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Distributions of new Stockholm Convention POPs in soils across South Korea

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ABSTRACT

In this study, we monitored the newly added Stockholm Convention persistent organic pollutants (POPs) HCHs, PeCBz, endosulfans, chlordecone, PBDEs, PBBs and PFCs in industrial, urban, and agricultural soils in South Korea, in order to evaluate their distributions and potential sources. These POPs were widely distributed throughout South Korea, and their concentrations and distributions were affected by land use, reflecting their sources. The overall concentrations of HCHs, PeCBz, endosulfans, PBDEs, and PFCs in soils were in the range of ND (non-detectable)–0.358 ng/g (average ± standard deviation: 0.060 ± 0.080 ng/g), ND–0.531 ng/g (0.083 ± 0.133 ng/g), 0.058–8.42 ng/g (2.19 ± 2.43 ng/g), 0.004–4.78 ng/g (0.68 ± 1.06 ng/g), and ND–1.62 ng/g (0.50 ± 0.46 ng/g), respectively. Agricultural soils showed the highest concentration of endosulfan, which was the most recently used pesticide monitored in this study. On the other hand, industrial soils contained the highest concentrations of PeCBz, PBDEs, and PFCs, which were mainly introduced to environment via the industrial activities.

1. Introduction

Environmental contamination by persistent organic pollutant (POP) is of serious concern due to their toxicity, persistence in the environment, bioaccumulation, and potential for long-range environmental transport (Jones and de Voogt, 1999; Wania and MacKay, 1996). Since POP contamination is a global environmental problem, POPs have been regulated under a global treaty, the Stockholm Convention on Persistent Organic Pollutants, which came into effect in 2004. In 2009 and 2011, following thorough evaluation, ten new POPs were added to the Stockholm Convention's annexes. These include hexachlorocyclohexanes (α-, β-, and γ-HCHs), chlordecone, pentachlorobenzene (PeCBz), endosulfans, polybrominated diphenyl ether (PBDEs), hexabromobiphenyls (PBBs), and perfluorooctane sulfonic acid (PFOS) (UNEP, 2009). Therefore, in order to implement the Stockholm Convention, it is necessary to conduct systematic assessments of the newly added chemicals in the environment.

Among the newly added POPs, HCHs, chlordecone, PeCBz and endosulfans are organochlorine pesticides (OCPs) that have been used widely across the world. Their production and use were banned in many countries due to their toxicity and environmental persistence, but they have been detected in various environmental media even in pristine mountain environment or in remote areas (Bailey et al., 2009; Li and Macdonald, 2005; Tao et al., 2011; Weber et al., 2010; Willett et al., 1998; Yang et al., 2013). HCHs have been detected at concentrations of 0.04–12.6 ng/g in soils of the Tibetan Plateau, which is one of the most remote and isolated regions in the world (Tao et al., 2011; Yang et al., 2013). Endosulfan (α-endosulfan) has been detected in air (0.01–16.5 pg/m^3), snow (0.09–1.09 ng/g), lake (0.001–0.137 ng/L), and sediment (0.04 ng/g) in the Arctic (Weber et al., 2010). Of the other compounds, PBDEs, PBBs, and PFCs have extensive industrial applications, and the continuous release of these compounds from various products has resulted in their ubiquitous distribution in the environment (Hites, 2004; Zareitalabad et al., 2013). Concentrations of these compounds in the environment are highly variable depending on their source locations. For example, PBDE concentrations in river sediment collected from 11 different countries are ranged from undetectable to 7190 ng/g (Hites, 2004). PFC concentrations in soils are ranged from 0.1 ng/g in agricultural areas to 58 ng/g in industrial areas (Zareitalabad et al., 2013). Soil can act as an important sink for POPs in the environment. POPs can be introduced to the soil either directly via point sources, or indirectly via atmospheric transport. Atmospheric POPs can accumulate in the surface environment via dry or wet deposition, even in remote mountain areas. In contrast, POPs in soil can be released to the atmosphere, surface water, and groundwater through volatilization, diffusion, leaching, and surface runoff. Thus, POP-contaminated soils are a potential long-term source of environmental pollution (Jones and de Voogt, 1999). Furthermore, bioaccumulation of POPs via food chain transfer from soil–plant–animal/human is an important pathway of human exposure. POPs that were heavily utilized in the past remain in soils for long periods of time owing to their environmental and biological persistence, and the residues continue to influence the environment and

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ecosystems (Jones and de Voogt, 1999). Therefore, investigation of POPs in soils is important in order to understand the fate and transport of POPs in the environment, and for risk assessment. However, compared to other environmental media monitoring of POPs in soils has not been extensively conducted yet.

In this study, we monitored soils throughout South Korea for the presence of POPs that were recently added to the Stockholm Convention's annexes, i.e., HCHs, PeCBz, endosulfans, chlordecone, PBDEs, PBBs, and perfluorinated compounds (PFCs), in order to evaluate their distributions and potential sources. The effects of land use on the levels and distributions of these POPs were evaluated at industrial, urban, and agricultural sites. This is the first nationwide monitoring study of these POPs in South Korea. Therefore, the findings can provide important information for the government's implementation of the Stockholm Convention.

2. Materials and methods

2.1. Sampling

Soil samples were collected at 33 sites, consisting of 8 industrial (i1–i8), 13 urban (u1–u13), 11 agricultural (a1–a11) and 1 control (c1) sites throughout South Korea, between April 2010 and May 2012 (Fig. 1). Industrial sites include major industrial complexes, where many petrochemical/chemical (i3, i6, i8), electronic (i4), vehicle (i7), and steel (i1, i2, i5) industries are concentrated. Urban sites consist of the 7 major big cities, Seoul (u2–4), Daejeon (u6), Daegu (u8), Gwangju (u9), and Pusan (u10), and 6 medium-sized cities across South Korea. Agricultural sites include cultivated land (a1, a2, a5–a8, a10), woodland (a3, a4), and grass-land (a9, a11). Control sample (c1) was collected near a meteorological observatory in Jeju Island, where no potential pollution sources are located nearby (Fig. 1). The detailed sampling information is summarized in Table 1. Averaged concentrations were reported for some sites, where sampling was conducted for consecutive years. At each site, five soil subsamples were taken from 0 to 5 cm below the surface, bulked into one sample, and homogenized to obtain a composite soil sample. The collected soil samples were stored in brown glass bottle at 4 °C, until further treatment.

2.2. Extraction and cleanup

The target compounds for analysis were eight OCPs, including α-HCH, β-HCH, γ-HCH, PeCBz, α-endosulfan, β-endosulfan, endosulfan sulfate, and chlordecone, and seventeen PBDE congeners (BDE-47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, and 191), five PBB congeners (BB-153, 154, 155, 156, and 169), perfluorooctanoic acid (PFOA), and PFOS. All soil samples were analyzed in duplicate. All reagents used for extraction and cleanup were above the high purity grade. Solvents were obtained from J.T. Baker® and their purities were 95% for hexane, 99.7% for toluene, 99.3% for acetone, 99.3% for methanol, and 99.9% for acetonitrile.

For OCP, PBDE, and PBB analysis, soil samples were extracted using Soxhlet extraction. Thirty grams of the soil samples was mixed with 10 g anhydrous sodium sulfate and Soxhlet extracted for 24 h with toluene/acetone (8:2, v/v) for OCPs and with toluene for PBDEs and PBBs. The extracted OCPs were cleaned and fractionated with Florisil

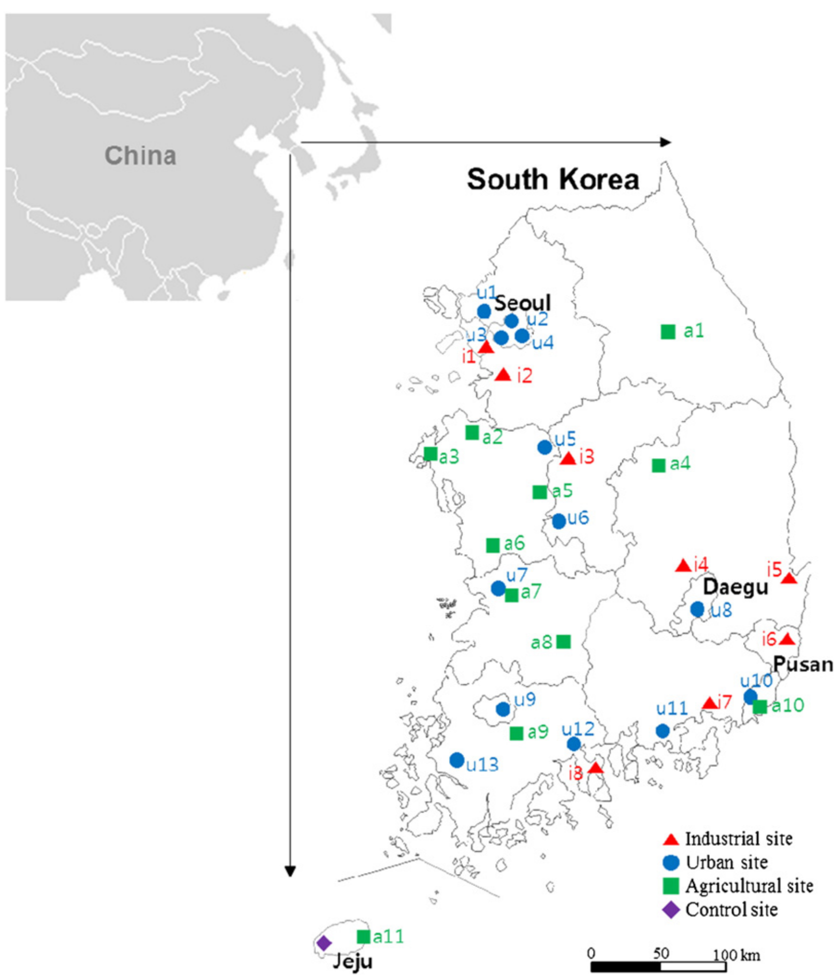

Fig. 1. Locations of soil sampling sites in South Korea.