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Is the long-term application of sewage sludge turning soil into a sink for organic pollutants?: evidence from field studies in the Czech Republic

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Abstract

Purpose Long-term microscale field experiments established at four sites in the Czech Republic (since 1996) were used for an assessment of the severity of the wide-scale contamination of treated soils by persistent organic pollutants (POPs) and pharmaceuticals and personal care products (PPCPs) as a result of the long-term regular pollutant load via sewage sludge and farmyard manure applications and for an estimation of the potential environmental risk caused by long-term pollutant inputs to agricultural soils.

Material and methods The experimental plots were treated as follows: (i) NPK mineral fertilization (NPK); (ii) sewage sludge (SS1); (iii) sewage sludge applied at three times the rate compared to SS1 (SS2); (iv) farmyard manure (FYM); and (v) untreated control. Except for antibiotics, which showed results for all analyses below the detection limit, all groups of the analyzed compounds showed measurable contents in the treated soils.

Results and discussion Among the POPs, the levels of organochlorine pesticides (OCPs) were detected at two locations at levels exceeding the Czech preventive values for their contents in agricultural soils (7.5 μg/kg for dichlorodiphenyl trichloroethane family, 20 μg/kg for hexachlorbenzene, and 10 μg/kg for α-hexachlorocyclohexane), regardless of the treatment. Similarly, elevated contents of polycyclic aromatic hydrocarbons (PAHs) were occasionally observed without any substantial relationship to the fertilizer application scenario. Thus, these contaminants are connected with atmospheric deposition in the given areas (PAHs) and their long-term stability (OCPs) even several decades after their ban; the role of the fertilizer composition was negligible.

Conclusions The levels of per- and polyfluoroalkylated substances, brominated flame retardants, and synthetic musk compounds tended to increase in the sewage sludge–treated plots, indicating that sewage sludge can contribute to the abundance of these compounds in soil, although the contaminant levels determined do not represent a direct environmental risk. The levels of these contaminants in sewage sludge and sludge-treated soils should be regularly monitored in further research.

Keywords Farmyard manure · Long-term trial · Persistent organic pollutants · Pharmaceuticals and personal care products · Sewage sludge

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1 Introduction

Li et al. (2016a) analyzed all of the publications on sewage sludge from 1991 to 2012 (using the Science Citation Index Expanded) and found that among the most popular disposal and treatment methods mentioned were composting and anaerobic digestion. However, the soil application was suggested as the most important approach to sewage sludge disposal. Although heavy metals were the contaminants of greatest concern for several decades, PPCPs (pharmaceuticals and personal care products) and PBDEs (polybrominated diphenyl ethers) showed comprehensive attention in recent years. McClellan and Halden (2010) showed that antibiotics such as triclocarban, triclosan, ciprofloxacin, and ofloxacin, followed by a number of tetracycline antibiotics, were the prevalent contaminants in biosolids. A comparison of different sludge processing methods showed galaxolide (representing musk compounds) and polybrominated diphenyl ether BDE-209 (representing PBDEs) among the substances most frequently detected under different treatment processes (Guerra et al. 2015). However, treatments such as composting or anaerobic fermentation should be at least partially effective for the elimination of PPCPs in biosolids and farmyard manure (Amarakoon et al. 2016; Ray et al. 2017; Spielmeyer et al. 2017).

Based on present knowledge, Roccaro and Vagliasindi (2014) assumed that the health risk related to the presence of PPCPs in biosolids used for land application is very low. However, the information concerning their toxicity, ecotoxicity, increased resistance of bacteria, possible synergistic effects due to the presence of emerging organic contaminant mixtures, etc., is limited and needs further research. In particular, the possible interrelationships between pollutants should be taken into account. For instance, risk elements such as Pb were observed by Li et al. (2011) to have an effect on the sorption of pharmaceuticals onto sediments. The potential transport of PPCPs and veterinary drugs into runoff after land application of biosolids from municipal treatment plants and manure from livestock or poultry production has already been investigated, as well (Topp et al. 2010). The suppressive effect of veterinary antibiotics on soil microbiota has already been documented. Yi et al. (2016) observed decreasing soil microbial cellulose decomposition activity and microbial respiration as well as ammonification with the addition of tetracycline, chlortetracycline, norfloxacin, and enrofloxacin, i.e., both human and veterinary antibiotics. The soil amended with a single application of antibiotics resulted in changed soil microbial diversity; however, communities appeared to converge over time, and no long-term significant effect was detected with the single application (Nelson et al. 2011). However, as a long-term effect of the antibiotics in the soil, an increased level of antibiotic resistance genes and shifts in the microbial community structure has been documented (Cleary et al. 2016).

For the most common persistent organic pollutants (POPs), such as polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), hexachlorocyclohexanes (HCHs) isomers, and the dichlorodiphenyl trichloroethane (DDT) family, the soil can represent an important reservoir of these compounds (Rychen et al. 2014; Clarke and Cummins 2015). In this context, sewage sludge is considered as the material that is able to increase the input of POPs into the soil (Elskens et al. 2013). The half-lives of PCBs and PCDD/Fs in sewage sludge vary between 9 and 12 years (Zennegg et al. 2013). Thus, the loads of these compounds in the soil can increase with repeated application of sewage sludge to the soil. In addition to these compounds, recently investigated pollutants such as PBDEs should be taken into account. The distribution of PBDE congeners in sewage sludge was published by Lee et al. (2014) who showed the dominant content of BDE-209 in all sludge samples. After BDE-209, relatively high levels were found for BDE-28 and -47 from industrial sludge, BDE-47 and -99 from domestic wastewater sludge, and BDE-206, -207, and -208 from livestock sludge. The contents of PBDEs in soils were measured at various industrial and electronic waste recycling sites. Total PBDE concentrations were dominated by BDE-209, while BDE-17, -85, -138, -191, -204, and -205 were the least abundant compounds (Li et al. 2016b).

Long-term (for several decades) fertilizer application and crop rotation experiments were established in many countries for the assessment of the sustainability of crop production on a particular soil type, in most cases to study the effects of different soil-climate conditions, the effects of various fertilizers, and crop rotation on soil properties and the nutrient content of crops (Körschens 2006; Madaras et al. 2013). However, a systematic assessment of the potential impact of fertilizers on the contents and accumulation of anthropogenically-derived organic pollutants is lacking. The fate and behavior of sewage sludge–derived contaminants in the soil, i.e., their persistence, mobility, leaching, plant uptake, and biodegradation depend on various factors such as soil properties, sewage sludge composition, contaminant properties, and interrelationships among the compounds (Oleszczuk 2007).

This experiment is based on the samples collected from four long-term established experimental sites in the Czech Republic with different soil and climate characteristics treated with various mineral and organic fertilizers, including sewage sludge. The main goal of our study was to investigate the direct as well as subsequent effects of different treatments on the accumulation of a large group of contaminants belonging to POPs and PPCPs and to assess the abundance of the individual compounds in the treated soils as a result of the long-term regular pollutant load via sewage sludge and farmyard manure applications.

2 Material and methods

2.1 Experimental sites, soil sampling, and characterization

The long-term field experiment (since 1996) established at four sites in the Czech Republic (Hněvčeves, Humpolec, Lukavec, Praha-Suchdol) with different soil and climate characteristics was used for this study. The whole design of the experimental tool and procedure as well as the main characteristics of the experimental sites and soils are described in detail elsewhere (Kulhánek et al. 2014; Vašák et al. 2015; Száková et al. 2018), and in the Supplementary material (Table S1, Electronic Supplementary Material—ESM). Composite soil samples consisting of ten subsamples collected throughout the plot to a depth of 30 cm were collected during April 2016; therefore, three composite soil samples were prepared for each treatment. Soil samples were air-dried and sieved through a 2-mm mesh. More detailed characteristics of the soils are summarized in the Supplementary material (Table S2—ESM). The individual treatments were as follows: (i) NPK mineral fertilization; (ii) sewage sludge with Lowe application, labeled SS1; (iii) sewage sludge with higher application rate, labeled SS2; (iv) farmyard manure, labeled FYM; and (v) untreated control, labeled Control.

2.2 Analytical methods

2.2.1 Chemicals

Certified standards with purity higher than 98% of PCBs (Nos. 28, 52, 101, 118, 138, 153, 170, and 180) dissolved in isooctane were provided by Dr. Ehrenstorfer, GmbH (Germany) as well as selected OCPs in the solid phase: isomers of hexachlorocyclohexane (α-, β-, γ-, δ-HCH), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (o,p'-, p,p'-DDT), dichlorodiphenyldichloroethan (o,p'-, p,p'-DDD), and dichlorodiphenyldichloroethylene (o,p'-, p,p'-DDE). Certified standards of selected synthetic musk compounds (SMs) were purchased from Neochema GmbH (Germany): galaxolide, tonalide, and cashmeran. Certified standards of 13 polybrominated diphenyl ethers congeners (# 47, 49, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, and 209) were provided by Wellington Laboratories, Inc. (Canada).

The following certified standards were purchased from Wellington Laboratories, Inc. (Canada): perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), and sodium salt of perfluorooctanesulfonic acid (linear and branched isomers of PFOS). Certified standards of 12 priority PAHs were supplied by the National Institute of Standards and Technology (NIST, Gaithersburg, USA): anthracene (AN), benz[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkFA), fluoranthene (FLT), benzo[b]fluoranthene (BbFA), chrysene (CHR), benzo[ghi]perylene (BghiP), dibenz[a,h]anthracene (DBahA), indeno[1,2,3-cd]pyrene (IP), phenanthrene (PHE), and pyrene (PY).

Methanol, acetonitrile, and ethyl-acetate were provided by Honeywell (USA). Hexane, dichloromethane, and isooctane were supplied by Sigma-Aldrich (Merck, Germany). Sodium chloride and magnesium sulfate were provided by Lach-Ner s.r.o. (Czech Republic).

The performance characteristics of all the following analytical methods are tabulated in Table S3 (ESM).

2.2.2 Determination of PCBs, OCPs, PAHs, SMs

A mixture of 10 g of soil sample and anhydrous sodium sulfate (Na_2SO_4) was prepared and transferred into a cellulose extraction thimble. Then, the sample was extracted for 7 h by dichloromethane. The extract was evaporated and dissolved in a mixture of cyclohexane:ethyl-acetate (1:1, v/v) and purified using gel permeation chromatography in a Bio-Beads S-X3 column (styrene-divinylbenzene copolymer) with a mixture of cyclohexane:ethyl-acetate (1:1, v/v) employed as the mobile phase. A purified extract was also evaporated to dryness, re-dissolved in isooctane, and transferred into a vial for analysis of PCBs, OCPS, BFRs, and SMs using gas chromatography coupled to (tandem) mass spectrometry (GC-MS(/MS)), as described by Száková et al. (2018). In the case of PAHs, a crude extract was purified separately also using a Bio Beads S-X3 column, and after evaporation, the collected fraction was re-dissolved in acetonitrile and analyzed using high-performance liquid chromatography with a fluorescence detector (HPLC-FLD), for details see Száková et al. (2018).

2.2.3 Determination of PFASs

A mixture was prepared by transferring 5 g of soil sample into a 50-mL polypropylene tube, adding 10 mL of acetonitrile and 10 mL of deionized water, and shaking the mixture for 1 min. Subsequently, 1.5 g of NaCl and 6 g of MgSO4 were added into the tube with the sample; the mixture was shaken once again for 1 min and then centrifuged for 5 min at 10,000 RPM. Into a second 50-mL PP tube, 5 mL of the upper organic layer was transferred, and the solvent was evaporated to dryness. The residue was re-dissolved in methanol and transferred into a vial for subsequent analysis by ultra-high performance chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS), see Száková et al. (2018).

2.2.4 Determination of antibiotics

Soil samples were prepared by dilution of a dry sample (5 g) with 2.5 mL of 0.05 M EDTA, 2.5 mL of McIlvaine buffer (pH 4), and 5 mL of methanol. Diluted samples were properly shaken for 1 min and then filtered using microfilters to ensure that all solid particles were removed prior to UHPLC-MS/MS analysis (Acquity UPLC with mass detector Xevo TQ-S (Waters, USA)).

3 Results and discussion

3.1 Polychlorinated biphenyls (PCBs)

The results showed detectable levels of all of the measured congeners in all of the analyzed samples, except for PCB 52 (detection frequency 95%), and the total PCB contents in the soils varied between 0.44 and 12.1 μg/kg dw (Table 1). In the Czech Republic, the preventive values of PCBs agricultural soils are given by the public notice characterizing the conditions for the protection of agricultural soil quality (Public Notice No. 153/2016 2016). The maximum values of the sum of seven congeners (PCB 28, 52, 101, 118, 138, 153, and 180) did not exceed the preventive value in soil, i.e., 20 μg/kg dw. Among the analyzed congeners, the highly chlorinated compounds presented the most important concentrations; No. 180 varied between 0.05 and 2.93 μg/kg dw, No. 153 between 0.08 and 3.42 μg/kg dw, and No. 138 between 0.11 and 3.63 μg/kg dw. The results also documented a difference between elevated PCB contents in the soil at the Suchdol location (in all of the samples including the untreated control) compared to the other locations with low levels of the sum of the investigated congeners in the untreated control samples. Profiles of PCBs Nos. 138, 153, and 180 and their levels were comparable between the Humpolec, Lukavec, and Hněvčeves locations and between the methods of fertilization and were 2–3 times lower compared to the Suchdol location. Moreover, the concentrations of all PCBs were very similar between the untreated control, fertilization with NPK, and fertilization with FYM, which shows that NPK and FYM are not significant sources of PCBs and their contribution to the overall levels of PCBs is negligible. The elevated overall levels of PCBs at the Suchdol location could be connected with the proximity of the most industrialized city in the Czech Republic, Prague. This statement could be supported by findings for urban soils in London, United Kingdom, where the sum of three congeners (Nos. 138, 153, and 180) reached up to 12.4 μg/kg dw (Vane et al. 2014). In this study, the maximum value of the sum of these three congeners in soil at the Suchdol location was 8.9 μg/kg dw, indicating similar levels of PCBs in both cities. Results originating from an industrial area in China (from 1.46 to 19.2 μg/kg dw) also showed the impact of industrial activities on the PCB level in agricultural soils (Zhu et al. 2014).

Regardless of the location, the results showed increased PCB contents in the soils treated with SS compared to all of the remaining variants, and the increase was related to the sludge application rate in the soil. The concentrations of PCBs were 1.8 times higher in the soil fertilized with SS2 compared to soil fertilized with SS1. The PCB content in the sludge exceeded the soil PCB levels ca. 150-fold, confirming that SS could be an important source of PCBs in agricultural soil. These statements are only speculative because the regularly applied SSs were not monitored from the beginning of the long-term experiment. However, the potential impact of SS application on the PCB levels in soils could be estimated according to the previously published results. Previous findings pointed out that the contents of dioxin-like PCBs (DL-PCBs) in various fertilizers in Belgium showed that the contents of these compounds in SS were the highest among both organic and inorganic fertilizers (Elskens et al. 2013). However, these authors assumed that their contribution to the overall soil contamination was low. Low PCB contents were reported by Abad et al. (2005) in various SSs for agricultural purpose in Spain, as well. Sludge from anaerobic wastewater stabilization ponds was even determined by Santos et al. (2009) to have no detectable PCB contents. Moreover, many authors have documented the degradability of SS-derived PCBs. For instance, a decrease in the soil PCB content was observed in composted SS-treated soil compared to the original soil before the treatment (Antolin-Rodriguez et al. 2016) indicating the positive stabilization effect of the SS-derived organic matter. Tillage could also be a factor in decreasing the accumulation of PCBs in the upper layer of soils (During and Gath 2002). The biodegradation rate of the SS-derived PCBs in soil can substantially decrease within 128 days of sludge amendment (Wilson et al. 1997). However, our results indicate substantial persistence of sludge-derived PCBs in the long-term trials if the sludge was regularly and repeatedly applied. Thus, the long-term experiment can allow us to make a more reasonable assessment of the potential impact of SS on the soil PCB levels. The long-term effect (39 years) of SS application on DL-PCBs in the soil was investigated by Umlauf et al. (2011). They found that the soils treated with SS showed higher values compared to those treated with a mineral fertilizer, but both were still below the guideline value of these compounds for arable land. Thus, they stated that the common practice of SS application in Germany does not pose a current threat to the agroenvironment with regard to DL-PCBs. However, they highlighted the necessity of investigation into the time-dependent changes in pollutant contents in long-term experiments. Our results could be concluded by the same statement: the PCB levels in the SS-treated soils do not represent a direct environmental risk, but regular

Table 1 Median concentrations of detected PCBs and OCPs in soils; $n = 3$; concentrations of HCBD, β-HCH, γ-HCH, and δ-HCH were below the limit of quantification or were detected in less than 50% of samples

	PCB28 (µg/kg)	PCB52 (µg/kg)	PCB101 (µg/kg)	PCB118 (µg/kg)	PCB138 (µg/kg)	PCB153 (µg/kg)	PCB170 (µg/kg)	PCB180 (µg/kg)	PeCB (µg/kg)	α-HCH (µg/kg)	HCB (µg/kg)	o,p'-DDE (µg/kg)	p,p'-DDE (µg/kg)	o,p'-DDD (µg/kg)	p,p'-DDD (µg/kg)	o,p'-DDT (µg/kg)	p,p'-DDT (µg/kg)
Hněvčeves																	
Control	0.08	0.01	0.03	0.03	0.19	0.17	0.08	0.12	0.02	0.02	0.95	0.01	1.63	0.04	0.29	0.11	2.14
SS1	0.13	0.03	0.16	0.09	0.68	0.63	0.29	0.45	0.03	0.03	1.56	0.01	1.60	0.04	0.41	0.16	3.33
SS2	0.20	0.11	0.36	0.18	1.28	1.25	0.57	0.92	0.04	0.04	1.58	0.02	1.92	0.05	0.44	0.12	2.82
FYM	0.12	0.02	0.05	0.03	0.25	0.24	0.11	0.15	<0.02	0.04	0.83	0.01	1.45	0.04	0.36	0.11	2.13
NPK	0.06	0.01	0.02	0.02	0.12	0.10	0.05	0.08	0.03	0.05	1.17	0.01	1.78	0.05	0.28	0.16	2.97
Humpolec																	
Control	0.07	0.02	0.09	0.06	0.35	0.31	0.14	0.23	0.03	0.02	2.57	0.31	31.1	0.69	3.27	4.04	13.5
SS1	0.18	0.07	0.21	0.13	0.77	0.72	0.33	0.57	0.04	0.03	2.63	0.17	12.7	0.51	3.85	1.78	11.8
SS2	0.21	0.08	0.36	0.22	1.44	1.37	0.63	1.07	0.04	0.02	2.85	0.08	5.64	0.31	1.29	0.65	2.85
FYM	0.08	0.01	0.05	0.03	0.18	0.15	0.06	0.10	0.02	0.03	2.22	0.22	24.6	0.62	2.82	2.18	8.78
NPK	0.05	0.01	0.03	0.02	0.13	0.11	0.04	0.07	0.02	0.02	1.66	0.19	22.0	0.43	2.12	2.67	13.8
Lukavec																	
Control	0.04	0.01	0.05	0.04	0.27	0.23	0.09	0.15	0.02	0.05	1.40	0.03	5.45	0.11	0.98	0.71	3.42
SS1	0.06	0.04	0.23	0.14	0.92	0.85	0.35	0.57	0.03	0.04	1.14	0.04	4.49	0.13	0.97	0.65	4.78
SS2	0.15	0.07	0.41	0.24	1.45	1.36	0.60	0.96	0.05	0.03	1.40	0.05	4.85	0.16	1.42	0.97	4.11
FYM	0.14	0.04	0.17	0.09	1.21	1.13	0.55	0.95	0.04	0.02	0.74	0.02	1.14	0.05	0.17	0.41	1.07
NPK	0.05	0.01	0.07	0.04	0.31	0.22	0.08	0.11	0.02	0.03	1.18	0.04	13.6	0.14	1.55	0.63	6.19
Suchdol																	
Control	0.08	0.01	0.10	0.06	0.98	0.93	0.42	0.70	<0.02	0.02	0.82	0.03	4.30	0.09	0.30	0.46	2.02
SS1	0.26	0.08	0.35	0.19	2.10	2.00	0.96	1.69	0.05	0.03	1.07	0.03	1.64	0.08	0.26	0.42	1.60
SS2	0.19	0.10	0.70	0.35	3.14	3.07	1.47	2.59	0.05	0.03	1.26	0.03	2.16	0.09	0.33	0.35	2.05
FYM	0.14	0.04	0.17	0.09	1.21	1.13	0.55	0.95	0.04	0.02	0.74	0.02	1.14	0.05	0.17	0.41	1.07
NPK	0.04	0.03	0.32	0.12	1.74	1.77	0.82	1.44	0.02	0.03	0.72	0.02	1.15	0.15	0.17	0.26	0.93

assessment of the potential changes in the PCB contents in the sludge-soil system should be carried out.

3.2 Organochlorinated pesticides (OCPs)

Except for HBCD, all of the targeted OCPs were found in the soil samples at detectable levels (Table 1). Among them, α-HCH, HCB, DDT isomers (*o,p′*-DDT, *p,p′*-DDT), DDE isomers (*o,p′*-DDE, *p,p′*-DDE), and one DDD isomer (*p,p′*-DDD) were identified in all of the analyzed samples. Minor amounts of *o,p′*-DDD and pentachlorobenzene were identified in 97% and 60% of the soil samples, respectively. The total OCP content in the soils varied between 3.31 and 51.3 μg/kg dw, and the most abundant compounds were DDE isomers representing from 23 to 60% of the total OCP content. Thus, the OCP contents did not exceed the preventive value of these compounds in soil given by Singh and Agrawal (2008), i.e., 75 μg/kg dw. In the Czech Republic (Public Notice No. 153/2016 2016), however, the preventive value of ∑DDTs is 7.5 μg/kg and for HCB and α-HCH, it is 20 μg/kg and 10 μg/kg, respectively. Although the HCB and α-HCH contents were far below these limits, the sum of DDTs exceeded these limits in all of the samples at the Humpolec location and in numerous samples at the Lukavec location. However, the data did not reach the value which can directly threaten human and animal health, i.e., 8 mg/kg (Public Notice No. 153/2016 2016).

Comparing the individual locations, the highest OCP contents varying between 21.5 and 51.3 μg/kg dw were found at the Humpolec location, regardless of the soil treatment. OCP contents at Hněvčeves and Lukavec were quite similar, varying within the range 7.02–13.9 and 9.91–16.0 μg/kg dw, respectively; however, these values were 2–4 times lower compared to Humpolec. The lowest concentrations of OCPs were measured in soil samples originating from the Suchdol location: 3.34–7.30 μg/kg dw, which is 3–16 times lower compared to the most contaminated area. The amounts of chlorinated pesticides in the SS-treated soils from long-term experiments in the United Kingdom typically ranged from 0.1 to 10 μg/kg dw, and the highest concentrations were found for γ-HCH and *p,p′*-DDE (Meijer et al. 2001). In this experiment, the proportions of HCH isomers in the sludge-treated soils did not exceed 2% of the total OCP content. Thus, the long-term impact of SS application on the soil OCP content seems to be negligible, and the concentrations of these compounds could be connected with their intensive application as pesticides in the past.

DDD and DDE are considered to be products of the partial degradation of DDT, and a ratio of the DDT content to the sum of DDE and DDD that is less than one indicates past application of DDT as an insecticide. This ratio was recorded for all of the locations except Hněvčeves, where the ratio of DDT/(DDD + DDE) was > 1 indicating either more recent application of DDT (although the application of DDT has been

banned for several decades), or a slow degradation rate of DDT compared to other locations. The last possibility should be supported by the presence of low content of total organic carbon (TOC) in this soil (Table S2—ESM), indicating possible lower activity of soil microbiome in these conditions. This speculation should be supported by the detailed microbiological analysis in further research. However, the results measured in the samples from this study did not reach the soil levels of DDD and DDE isomers observed in an area affected by the illegal application of these compounds (79 μg/kg dw) in Uganda (Sseburege et al. 2010). Odukkathil and Vasudevan (2013) summarized and reviewed the behavior of chlorinated pesticides in soils. According to the previous investigations, chlorinated pesticides like DDT and HCH are persistent in soil, and their half-lives range from 100 to 200 days. In this experiment, however, the detectable OCP contents were found many years after the application ban. Unfortunately, the application rates and/or duration of the application of OCPs at the individual locations during the period of permitted application of these chemicals before the establishment of the long-term experiment was not documented. Thus, we can only speculate that the locations differed in their OCP contents due to their different DDT rates.

3.3 Per- and polyfluoroalkylated substances (PFASs)

Among the 19 targeted PFASs, only branched isomers of PFOS (br-PFOS), linear PFOS (L-PFOS), PFOA, and PFHpA were detected in 90%, 83%, 43%, and 3% of the samples, respectively. Concentrations of the remaining PFASs were below the quantification limit (LOQ). The total PFOS content varied between < 0.1–2.46 μg/kg dw and that of PFOA between < 0.3–0.97 μg/kg dw (Table 2). The results showed no significant difference in the PFAS content among all of the locations, but fertilization of the soil with SS was the highest contributor to soil pollution with PFASs. These results indicate that SS is a significant source of these compounds and therefore has to be carefully checked before possible application to soil. No differences were observed in the PFAS content in the control soil and soil fertilized with the FYM or NPK. Another interesting fact is that the ratio between br- and L-PFOS was 1:4 in all locations and all types of fertilization, which corresponds to the ratio of PFOS isomers in the technical mixture. This result indicates that PFOS probably does not undergo transformation between its forms in soil.

Higher contents of PFOA and PFOS in soil were observed in a study from the USA (Xiao et al. 2015). PFOA and PFOS were detected in all samples, and concentrations ranged between 0.2–28.2 μg/kg dw for PFOA and 5.5–125.7 μg/kg dw for PFOS. Similar to our study, concentrations of PFOS were higher compared to PFOA. Another trend was identified in a study from Sweden (Plassmann and Berger 2013) in which the concentrations of PFOA (< 1.67–3.26 μg/kg dw) were higher

Table 2 Median concentrations of detected PFASs and BFRs in soils; $n = 3$; concentrations of PFBA, PFPeA, PFHxA, PFNA, PFUDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFHxS, PFDS, PFOSA, N-MeFOSA, N-EtFOSA, BDE 28, BDE 66, BDE 85, BTBPE, DBDPE, HBB, α-HBCD, β-HBCD, γ-HBCD, OBIND, PBEB, and PBT were below the limit of quantification or were detected in less than 50% of samples

	PFHpA (µg/kg)	PFOA (µg/kg)	PFDA (µg/kg)	Br-PFOS (µg/kg)	L-PFOS (µg/kg)	BDE 47 (µg/kg)	BDE 49 (µg/kg)	BDE 99 (µg/kg)	BDE 100 (µg/kg)	BDE 153 (µg/kg)	BDE 154 (µg/kg)	BDE 183 (µg/kg)	BDE 196 (µg/kg)	BDE 197 (µg/kg)	BDE 203 (µg/kg)	BDE 206 (µg/kg)	BDE 207 (µg/kg)	BDE 209 (µg/kg)
Hněvčeves																		
Control	<0.3	<0.3	<0.3	0.07	0.28	0.02	<0.01	0.02	0.02	0.02	<0.01	0.04	0.07	0.04	0.04	0.89	1.11	5.91
SS1	<0.3	0.56	<0.3	0.26	0.89	0.16	0.01	0.16	0.05	0.04	0.02	0.10	0.11	0.11	0.03	0.71	0.85	2.57
SS2	<0.3	0.80	0.37	0.35	1.39	0.35	0.01	0.38	0.10	0.06	0.04	0.09	0.12	0.10	0.03	0.38	0.43	1.92
FYM	<0.3	<0.3	<0.3	0.07	0.23	0.04	<0.01	0.04	0.02	0.02	0.01	0.03	0.03	0.04	<0.02	0.31	0.31	<1
NPK	<0.3	<0.3	<0.3	0.04	0.18	0.01	<0.01	0.01	<0.01	0.04	<0.01	0.05	0.17	0.07	0.03	4.14	3.58	8.57
Humpolec																		
Control	<0.3	0.34	<0.3	0.07	0.25	0.03	<0.01	0.04	0.03	<0.01	0.01	<0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1
SS1	<0.3	0.48	<0.3	0.21	0.69	0.19	0.01	0.22	0.07	0.03	0.02	0.05	0.15	0.07	0.04	0.81	0.81	2.94
SS2	<0.3	0.91	0.43	0.40	1.49	0.35	0.02	0.41	0.10	0.06	0.04	0.14	0.13	0.16	0.04	0.34	0.67	4.38
FYM	<0.3	<0.3	<0.3	0.04	0.14	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1
NPK	<0.3	<0.3	<0.3	<0.03	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.03	0.04	<0.02	0.44	0.39	2.13
Lukavec																		
Control	<0.3	<0.3	<0.3	0.05	0.19	0.02	<0.01	0.02	0.01	0.01	<0.01	<0.01	0.06	0.02	0.03	1.80	1.28	3.17
SS1	<0.3	0.49	<0.3	0.20	0.88	0.18	0.01	0.17	0.09	0.04	0.03	0.05	0.08	0.06	<0.02	<0.1	<0.1	<1
SS2	<0.3	0.79	0.39	0.41	1.93	0.38	0.02	0.41	0.10	0.06	0.05	0.16	0.12	0.13	<0.02	0.31	0.25	<1
FYM	<0.3	0.31	<0.3	0.10	0.46	0.05	0.03	0.04	0.02	0.01	0.01	0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1
NPK	<0.3	<0.3	<0.3	0.19	0.68	0.04	<0.01	0.05	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1
Suchdol																		
Control	<0.3	<0.3	<0.3	0.05	0.24	0.02	<0.01	0.01	0.02	<0.01	<0.01	0.02	<0.01	<0.01	<0.02	<0.1	<0.1	<1
SS1	0.31	0.49	<0.3	0.21	0.88	0.21	0.01	0.21	0.08	0.03	0.03	0.08	0.04	0.04	<0.02	0.40	0.29	1.51
SS2	<0.3	0.80	0.34	0.40	1.46	0.38	0.03	0.40	0.19	0.04	0.04	0.09	0.09	0.06	0.03	0.53	0.54	1.09
FYM	<0.3	0.31	<0.3	0.10	0.46	0.05	0.03	0.04	0.02	0.01	0.01	0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1
NPK	<0.3	<0.3	<0.3	0.04	0.14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.1	<0.1	<1

compared to PFOS (< 0.147–0.272 μg/kg dw) but lower than in our study. In another survey conducted in Korea (Naile et al. 2013), higher concentrations of PFOA (< 0.2–6.4 μg/kg dw) compared to PFOS (< 0.2–1.7 μg/kg dw) were also measured. The results from Korea are comparable with the data from our study. It should be noted that accumulation of PFASs strongly depends on the soil organic carbon content and the available cations (Higgins and Luthy 2006; Hong et al. 2013), and this is probably the reason why the concentrations of PFASs among several studies are so different. In this experiment, however, the TOC levels of the untreated soils (Table S2— ESM) varied in relatively narrow range, between 0.93 (Hněvčeves) and 1.76% (Suchdol), thus, differences similar to the cited studies were not expected.

3.4 Brominated flame retardants (BFRs)

Among the group of BFRs, 15 compounds representing brominated diphenyl ethers (PBDEs) and other flame retardants (PBT and PBEB) and isomers of HBCD were detected in the examined soil samples, where the total contents of these compounds varied between 0.69 and 16.9 μg/kg dw (Table 2). The most abundant PBDEs were BDE-47 and -99 (both identified in 78% of the samples), γ-HBCD (68% of the samples), BDE-100 (62% of the samples), and BDE-183 (57% of the samples); the remaining congeners occurred at detectable levels in less than 50% of the samples. The individual congeners with highest contents were BDE-209 (from 0.5 to 5.88 μg/kg dw) and BDE-206 (from 0.05 to 2.78 μg/kg dw), but they were only detected in 30% of the samples. On the other hand, the concentrations of BDE-28, HBB, BTBPE, OBIND, and DBDPE were below the LOQ. Concentrations of BDE 47 and BDE 99 were somewhat higher in soil from the Suchdol location compared to other locations, whereas the concentrations in soil from Lukavec, Humpolec, and Hněvčeves were similar. The results also indicated the impact of SS application on the PBDE levels in the soil: increasing PBDE contents were observed with increasing sludge application rate. On the contrary, the PBDE levels in the soils treated by FYM and NPK did not differ from the control variants. Among the locations, the levels at Hněvčeves tended toward higher values compared to all of the remaining sites.

PBDE content is one of the soil quality parameters that is often investigated, and the levels determined by investigators are highly variable. Low contents of BDE-47 and -99 (not exceeding 1 μg/kg dw) were found in long-term sludge-treated soils in Sweden (Österas et al. 2015), whereas higher values (up to 17 μg/kg dw) were determined in rice fields in China (Wang et al. 2011). Similar to PCBs and OCPs, BFRs showed long persistence in the soil. Venkatesan and Halden (2014) found that the initial BFR amount in sludge/soil mixtures (1:2) persisted over the monitoring duration of 3 years. Thus, the repeated application of SS can be a source of

potential accumulation of these compounds in soil. The possible enrichment of soils with BFRs should be regularly monitored also because of the potential intake of these compounds into the food chain. Uptake and transformation of BDE-99 by *Oryza sativa*, *Triticum aestivum*, and *Glycine max* have been observed via recordings of the corresponding homologous methoxylated metabolites (Chow et al. 2015; Pan et al. 2016).

3.5 PAHs

All 12 targeted compounds from the PAHs group were detected in all samples. PAHs are one of the main contributors to soil pollution, and their concentrations varied between 54.1 and 1443 μg/kg dw (Table 3). The public notice No. 153/2016 (2016) gives the preventive value of ∑12 PAHs in the soil at the level 1000 μg/kg. Fluorathene and pyrene were the most abundant PAHs, representing 12–22% and 11–17% of the total PAH content, respectively. The highest concentrations of PAHs, occasionally exceeding the preventive value, were found in soil samples from the Humpolec location, and concentrations in this location were 2–5 times higher compared to the others. These results imply a probable local source of PAHs pollution in Humpolec. No difference in the PAH contents was observed between the different types of fertilization, indicating that the pollution of soil with PAHs is more likely caused through atmospheric deposition than by fertilization, and SS represents only a negligible risk. The ratio between all PAHs in all samples is quite similar, and the ratio between B[a]A, CHR, B[b]F, and B[a]P was approximately 1:1:1:1 in all samples and all locations with no significant differences.

3.6 Musk compounds

Among the targeted SMs, only galaxolide (most abundant, identified in 88% of the soil samples), tonalide (70% of the soil samples), and cashmeran (28% of the soil samples) were detected (Table 3). The total content of the determined compounds varied between 6.22 and 80.9 μg/kg dw. The predominant compound in all of the samples was galaxolide, varying between 1.6 and 58.9 μg/kg dw. Although the differences among the individual locations were negligible, the content of musk compounds increased with increasing SS application rate at all of the locations. Monitoring of PPCP contents in SSs from wastewater treatment plants in the United Kingdom showed a few high contents of total SMs ranging from 2.1 to 86 mg/kg dw. Thus, SS could be an important source of musk compounds in soil, where assessment of the potential environmental risk is aggravated by the high variability of these pollutants in sludge. The variability of musk compound levels in SS could be documented by the musk compound levels in the SS-treated soils as presented by other authors. Chen et al. (2014a) determined galaxolide and tonalide levels in Chinese soils reaching up to 82.4 μg/kg, whereas

Table 3 Median concentrations of detected PAHs and SMs in soils; $n = 3$; concentrations of Celestolide, Musk Ambrette, Musk Ketone, Musk Moskene, Musk Tibetene, Musk Xylene, Phantolide, and Traseolide were below the limit of quantification

	PHE (µg/kg)	AN (µg/kg)	FLT (µg/kg)	PY (µg/kg)	BaA (µg/kg)	CHR (µg/kg)	BbFA (µg/kg)	BkFA (µg/kg)	BaP (µg/kg)	DBahA (µg/kg)	BghiP (µg/kg)	IP (µg/kg)	Cashmeran (µg/kg)	Galaxolide (µg/kg)	Tonalide (µg/kg)
Hněvčeves															
Control	6.2	0.6	11.6	11.2	6.0	8.6	8.8	4.2	6.9	1.0	7.4	6.4	11.9	0.37	0.37
SS1	7.9	0.7	13.2	13.9	8.9	10.9	12.0	6.3	11.0	1.6	11.4	9.7	1.49	5.98	2.09
SS2	11.1	2.0	23.4	21.2	13.4	15.2	15.2	8.2	14.6	1.9	15.3	12.6	2.81	4.16	2.69
FYM	5.6	0.5	11.8	11.8	6.0	7.6	8.4	4.2	7.3	0.9	8.1	7.0	1.08	2.14	0.37
NPK	7.8	0.7	13.3	12.8	7.2	9.3	9.8	5.0	8.4	1.2	8.5	7.4	4.05	2.21	0.37
Humpolec															
Control	64.3	5.8	100.4	85.8	42.6	54.7	43.1	24.1	37.4	5.1	39.7	30.7	<0.75	2.19	1.49
SS1	60.0	8.0	110.2	94.8	51.4	60.5	49.0	26.5	46.3	6.1	43.4	34.7	<0.75	4.28	4.60
SS2	61.2	7.0	125.6	88.3	60.1	73.0	61.1	27.6	60.1	7.4	57.3	46.5	1.10	49.9	23.7
FYM	43.9	4.6	87.3	77.2	41.2	51.3	43.1	23.9	41.5	5.0	39.7	31.3	<0.75	2.05	0.76
NPK	46.7	4.6	86.4	75.5	38.3	48.7	38.4	21.8	37.7	4.3	34.1	27.8	2.07	2.03	0.37
Lukavec															
Control	51.2	1.7	40.4	39.3	19.7	24.9	22.3	11.9	20.7	2.6	20.4	17.8	<0.75	2.91	2.07
SS1	16.1	1.3	32.4	30.9	15.6	19.6	19.0	10.2	17.2	1.8	17.6	15.7	<0.75	6.21	4.94
SS2	16.7	1.6	32.5	30.7	17.0	21.5	21.9	11.2	18.2	1.8	20.3	16.9	<0.75	26.0	12.3
FYM	11.4	1.5	16.4	15.9	17.4	21.4	13.9	11.8	12.0	2.4	24.8	11.4	0.92	5.52	5.14
NPK	20.2	2.1	46.2	45.2	24.5	29.6	25.5	12.6	25.4	2.2	22.4	19.2	<0.75	1.12	0.37
Suchdol															
Control	20.6	2.0	39.9	37.7	22.3	26.7	25.9	14.2	25.6	3.0	29.3	21.5	<0.75	1.25	0.37
SS1	24.9	2.0	37.1	34.2	22.3	26.7	26.8	12.9	25.9	3.1	30.8	22.3	1.29	25.1	12.1
SS2	29.6	2.1	36.0	35.4	19.8	25.1	27.5	13.1	24.2	3.3	30.8	23.1	1.15	23.1	5.60
FYM	11.4	1.5	16.4	15.9	17.4	21.4	13.9	11.8	12.0	2.4	24.8	11.4	0.92	5.52	5.14
NPK	11.8	1.2	23.0	21.0	13.3	15.5	15.1	8.3	13.9	2.0	18.5	11.7	<0.75	2.28	0.37

Fig. 1 A comparison of the sums
of the individual groups of
pollutants at the individual
locations as affected by the
individual treatments
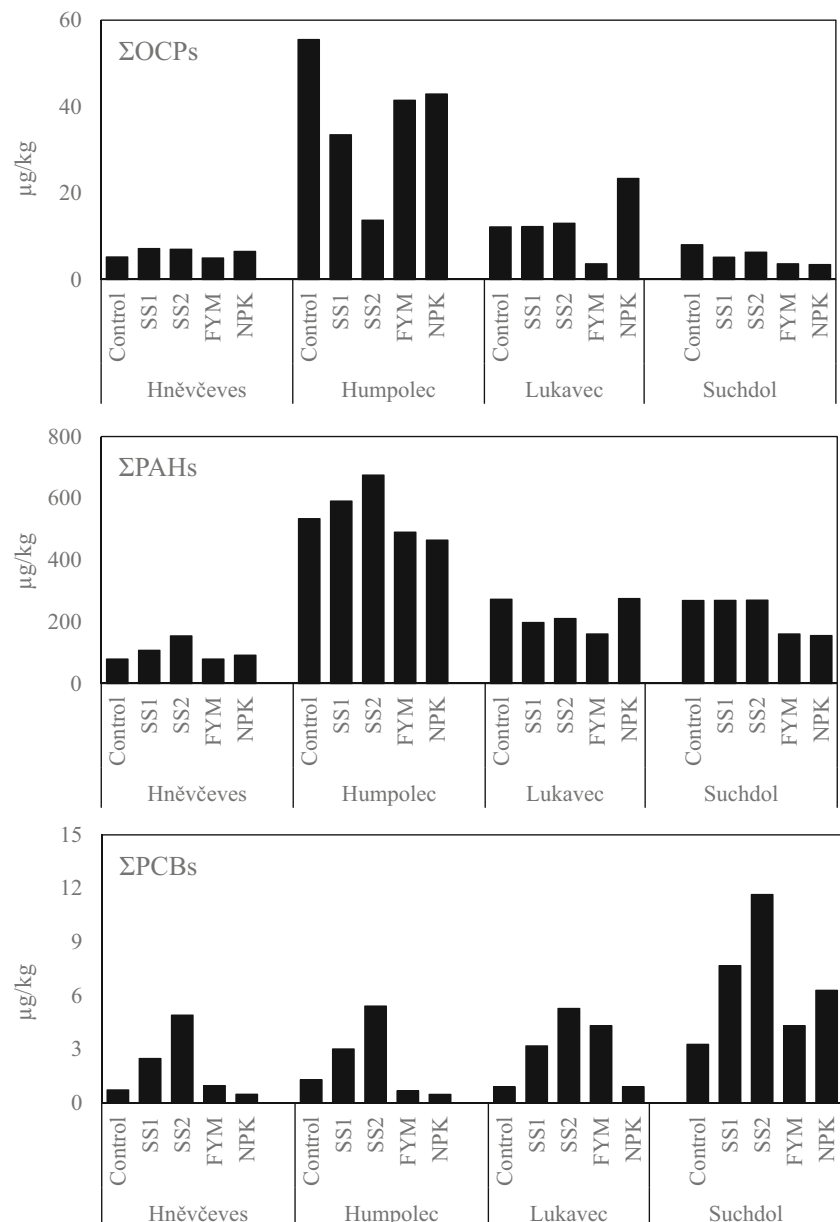
Yang and Metcalfe (2006) found levels of these compounds
up to only 4.6 µg/kg in SS-treated soils in Canada.

The potential risk of the intake of SMs into the terrestrial
food chain needs to be taken into account as well. The potential
uptake of PPCPs by plant roots has already been proved. The
introduction of persistent semi- and nonpolar pollutants such as
musk compounds (galaxolide, tonalide) into the food chain via
edible plants like carrots could be of particular relevance when
sludge is applied as fertilizer (Macherius et al. 2012). The
potential relationships of musk compounds (galaxolide) and
risk elements (Cd) have also been observed in regard to the
uptake of these substances by plants (Chen et al. 2014b). Thus,
the uptake and translocation of risk elements by plants and
their interactions with sludge-derived organic contaminants

should also be included in comprehensive assessments of the
potential impact of SS on agricultural soils.

3.7 Antibiotics

Within this contaminant group, ten chemicals, i.e., sulfadia-
zine, sulfathiazole, sulfamerazine, sulfamethoxazole,
sulfadimidine, norfloxacin, enrofloxacin, tetracycline,
oxytetracycline, and chlortetracycline, were targeted but not
detected at concentrations above the LOQ. Hou et al. (2016)
monitored the contents of human antibiotics including tetracy-
clines within the processing stages in pharmaceutical wastewa-
ter treatment plants, and although the antibiotics were partially
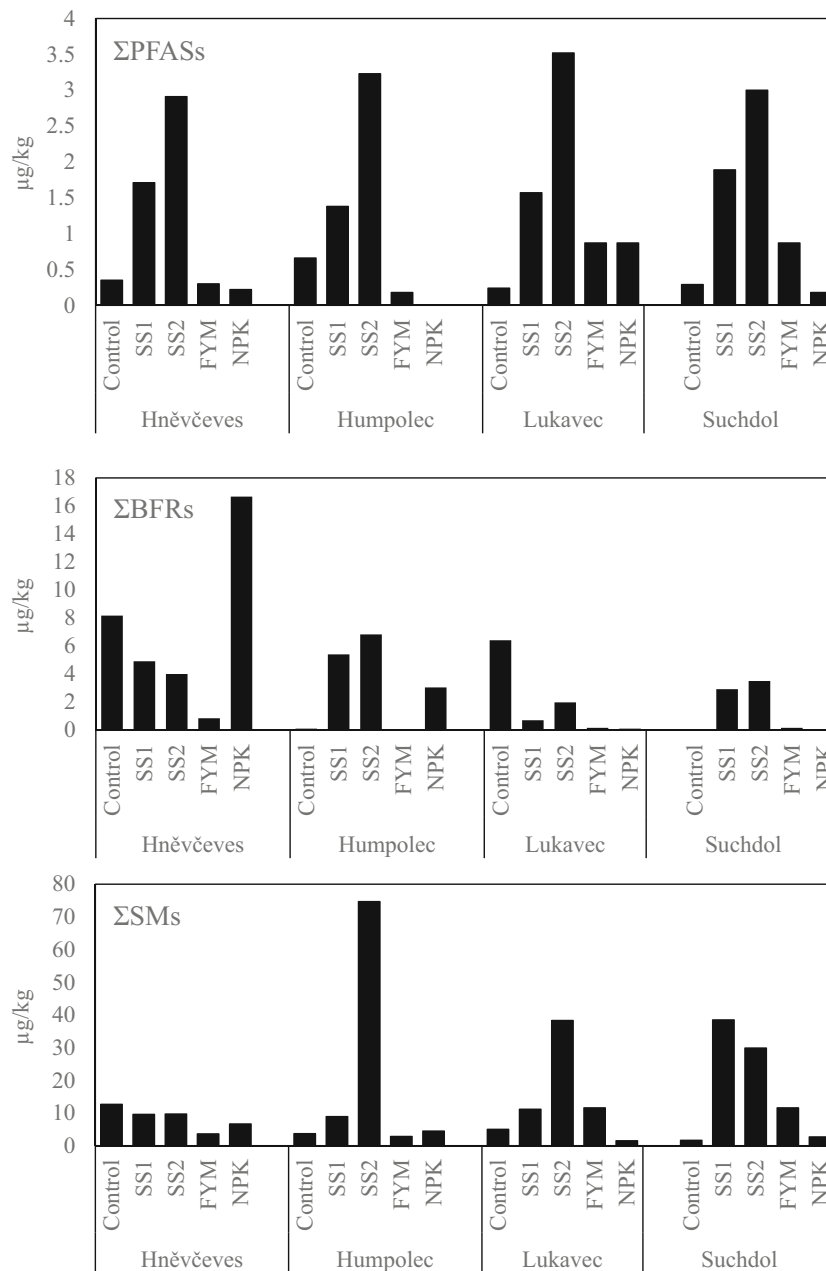degraded during the procedure, large amounts of tetracyclines

Fig. 1 continued.

were still discharged through the effluent (up to 32.0 ± 6.0 mg/L) and dewatered SS (up to 5481 ± 123 mg/kg). Limited biodegradation of human antibiotics in wastewater treatment plants was observed also by Plosz et al. (2010). On the contrary, Gao et al. (2012) showed the high efficiency of removal of antibiotics via biotransformation during the wastewater cleaning procedure and observed only an insignificant role of the sorption of these compounds onto the SS.

The contents of tetracyclines and sulfonamides in manures were monitored by An et al. (2015) in northeast China, where the highest concentration of antibiotics in manure was 143.9 mg/kg for chlortetracycline. In the manure-treated soils,

the concentrations of antibiotics varied from 2.56 μg/kg dw of sulfadimidine to 1590 μg/kg dw of chlortetracycline. Ostermann et al. (2014) identified the hotspots of antibiotic-contaminated soils in China, where the concentrations reached 110 μg/kg of sulfamethazine, 111 μg/kg dw of chlortetracycline, and 62 μg/kg dw of enrofloxacin in the topsoil of agricultural fields.

The screening provided by Xiang et al. (2016) showed that a wide range of tetracycline compounds (oxytetracycline, tetracycline, chlortetracycline, and doxycycline) was present in the soil, ranging from 0.04 to 184.8 μg/kg dw. Ding et al. (2016) investigated the potential biodegradation of antibiotics

and found that the removal of these substances from the soil solution showed complementary effects on the laccase-mediated oxidation and soil adsorption with the adsorption rate depending on the chemical structure of the antibiotics. Moreover, Allaire et al. (2006) observed that sorption of chlortetracycline in sandy loam and clay occurs very fast: more than 95% of the chlortetracycline adsorption was completed within 10 min. However, the sorption/desorption behavior of antibiotics (oxytetracycline) was substantially affected by the soil type and physicochemical properties (Feng et al. 2016). In contrast to the previous investigations, this study showed that neither manure nor SS application represents a risk for long-term loads of these contaminants in the treated soils. The lower use of antibiotics in the Czech Republic compared to other countries, and/or the degradation of these compounds within the wastewater cleaning procedure or in soil after SS and manure application can be speculated as the reasons for the low antibiotic contents in the long-term treated soils.

4 Conclusions

Regardless of the location and fertilizer application, the results showed two major patterns of the fate of contaminants in the soils (Fig. 1): (i) For PAHs and OCPs (especially the DDT family), the results indicated long-term soil contamination, most probably originating from the past before the establishment of the long-term experiment, as also stated by Száková et al. (2018). The DDT levels especially documented high persistence and low biodegradability even a few decades after the application ban. We can also speculate that the differences in the DDT contents among the individual locations are determined by the different loads of the contaminants at the individual locations rather than the potential differences in the biodegradability of the pollutants due to the different soil physicochemical and biological properties. (ii) For PFASs, BFRs, and SMs, the results indicated that the soil could become a sink for these compounds due to the application of sewage sludge, confirming the original assumption. Evidently, none of the levels of the targeted contaminants represent a direct environmental risk. However, the potential sorption/desorption and/or potential degradation pattern should be more intensively investigated to elucidate the potential risk of sewage sludge-derived pollution from the long-term perspective. Moreover, contaminants such as PFASs, BFRs, and SMs should be regularly monitored in the soils and sewage sludge together with the "classical" contaminants (PAHs, OCPs, PCBs), i.e., compounds already monitored following the Public notice No. 153/2016 (2016).

References

Abad E, Martinez K, Planas C, Palacios O, Caixach J, Rivera J (2005) Priority organic pollutant assessment of sludges for agricultural purposes. Chemosphere 61:1358–1369

Allaire SE, Del Castillo J, Juneau V (2006) Sorption kinetics of chlortetracyline and tylosin on sandy loam and heavy clay soils. J Environ Qual 35:969–972

Amarakoon ID, Zvomuya F, Sura S, Larney FJ, Cessna AJ, Xu SW, McAllister TA (2016) Dissipation of antimicrobials in feedlot manure compost after oral administration versus fortification after excretion. J Environ Qual 45:503–510

An J, Chen HW, Wei SH, Gu J (2015) Antibiotic contamination in animal manure, soil, and sewage sludge in Shenyang, Northeast China. Environ Earth Sci 74:5077–5086

Antolin-Rodriguez J, Sanchez-Bascones M, Martin-Ramos P, Bravo-Sanchez CT, Martin-Gil J (2016) Estimation of PCB content in agricultural soils associated with long-term fertilization with organic waste. Environ Sci Pollut Res 23:12372–12383

Chen F, Ying G, Ma Y, Chen Z, Lai H, Peng F (2014a) Field dissipation and risk assessment of typical personal care products TCC, TCS, AHTN and HHCB in biosolid-amended soils. Sci Total Environ 470-471:1078–1086

Chen CH, Zhou QX, Cai Z (2014b) Effect of soil HHCB on cadmium accumulation and phytotoxicity in wheat seedlings. Ecotoxicology 23:1996–2004

Chow KL, Man YB, Tam NFY, Liang Y, Wong MH (2015) Uptake and transport mechanisms of decabromodiphenyl ether (BDE-209) by rice (*Oryza sativa*). Chemosphere 119:1262–1267

Clarke RM, Cummins E (2015) Evaluation of "classic" and emerging contaminants resulting from the application of biosolids to agricultural lands: a review. Hum Ecol Risk Assess 21:492–513

Cleary DW, Bishop AH, Zhang LH, Topp E, Wellington EMH, Gaze WH (2016) Long-term antibiotic exposure in soil is associated with changes in microbial community structure and prevalence of class 1 integrons. FEMS Microbiol Ecol 92:fiw159

Ding HY, Wu YX, Zou BC, Lou Q, Zhang WH, Zhong JY, Lu L, Dai GF (2016) Simultaneous removal and degradation characteristics of sulfonamide, tetracycline, and quinolone antibiotics by laccase-mediated oxidation coupled with soil adsorption. J Hazard Mater 307:350–358

During RA, Gath S (2002) Tillage effects on the accumulation of polychlorinated biphenyls in biosolid-amended soils. J Plant Nutr Soil Sci 165:299–304

Elskens M, Pussemier L, Dumortier P, Van Langenhove K, Scholl G, Goeyens L, Focant JF (2013) Dioxin levels in fertilizers from Belgium: determination and evaluation of the potential impact on soil contamination. Sci Total Environ 454:66–372

Feng Y, Li ZJ, Hao XQ (2016) Impacts of soil organic matter, iron-aluminium oxides and pH on adsorption-desorption behaviors of oxytetracycline. Res J Biotechnol 11:121–131

Gao P, Ding YJ, Li H, Xagoraraki I (2012) Occurrence of pharmaceuticals in a municipal wastewater treatment plant: mass balance and removal processes. Chemosphere 88:17–24

Guerra P, Kleywegt S, Payne M, Svoboda ML, Lee HB, Reiner E, Kolic T, Metcalfe C, Smyth SA (2015) Occurrence and fate of trace

contaminants during aerobic and anaerobic sludge digestion and dewatering. J Environ Qual 44:1193–1200

Higgins CP, Luthy RG (2006) Sorption of perfluorinated surfactants on sediments. Environ Sci Technol 40:7251–7256

Hong S, Khim JS, Park J, Kim M, Kim WK, Jung J, Hyun S, Kim JG, Lee H, Choi HJ, Codling G, Giesy JP (2013) In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River estuaries of South Korea. Sci Total Environ 445-446:136–145

Hou J, Wang C, Mao DQ, Luo Y (2016) The occurrence and fate of tetracyclines in two pharmaceutical wastewater treatment plants of northern China. Environ Sci Pollut Res 23:1722–1731

Körschens M (2006) The importance of long-term field experiments for soil science and environmental research-a review. Plant Soil Environ 52:1–8

Kulhánek M, Balik J, Černý J, Vašák F, Shejbalová Š (2014) Influence of long-term fertilizer application on changes of the content of Mehlich-3 estimated soil macronutrients. Plant Soil Environ 60: 151–157

Lee HJ, Kim CJ, Hong GH, Hong SH, Shim WJ, Kim GB (2014) Congener-specific accumulation and environmental risk assessment of polybrominated diphenyl ethers in diverse Korean sewage sludge types. Environ Sci Pollut Res 21:7480–7488

Li JH, Zhou BX, Xue B, Mo QL, Cai WM (2011) Influence of heavy metals and surfactants on the adsorption of tetracyclines to sediment. Res J Chem Environ 15:71–76

Li YY, Shi S, Zhang L, Liu YS (2016a) Global trends and performances of publication on sewage sludge from 1991 to 2012. In: Li J, Dong F (eds) Selected proceedings of the tenth international conference on waste management and technology Book Series: Procedia Environmental Sciences 31:65–74

Li WL, Ma WL, Jia HL, Hong WJ, Moon HB, Nakata H, Minh NH, Sinha RK, Chi KH, Kannan K (2016b) Polybrominated diphenyl ethers (PBDEs) in surface soils across five Asian countries: levels, spatial distribution, and source contribution. Environ Sci Technol 50:12779–12788

Macherius A, Eggen T, Lorenz WG, Reemtsma T, Winkler U, Moeder M (2012) Uptake of galaxolide, tonalide, and triclosan by carrot, barley, and meadow fescue plants. J Agric Food Chem 60:7785–7791

Madaras M, Stehlíková I, Teplá M (2013) The long-term field experiments and their merit for sustainable agriculture. Crop Research Institute, Prague (in Czech)

McClellan K, Halden RU (2010) Pharmaceuticals and personal care products in US biosolids. In: Halden RU (Ed) Contaminants of emerging concern in the environment: ecological and human health considerations. Book Series: ACS Symposium Series 1048:199–211

Meijer SN, Halsall CJ, Harner T, Peters AJ, Ockenden WA, Johnston AE, Jones KC (2001) Organochlorine pesticide residues in archived UK soil. Environ Sci Technol 35:1989–1995

Naile JE, Khim JS, Hong S, Park J, Kwon BO, Ryu JS, Hwang JH, Jones PD, Giesy JP (2013) Distributions and bioconcentration characteristics of perfluorinated compounds in environmental samples collected from the west coast of Korea. Chemosphere 90:387–394

Nelson KL, Brozel VS, Gibson SA, Thaler R, Clay SA (2011) Influence of manure from pigs fed chlortetracycline as growth promotant on soil microbial community structure. World J Microbiol Biotechnol 27:659–668

Odukkathil G, Vasudevan N (2013) Toxicity and bioremediation of pesticides in agricultural soil. Rev Environ Sci Biotechnol 12:421–444

Oleszczuk P (2007) Organic pollutants in sewage sludge-amended soil part I. General remarks. Ecol Chem Eng 14:65–76

Österas AH, Allmyr M, Sternbeck J (2015) Screening of organic pollutants in sewage sludge amended arable soils. Swedish Environmental Protection Agency

Ostermann A, Gao J, Welp G, Siemens J, Roelcke M, Heimann L, Nieder R, Xue QY, Lin XY, Sandhage-Hofmann A (2014) Identification of soil contamination hotspots with veterinary antibiotics using heavy metal concentrations and leaching data-a field study in China. Environ Monit Assess 186:7693–7707

Pan LL, Sun JT, Wu XD, Wei Z, Zhu LZ (2016) Transformation of hydroxylated and methoxylated 2,2 ',4,4 ',5-brominated diphenyl ether (BDE-99) in plants. J Environ Sci 49:197–202

Plassmann MM, Berger U (2013) Pefluoroalkyl carboxylic acids with up to 22 carbon atoms in snow and soil samples from a ski area. Chemosphere 91:832–837

Plosz BG, Leknes H, Liltved H, Thomas KV (2010) Diurnal variations in the occurrence and the fate of hormones and antibiotics in activated sludge wastewater treatment in Oslo, Norway. Sci Total Environ 408:1915–1924

Public notice No. 153/2016 (2016) About the conditions for the protection of the agricultural soil quality. Legal code of The Czech Republic, pp 2692–2699

Ray P, Chen CQ, Knowlton KF, Pruden A, Xia K (2017) Fate and effect of antibiotics in beef and dairy manure during static and turned composting. J Environ Qual 46:45–54

Roccaro P, Vagliasindi FGA (2014) Risk assessment of the use of biosolids containing emerging organic contaminants in agriculture. In: Ranzi E, Kohse Hoinghaus K (eds) ICONBM: international conference on biomass, PTS 1 and 2. Book Series: Chemical Engineering Transactions 37:817–822

Rychen G, Jurjanz S, Fournier A, Toussaint H, Feidt C (2014) Exposure of ruminants to persistent organic pollutants and potential of decontamination. Environ Sci Pollut Res 21:6440–6447

Santos JL, Aparicio I, Santos A, Alvarez F, Lopez-Artiguez M, Olano D, Garcia S, Alonso E (2009) Presence of organic pollutants in sludge from anaerobic wastewater stabilization ponds. Desalin Water Treat 4:116–121

Singh RP, Agrawal M (2008) Potential benefits and risks of land application of sewage sludge. Waste Manag 28:347–358

Spielmeyer A, Stahl F, Petri MS, Zerr W, Brunn H, Hamscher G (2017) Transformation of sulfonamides and tetracyclines during anaerobic fermentation of liquid manure. J Environ Qual 46:160–168

Sseburege P, Wasswa J, Mbabazi J, Nyanzi SA, Kiremire BT, Marco JAM (2010) Organochlorine pesticides in soils from south-western Uganda. Chemosphere 78:1250–1255

Száková J, Pulkrabová J, Černý J, Mercl F, Švarcová A, Gramblička T, Najmanová J, Tlustoš P, Balík J (2018) Selected persistent organic pollutants (POPs) in the rhizosphere of sewage sludge-treated soil: implications for the biodegradability of POPs. Arch Agron Soil Sci:1–16. https://doi.org/10.1080/03650340.2018.1543945

Topp E, Metcalfe CD, Boxall AB, Lapen DR (2010) Transport of PPCPs and veterinary medicines from agricultural fields following application of biosolids or manure. In: Halden RU (ed) Contaminants of emerging concern in the environment: ecological and human health considerations. Book Series: ACS Symposium Series 1048:227–240

Umlauf G, Christoph EH, Lanzini L, Savolainen R, Skejo H, Bidoglio G, Clemens J, Goldbach H, Scherer H (2011) PCDD/F and dioxin-like PCB profiles in soils amended with sewage sludge, compost, farmyard manure, and mineral fertilizer since 1962. Environ Sci Pollut Res 18:461–470

Vane CH, Kim AW, Beriro DJ, Cave MR, Knights K, Moss-Hayes V, Nathanail PC (2014) Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of greater London, UK. Appl Geochem 51:303–314

Vašák F, Černý J, Buráňová Š, Kulhánek M, Balík J (2015) Soil pH changes in long-term field experiments with different fertilizing systems. Soil Water Res 10:19–23

Venkatesan AK, Halden RU (2014) Brominated flame retardants in US biosolids from the EPA national sewage sludge survey and chemical persistence in outdoor soil mesocosms. Water Res 55:133–142

Wang Y, Luo C, Li J, Yin H, Li X, Zhang G (2011) Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China. Environ Pollut 159:2443–2448

Wilson SC, Alcock RE, Sewart AP, Jones KC (1997) Persistence of organic contaminants in sewage sludge-amended soil: a field experiment. J Environ Qual 26:1467–1477

Xiang L, Wu, XL, Jiang YN, Yan QY, Li YW, Huang XP, Cai QY, Mo CH (2016) Occurrence and risk assessment of tetracycline antibiotics in soil from organic vegetable farms in a subtropical city, south China. Environ Sci Pollut Res 23:13984–13995

Xiao F, Simcik MF, Halbach TR, Gulliver JS (2015) Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: migration and implications for human exposure. Water Res 72:64–74

Yang J, Metcalfe CD (2006) Fate of synthetic musks in a domestic wastewater treatment plant and in an agricultural field amended with biosolids. Sci Total Environ 363:149–165

Yi LY, Zhao HH, Yuan Z, Zhou DL, Liang YT (2016) Depression of soil microbial respiration, ammonification and cellulose degradation under the stress of antibiotic residuals. Environ Eng Manag J 15:2189–2194

Zennegg M, Munoz M, Schmid P, Gerecke AC (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012). Environ Int 60:202–208

Zhu Z, Chen S, Zheng J, Tian M, Feng A, Luo X, Mai B (2014) Occurrence of brominated flame retardants (BFRs), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs) in agricultural soils in a BFR-manufacturing region of North China. Sci Total Environ 481:47–54