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Temporal trends of chlorinated paraffins and polychlorinated biphenyls in Swiss soils☆

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ABSTRACT

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), are ubiquitous environmental contaminants that have been targeted by national regulations since the 1970–1980s, followed in 2004 by the worldwide regulation under the Stockholm Convention on POPs. However, concerns are growing regarding the emergence of additional POP-like substances, such as chlorinated paraffins (CPs), which have particularly large production volumes. Whereas short-chain CPs (SCCPs) have recently been restricted in Europe and are currently under evaluation for inclusion into the Stockholm Convention, medium-chain CPs (MCCPs) have received little attention. On the one hand, temporal trends of CPs in the environment have hardly been investigated. On the other hand, the effectiveness of the Stockholm Convention on environmental levels of PCBs is still a matter of debate. Here, we reconstructed temporal trends of SCCPs, MCCPs, and PCBs in archived soil samples from six sampling sites in Switzerland, covering the period 1989–2014 (respectively 1988–2013 for one site). Concentrations of SCCPs have decreased in soil since 1994, which indicates positive effects of the reduction of production of SCCPs in Europe and the increasingly stringent regulation. However, the decline in soil is slow with a halving time of 18 years. Concentrations of MCCPs have continuously increased in soil over the entire period 1989–2014, with a doubling between 2009 and 2014. The concentrations of MCCPs have surpassed those of SCCPs, showing their relevance today, partly as replacements for SCCPs. Soil concentrations of PCBs peaked in 1999, i.e. three decades later than worldwide production and use of PCBs, but earlier than the entry into force of the Stockholm Convention. PCBs follow a decline in soil with a halving time of approx. 8 years. This study shows the usefulness of sample archives for the reconstruction and interpretation of time trends of persistent environmental contaminants.

1. Introduction

Persistent Organic Pollutants (POPs) are anthropogenic compounds that are highly resistant to environmental degradation (persistence, P), accumulate in biota and humans (bioaccumulation, B), and have negative health effects (toxicity, T). POPs undergo long-range atmospheric transport (LRAT), resulting in their global distribution in the environment (Ballschmiter et al., 2002). Because of their negative properties, POPs have been targeted by several national and international regulations. The Stockholm Convention on POPs entered into force in 2004 and has been signed by more than 150 countries worldwide, with the goal to eliminate or reduce the emissions of POPs and their adverse effects in the environment (UNEP, 2001). Among the 26 substances or substance classes currently recognized as POPs by the Stockholm Convention, polychlorinated biphenyls (PCBs) represent a particularly relevant compound class ubiquitously distributed in the environment. PCBs have been widely used in the 1950s–1980s as dielectrics in capacitors and transformers and as plasticizers in paints and joint sealants (Erickson and Kaley, 2011).

The Stockholm Convention also foresees the inclusion of additional substances with POP-like properties (P, B, T, LRAT). Currently, short-chain chlorinated paraffins (SCCPs) are under evaluation as POP-candidates under the Stockholm Convention (UNEP, 2015). SCCP are complex mixtures of chlorinated *n*-alkanes with a carbon

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chain length of C10 to C13 and a chlorination degree typically between 30% and 70% (weight percentage of chlorine). The main application of SCCPs include their usage as high-pressure additives in metal working fluids and as flame retardants and softeners in plastics (e.g., PVC, polyester, neoprene) and rubber (Glüge et al., 2016b). SCCPs are also partly used as replacements for PCBs, as plasticizers and adhesives in sealants and paints (Fiedler, 2010). Although, in Europe the production of SCCPs has been discontinued since the early 2000 (UNEP, 2015) and the use of SCCPs has been restricted in the EU since 2015 (EC, 2004), their global production is expected to continuously increase and exceeds currently 160,000 t/a (Glüge et al., 2016b).

The most widely used alternatives to SCCPs today are medium-chain chlorinated paraffins (MCCPs), which have a chain length of C14 to C17 (UNEP, 2016). The knowledge about the properties of MCCPs is very scarce and they have not been regulated so far. However, indications about their persistence and potential for bioaccumulation are available (EC, 2005, 2011). Particularly worrisome are the enormous production amounts of MCCPs, representing a major share of the total CP production, which is currently exceeding 1 million t/a (Glüge et al., 2016b).

The large production and use of persistent chemicals leads also to their emissions into the environment and concentrations measurements are an important tool to monitor these releases. Data sets on temporal trends of POPs represent a particularly precious piece of information when assessing the past and present efficacy of emission control measures. The Stockholm Convention also requests the signatory countries to evaluate the effectiveness of the Convention by performing long-term monitoring of POPs in environmental matrices. However, temporal trends are very difficult to obtain, because long-term monitoring programs are expensive and require a durable financial and personal commitment. Additionally, the comparability of analytical methods has to be warranted over the entire monitoring period. Therefore, environmental specimen banks represent a valuable alternative to continuous monitoring efforts.

For PCBs, a few long-term monitoring programs exist and show a general decreasing trend of concentrations in air (e.g., Hung et al., 2016; Kong et al., 2014; Wöhrnschimmel et al., 2016), biota (e.g., Bignert et al., 1998; Braune, 2007; Fangstrom et al., 2005; Park et al., 2009), or humans (e.g., Lignell et al., 2009; Solomon and Weiss, 2002). However, because of the long lifetime of former applications (e.g., building materials), PCBs have still an appreciable reservoir and continue to be emitted from numerous diffusive sources (Bogdal et al., 2014; Breivik et al., 2007; Diamond et al., 2010; Diefenbacher et al., 2015a, 2016). For SCCPs and particularly for MCCPs, only very few data are available (e.g., Diefenbacher et al., 2015b), mainly due to their extremely challenging analysis methods (Tomy, 2010). Recent studies on temporal trends of SCCPs are only available from China, where sediment concentrations are still increasing (Li et al., 2014; Zeng et al., 2012, 2013). In Europe and North America, studies on temporal trends of SCCPs in sediment date back to more than a decade ago and indicated a leveling off (Iozza et al., 2008; NCP, 2003; Stern et al., 2005; Tomy, 1997; Tomy et al., 1999a). About temporal trends of MCCPs in the environment, no recent study is available. MCCPs have only been analyzed in one dated sediment core in Switzerland covering samples up to 2004 and showing, at that time, clearly increasing concentrations (Iozza et al., 2008).

Here, we present temporal trends of SCCPs, MCCPs, and PCBs in archived soil samples from six selected sites in Switzerland covering the period 1989–2014. The samples have been obtained from the Swiss Soil Monitoring Network (NABO), which is a reference measurement network assessing long-term trends of soil pollution and the success of environmental protection measures (Desaules et al., 2008; Gubler et al., 2015; Schmid et al., 2005). In this study, SCCPs and MCCPs represent current-use high-production volume chemicals with an urgent need for more information on their time trends. PCBs have been included as representatives for the legacy POPs with existing national and global regulations.

2. Materials and methods

2.1. Soil samples

2.1.1. Sampling sites

The NABO monitoring network operates long-term monitoring sites throughout Switzerland. Since the first sampling in the 1980s, each site has been re-sampled every five years. In this study, six sites were selected with the goal to include sites from different regions in Switzerland, with different land uses, but with similar soil properties (mainly the organic carbon content). The selected sites Langenthal and Unterschächen are located north of the Alps, Visp is situated in an Alpine valley, whereas the sites Sant'Antonino, Lugano, and Coldrerio are located south of the Alps (Fig. 1). These sites are characterized by different land uses, including coniferous forest (Visp and Langenthal), extensive grassland (Unterschächen), horticulture (Sant'Antonino), arable land (Coldrerio), and urban park (Lugano). Further properties of the soil samples and potential sources of environmental pollution at the six sampling sites are provided in the Supplementary Material (Table S1).

2.1.2. Soil sampling

For each sampling campaign and for each site, four replicate samples were collected from the upper 20 cm of the soil, including the top organic humus layer. Each sample consists of 25 pooled subsamples, which were taken using a steel gouge auger and which cover together a sampling area of 10 m by 10 m. Further information about the sampling, the procedure of drying, sieving, grinding, and homogenizing the soil samples have been reported in earlier investigations on organic pollutants in NABO soils (Desaules et al., 2008; Gubler et al., 2015; Schmid et al., 2005). Here, in total 35 archived soil samples were analyzed, covering a period of 25 years. Samples were available in 5 years interval, covering the years 1989–2014 for Visp, Langenthal, Lugano, and Coldrerio (series of six samples), the years 1988–2013 for Sant'Antonino (series of six samples), and the years 1989–2009 for Unterschächen (series of five samples).

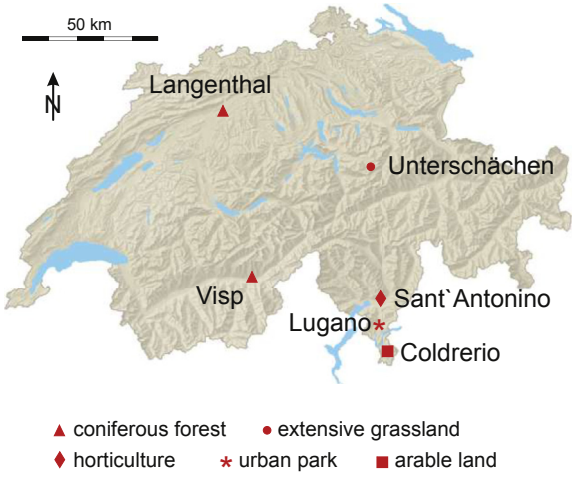

Fig. 1. Map of Switzerland with the location of the six sampling sites included in this study and covering different land uses as indicated on the map with different symbols. © 2016 swisstopo (JD100042).