0.9	1.0	0.7	0.8	0.7	> 0.7

n.a. not applicable

(1) Anthracene/(anthracene + phenanthrene)

(2) Fluoranthene/(fluoranthene + pyrene)

(3) Benzo[a]anthracene/(benzo[a]anthracene + chrysene)

3.2 Emerging organic pollutants

In addition to well-known sewage sludge constituents, also rarely reported organic contaminants were identified exhibiting higher specificity and potential for fingerprinting (examples see Fig. 2). The identified emerging pollutants belonged to different application groups, namely (synthetic) fragrances, pharmaceutical educts, vitaminoids and their metabolites, surfactant residues and technical additives and compounds of biogenic origin. For a better preliminary estimation of their environmental behavior and risk potential, the log K_{OW} values and the bioaccumulation factor (BCF) for selected compounds are given in Fig. 2.

Three compounds were detected from the group of (synthetic) fragrances (Table 2). Methyl-2-phenylacetate (No. 2) has an intense odor of honey or jasmine and is used as fragrance, mal-odor reducing agent and as flavor [53, 54]. The compound occurred in three WWTP with a maximum concentration of 46 mg kg⁻¹. 4-*tert*-Butylcyclohexanol (No. 3) is in use as fragrance in soaps, detergents, perfumes, creams and lotions [55] and was previously reported as environmental contaminant in river water [56]. A relatively low total degradation rate during wastewater treatment for this compound was reported (7.6%) splitted into biodegradation of 0.13% and sludge adsorption of 6.36% [51]. In this study, the fragrance was detected only in one WWTP with a concentration of 2 mg kg⁻¹. Phenylpropanoic acid (No. 4) has a sweet odor and occurs naturally e.g. in fruits, cinnamon and wine. It is used as fragrance and as food flavor (Burdock [55]) and was detected in two WWTP with a comparably high maximum concentration of 270 mg kg⁻¹.

Aminoacetophenone (No. 5) is an important educt in the production of pharmaceuticals such as aminophenylchloroquinolines [57]. It is also used for the synthesis of further industrial products such as agrochemicals (e.g. [58, 59]) but it has been described as a volatile marker in the breath of humans infected with *Pseudomonas aeruginosa* [59]. Its log K_{OW} and BCF values indicate that aminoacetophenone is not expected to adsorb to suspended solids and sediment. Also, the potential for bioconcentration in aquatic organisms is low [52]. Aminoacetophenone was detected in other studies in the effluents of a chemical manufacturing plant [60] and in raw sewage samples of a WWTP [61]. In this study, aminoacetophenone was identified at a low concentration of 0.3 mg kg⁻¹ in one sewage sludge sample from a WWTP that receives industrial and municipal wastewaters (Table 2).

Naphthalene-1,4-dione derivatives are used for the synthesis of pharmaceuticals, e.g. of compounds with antimycobacterial activities which are used for the treatment of tuberculosis [62]. Dimethylnaphthalenedione (No. 6) was detected in one sewage sludge sample from a German WWTP. However, any detailed information on the occurrence in sewage or technical application of this dimethylated derivative is missing.

In the group of vitaminoids and their metabolites two emerging contaminants, have been identified. One compound is menadione (No. 7). The menadione production and its use in pharmaceuticals and animal feed additives

may result in its release to the environment through WWTP. Its former production and use in fungicides may have resulted in its direct release to the environment [63, 64]. The partition characteristics, especially the $\log K_{OW}$ value [65, 66], indicate that menadione is not expected to adsorb to suspended solids and sediment. The potential for bio-concentration in aquatic organisms is low, too. Menadione was identified in one Bavarian sewage sludge sample in a WWTP with a capacity of 35,000 PE with a concentration of 1 mg kg^{-1} (Table 2). Pthiocol has a vitamin K-like physiological effect [67] and an antibiotic activity [68]. To the best of our knowledge, this physiological active compound has to date not been reported to occur in wastewaters, sewage sludge or in the environment. Noteworthy are the very high concentration levels of pthiocol in the sludge samples from China and Germany that ranged between 36 and 586 mg kg^{-1} (Table 2).

The technical additives di-*iso*-propylnaphthalenes (DIPN, No. 15) are used as non-chlorinated substitutes for polychlorinated biphenyls (PCBs) and they are employed as colour sensitizers for manufacturing of thermal papers [69]. The eight different DIPN isomers were characterized in earlier studies [70]. DIPN were identified in process waters of paper manufacturing factories [69] and in water and fish sampled at the outfall of paper-recycling facilities [71, 72]. They occurred in all sewage sludge samples from Germany (WWTP A–D) with a maximum concentration of 18 mg kg^{-1} , but interestingly not in the samples from China. WWTP B and C receive only municipal sewage (Table 1). The input pathway of DIPN into municipal sewage remains unclear at this moment, because to date only the industrial application of DIPN was reported. One possibility could be the usage of DIPN-containing paper products in households, e.g. toilet paper made from recycled paper.

A further compound of this group is isocyanatocyclohexane (No. 16). The compound is a relevant contaminant in urban and industrial air, because it is used in high amounts in automobile industry and building insulation, as well as in the manufacture of foams, rubber, paints and varnishes [73]. Isocyanatocyclohexane was detected in one German WWTP at a concentration of 7 mg kg^{-1} .

In the group of substances with biogenic origin, dehydroabietin and tetrahydroretene were detected, which are known as biomarkers for the input of organic materials derived from wood (e.g. [74]). Both compounds typically occur in the wastewaters of paper mills [75]. Dehydroabietin and tetrahydroretene were detected in WWTP which receive municipal inputs (Tables 1, 2).

3.3 Differences of the WWTP in China and Germany

In the following, the appearance and quantitative data of individual substances as fingerprints are discussed with respect to the different characteristics of the WWTP. Overall, the quantified substances showed no systematic pattern (Table 2).

Substances of the application group of plasticizers and flame retardants as well as DIPN could not be detected in Chinese sewage sludge samples. Substances from the groups of surfactants (LABs) as well as polycyclic aromatic hydrocarbons and the fecal steroid coprostanol were identified in all WWTP from Germany and China, with similar concentration levels. WWTP A and D have contributions from industrial wastewaters (see Table 1). Only the fragrance phenylpropanoic acid (No. 4) was solely found in the sludge from these two WWTP. Further compounds with a potentially industrial origin were not found.

WWTP A, WWTP E and WWTP F have slightly different annual water flows (Table 1) in relation to the capacities and are up to 25% higher in comparison to WWTP B, C and D. This might lead to higher pollutant concentrations in sewage sludge from WWTP A, E and F, but the compounds appeared in relevant concentrations in all WWTP (e.g. methyl 2-phenylacetate or vitamin E acetate). This widespread appearance do not support the assumption. One higher concentration level for the substance pthiocol has been identified in WWTP E, but systematic higher concentration levels in WWTP A, E and F were not evident. WWTP B is the treatment plant with the fewest capacity and annual flow, but most loaded WWTP with partially highest concentrations (for example for triethylphosphate). Hence, for all WWTPs very individual patterns or fingerprints were visible.

4 Conclusions

Non-target screening analyses are an important tool for the evaluation of the environmental pollution that is caused often by multiple anthropogenic organic contaminants. In this study, screening analyses of sewage sludge samples from wastewater treatment plants of varying capacities and characteristics in Germany and China have been conducted to identify a broad range of anthropogenic organic pollutants. Selected compounds with a specific application or relevance as marker compound were quantified. Several emerging pollutants including some fragrances, pharmaceutical educts, vitaminoids, technical additives and compounds of biogenic origin have rarely been reported as environmental pollutants in sewage sludge. They are relevant candidates for more specific assessments including long-term ecotoxicological effects. The spectrum of contaminants was not related to classic characteristics of the wastewater treatment plants like capacity or water flow. Hence, unique patterns have been identified as fingerprints. However, the basic reason for the pattern variations remains unclear. Beside different spectra of technical application and commercial usage of products, also diverse treatment technology may be responsible for varying fingerprints.

Based on the results of this study, non-target screening analyses should be established as tool for the identification of anthropogenic organic constituents and further investigation of emerging pollutants in the challenging matrix sewage sludge.

Authors' contributions LC, YH: laboratory analytical work, data processing and evaluation. A-KW, LD: data processing and evaluation, preparation of manuscript. JS: data processing and evaluation, supervision, preparation of manuscript.

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Data availability All data generated or analysed during this study are included in this published article [and its supplementary information files].

Declarations

Competing interests The authors declare no competing interests.

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