Environment International 60 (2013) 202–208

Contents lists available at ScienceDirect

Environment International

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

Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012)

Markus Zennegg [a], Maria Munoz [a,b], Peter Schmid [a], Andreas C. Gerecke [a,*]

[a] Empa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Dübendorf CH-8600, Switzerland
[b] Chemical Engineering Department, University of Alicante, Ap. 99, 03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 11 June 2013
Accepted 26 August 2013
Available online 23 September 2013

Keywords:
Biosolids
PCB
PCDD/FBFR
PBDE
PFOS

ABSTRACT

The analysis of temporal trends is a key tool to assess the success of national and international regulations on chemical pollution. Persistent organic pollutants (POPs) are chemical pollutants, which are not only harmful, but also because of their slow environmental degradation they pose a long-time risk.
In this study, concentrations of selected POPs were measured between 1993 and 2012 in digested sewage sludge from eight municipal waste water treatment plants. Polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-dioxins and furans (PCDD/Fs), which have been banned or restricted for decades, exhibited decreasing trends with apparent half-lives between 9 and 12 years. Polybrominated diphenyl ethers (PBDEs) and long-chain perfluorinated acids showed no clear trend, which reflects the recent introduction of regulations. The analysis of octabromodiphenyl ethers did not reveal indications for reductive debromination of decabromodiphenyl ether; however the analysis of total bromine showed that up to 14% of the total bromine load in sewage sludge originated from PBDEs (average 2%). This is the first study to report temporal trends for more than 20 years of series POPs in sewage sludge.

1. Introduction

Persistent organic pollutants (POPs) are anthropogenic chemicals, which possess harmful properties and which degrade slowly in the environment. Therefore, POPs pose a long-term threat to human health and the environment. POPs have multiple purposes such as insecticides (e.g., DDT) or industrial chemicals; chlorinated dibenzo-dioxINS and -furans are POPs, which are formed as side-products during synthesis or combustion. Because of their negative properties many POPs are currently banned or restricted, but others are still in use (Howard and Muir, 2010; Muir and Howard, 2006). The Stockholm Convention on Persistent Organic Pollutants regulates the most important POPs at a global scale (UNEP, 2001). The convention asks for action to reduce the reservoir of banned POPs and for plans to evaluate the success of the regulatory measures.

Sewage sludge has been proposed to measure the emissions of hydrophobic contaminants from human activity in cities and villages, or more general from the anthroposphere (Harrison et al., 2006; Kupper et al., 2004). Sewage sludge incorporates hydrophobic compounds, which enter the waste water treatment plants via the sewer system. Sources include atmospheric deposition and wash-off by rain into combined sewer systems, human excretions and washing of textiles and other materials. Two main advantages of sewage sludge as sampling medium are that sewage sludge integrates pollution over whole catchment areas and that sewage sludge is much more easily available than other matrices such as sediments or biological samples, which also have been used to monitor temporal trends of POPs (de Boer et al., 2010; Kohler et al., 2008; Norén and Meironyte, 2000; Zennegg et al., 2007). Additionally, sewage sludge is applied to agricultural soils in many countries, but not in Switzerland, which makes it important to know the concentrations and temporal trends of pollutants (Passuello et al., 2010).

Despite the advantages of sewage sludge and the need for data on temporal trends, only a few papers investigated temporal trends of selected compounds in sewage sludge (polybrominated diphenyl ethers) (PBDEs) (Hale et al., 2012), and perfluorinated acids (PFOS and PFOA) (Sun et al., 2011). Recently, there was a first study that systematically investigated temporal trends of a large number of organic compounds in sewage sludge (Olofsson et al., 2012). Of the investigated 77 compounds, 18 showed statistically significant trends, thereof 75% decreasing. However, the observed time period comprised only seven years (2004–2010) and thus long time-trends could not be observed.

In this paper, we wanted to expand the knowledge on temporal trends of POPs by investigating sewage sludge over a time period of more than 20 years. Thereby we selected two classes of POPs, which have been banned or restricted more than three decades ago, i.e. polychlorinated biphenyls (PCBs; used as plasticizers and isolating fluids) and polychlorinated dibenzo-dioxINS and -furans (PCDD/Fs; by-products of combustion and synthesis processes). And we investigated two classes

* Corresponding author. Tel.: +41 58 765 4953.
E-mail address: andreas.gerecke@empa.ch (A.C. Gerecke).

0160-4120/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.08.020

of compounds for which bans and/or restrictions were put into force only in the last decade, i.e. polybrominated diphenyl ethers (PBDEs; used as flame retardants) and long-chain perfluorinated acids, used as surface chemicals. To reflect differences in the catchment of waste water treatment plants, we investigated sewage sludge from eight plants, which serve between 4000 and 115,000 residents. The data enable a comparison between compounds, which have been regulated for years, and compounds, which have been regulated recently. In addition, the detailed analysis of congener patterns and the total bromine content enables conclusions on the sources and fate of PBDEs and PCDD/Fs.

2. Materials and methods

2.1. Sampling and sampling stations

Single samples ($n = 1$) of anaerobically stabilized sewage sludge (digested sludge) were collected from eight municipal waste water treatment plants (plants A–H, see Table S1) in the greater Zürich area in 1993, 2002, 2007 and 2012 (2008 instead of 2007 for PFOS and PFOA). The treatment plants served between 4000 and 115,000 people. In all treatment plants residential waste water was the most important source; no treatment plant served a heavily industrial area (see Table S1). The samples consisted of digested sewage sludge, which was taken before dewatering. The sewage sludge samples had a water content of approximately 95%. Samples were filled in pre-cleaned glass bottles and shipped directly to the laboratory. Upon arrival in the laboratory, samples were dried and ground. The dried samples were stored in the dark at room temperature until analysis. The concentrations of the analytes are given per dry mass (dm).

2.2. Analysis of PCDD/F, PCB and PBDE

The analysis of PCDD/F, PCB and PBDE was simultaneously carried out. About 10 g of dried sewage sludge was Soxhlet extracted with a mixture of acetone and hexane (1:1, v/v) during 24 h. The extract was poured into a flask and the volume adjusted to 250 ml. An aliquot of 50 ml was spiked with internal standards (the 17 $^{13}C_{12}$-labeled PCDD/F (EDF-4067, Cambridge Isotope Laboratories, Andover, MA, USA), the $^{13}C_{12}$-labeled mono- and non-ortho substituted PCB (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), (EC-4937, Cambridge Isotope Laboratories, Andover, MA, USA), the $^{13}C_{12}$-labeled indicator-PCB (i-PCB = PCB-28, -52, -101, -138, -153, and -180), (EC-4058, Cambridge Isotope Laboratories, Andover, MA, USA) and the $^{13}C_{12}$-labeled PBDE (mixture of 9 tri- through deca-BDE congeners, all from Cambridge Isotope Laboratories, Andover, MA, USA)).

The clean-up procedure consisted of three steps with a previous step of solvent exchange to hexane. First, a liquid–liquid extraction with fuming sulfuric acid (7% SO_3 in conc. H_2SO_4) was carried out to eliminate basic and oxidizable compounds. Second, the extract was treated with gel permeation chromatography (Biobeads SX-3 beads 35 cm × 2.5 cm i.d. column) to eliminate high molecular weight compounds and sulfur, which would otherwise interfere in the analysis. Then, the extract was passed through a multilayer silica gel column (4 g acidic silica (30% conc. sulfuric acid), 2 g basic silica (23% 1 M sodium hydroxide) and 3 g of neutral silica (deactivated with 10% water with n-hexane), and then the eluate was directed to a basic alumina column (12.5 g Alumina Super B1 conditioned at 600 °C for 16 h)).

The mono-ortho and di-ortho substituted PCB were eluted from the basic alumina column with a solution of 4% dichloromethane in n-hexane. PBDE were eluted from the basic alumina columns with a solution of 50% dichloromethane in n-hexane. For retention of the PCDD/F, a carbon column (0.275 g of 8% carbon PX-21 on Celite 545-AW) was placed in series. Finally, PCDD/F and non-ortho substituted PCB (77, 81, 126, and 169) were eluted from the carbon column by back flush with toluene. After addition of the recovery standards ($^{13}C_{12}$-PBDE 126 for PBDEs, $^{13}C_{12}$-1,2,7,8-TCDF for PCDD/F and $^{13}C_{12}$-PCB 70 for PCB), the fractions were analyzed by HRGC/MS using a 60 m × 0.25 mm DB-Dioxin column (film thickness 0.15 μm). Analysis of PBDE was carried out on a 30 m × 0.25 mm RTX-5 Sil MS capillary column (film thickness 0.10 μm). The resolution of the mass spectrometer was tuned to 8000–9000.

2.3. Analysis of PFAS (PFOS and PFOA)

The analysis of PFAS was described in detail in Sun et al. (2011). In brief, the sludge samples were spiked with ^{13}C-labeled internal standards and extracted three times with methanol. Each extraction was performed by shaking the slurry for 10 min, sonication for 20 min at 40 °C and centrifugation at 3500 rpm for 8 min. After addition of the Envicarb graphitized carbon adsorbent (300 mg), the combined extracts were gently shaken for 20 min and then centrifuged at 3500 rpm for 30 min. Before analysis, NH_4OH aqueous solution was added to obtain better chromatographic peak shape. Analysis of the target compounds was performed by a Varian 1200 LC-MS/MS. Separation was achieved by a 70 mm (length) × 2 mm (diameter) × 3 μm (particle size) Nucleodur C18 Gravity Column (Macherey- Nagel). The injection volume was 20 μL. A gradient mobile phase of 2.5 mM NH_4Ac in methanol/water 95:5 (A) and 2.5 mM NH_4Ac in water/methanol 95:5 (B) were used.

The MS/MS was operated in the electrospray negative ionization mode. Quantification of PFAS was performed through multiple reaction monitoring on the most intense two ions.

2.4. Analysis of total bromine content

The determination of total bromine (organic and inorganic) in the sewage sludge samples was carried out following the US EPA Method 5050 "Bomb preparation method for solid waste" (US EPA, 1994a) using an AC-350 calorimetric bomb (Leco Corporation, St. Joseph, MI, USA) and Method 9056 "Determination of inorganic anions by chromatography" (US EPA, 1994b) using a Dionex DX 500 Ion Chromatograph (Dionex Corp., CA, USA)

In brief, 0.5–1 g of sample was placed in the crucible of a calorimetric bomb. The bomb was filled with 10 mL of a sampling solution (HCO_3^{2-}/CO_3^{2-}). After completion of the combustion, a known amount of the solution is analyzed by ion chromatography. To calculate the concentration of the bromide ions in the solution, a four point calibration curve was used.

3. Results and discussion

3.1. Development of waste water treatment plant

In all investigated treatment plants, the population has been growing steadily in the past 20 years (see Table S1). The average increase per treatment plant was 25% (min. 14%, max. 48%). The total number of people in the catchment of the eight plants increased by 18%, which is very comparable to the population growth of 16% of Switzerland for the same time period. The dry sludge mass increased only by 7% from 1993 to 2012 in the eight plants. The amount of sludge per person decreased to 85% of the 1993 value. Thus, for compounds that had a steady emission per capita during the observation period, the concentration in the sludge should have increased by almost 18%.

3.2. POP concentrations and total fluxes to sewage sludge

In the most recent sampling campaign, DecaBDE exhibited the highest concentrations (median concentration 410 ng/g dry mass (ng/g dm)). The concentrations of the indicator PCB (Σ i-PCB) and PentaBDE were