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Long-range atmospheric transport of persistent organic pollutants to remote lacustrine environments

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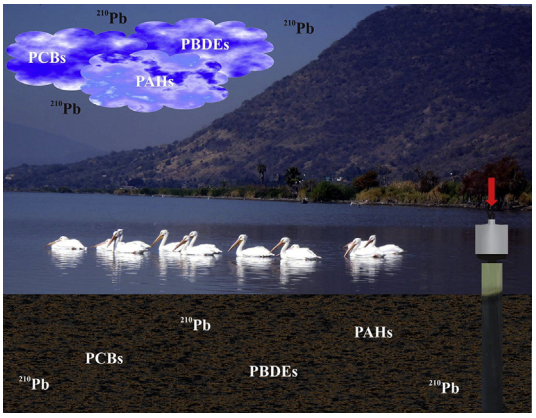
HIGHLIGHTS

- Persistent organic pollutants in soils and ^{210}Pb-dated lake cores from Central Mexico
- PCB and PBDE concentrations showed ongoing increasing contamination trends.
- Light brominated BDEs and lower chlorinated CBs abounded in soils and sediments.
- The prevalent POP source to lake sediments is long range atmospheric transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentrations, temporal trends and fluxes of persistent organic pollutants (POPs: PAHs, PCBs and PBDEs) were determined in soil and ^{210}Pb-dated sediment cores from remote lacustrine environments (El Tule and Santa Elena lakes) in rural areas of Central Mexico. In both areas, the concentrations of target analytes in soil and sediment samples were comparable and indicative of slightly contaminated environments. The prevalence of low-molecular-weight PAHs in soils suggested their mainly atmospheric origin, in contrast to the aquatic sediments where runoff contribution was also significant. Increasing contamination trends of PCBs and PBDEs were evident, showing maximum fluxes of 4.8 ± 2.1 and 0.3 ± 0.1 ng cm^{-2} a^{-1} for PCBs and PBDEs, respectively.

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The predominance of lower-brominated PBDEs and lower-chlorinated PCBs in soils and sediments indicated that their presence is mostly due to long-range atmospheric transport.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs) that are ubiquitous owing to their volatility, multiplicity of sources and transport mechanisms. They also show strong biomagnification potential in fish and mammals, from which they can be transferred to humans through consumption of contaminated food (Jones and de Voogt, 1999).

PAHs may enter the environment from both natural sources (e.g. plant synthesis, organic matter diagenesis, and forest and prairie fires) and anthropogenic processes such as the release of petrogenic PAHs through accidental oil spills and urban runoff, and of pyrogenic PAHs produced by the combustion of biomass and fossil fuel (Yunker et al., 2002). Some PAHs are considered to be potential human mutagens and carcinogens (ATSDR, 1995).

First synthesized in 1881 (Myers, 2007), PCBs were produced in the USA from 1929 onwards under the commercial name of Aroclors, until Monsanto voluntarily stopped production in the late 1970s. Other countries followed this decision (e.g. in Germany production of PCBs was stopped in 1983). PCBs were used in electrical transformers and capacitors as dielectric fluids, and in carbonless copy papers and inks (Harrison, 2001). Although no longer produced, PCBs may be released into the environment through improper disposal or leakage from older electrical equipment, the incineration of PCB-containing wastes, vehicular emissions and storm-water runoff (ATSDR, 2011). Potential adverse effects of PCBs include reduced hatchability, embryonic deformities, immune suppression and mortality in top predators (Skaare et al., 2000; Su et al., 2014) as well as neurobehavioral effects in humans due to prenatal exposure to PCBs (Suzuki et al., 2010).

PBDEs are used as flame retardants in a wide range of products including polyurethane foam, plastics, textiles and electronics. They were introduced commercially in the 1970s, produced as three commercial mixtures (penta-BDE, octa-BDE and deca-BDE) which have been used as additives, i.e. not chemically bound to the substrates, and are thus prone to leak into the environment (Barrera-Cordero et al., 2004). The commercial use of penta-BDE and octa-BDE mixtures has been banned in the USA and Europe since 2004 (USEPA, 2013); deca-BDE has been banned in electrical and electronic applications in Europe since 2008 and has been phased out for all applications in the USA and Canada since 2013 (BSEF, 2014). Nonetheless, since many products manufactured with PBDEs remain in use, volatilization becomes a diffuse source of PBDEs to the air, even more significant than point sources (Song et al., 2004). The major point sources of PBDEs are the incineration of disposed commercial products, sewage and sludge releases, and leaching from landfills (Darnerud et al., 2001). Several studies have found associations between human body burdens of PBDEs (primarily penta-BDE) and health effects such as thyroid hormone and androgen abnormalities, cryptorchidism, and low birth weights (Stapleton et al., 2009).

POPs may enter the gas phase under environmental temperatures, and hence may volatilize from soils, vegetation and water bodies to the atmosphere, where POPs can attach to aerosols, depending on the ambient temperature and the physico-chemical properties of the contaminant. Owing to their resistance to breakdown reactions in air, POPs can travel long distances, and the cool temperatures at higher latitudes and altitudes favor deposition from the atmosphere onto soil and water (Jones and de Voogt, 1999, Wania and Mackay, 1996).

Hydrophobic in nature, POPs are easily sequestered by settling particles in aquatic environments and they accumulate in sediments, which may become environmental archives of contaminant inputs. The study of undisturbed dated sediment cores is useful for the assessment of long-term temporal trends of POP concentrations and fluxes, and for identifying their provenance. Sedimentary records of POPs from urban lakes mainly reflect direct inputs of contaminants from wastewater effluents and municipal runoff, whereas in remote lakes the different transportation pathways could have considerable effects on the composition of POPs in different environmental settings (Macdonald et al., 2000). Thus, lake sediment cores collected from non-urbanized areas, far from point sources and where atmospheric transport and deposition can be the major input pathway for POPs (Shen et al., 2006), can provide a record useful in the evaluation of POP contamination due to long-range atmospheric transport.

The global temporal trends and the composition of the POP assembly in sediments have often varied according to the documented history of environmental releases of POPs, related to i) global transitions among chief energy sources; i.e. wood, coal, oil and natural gas, and economic development phases (e.g. PAHs), or ii) the production, commercialization and banning of those groups without known natural sources (e.g. PCBs and/or PBDEs). For instance, the global pattern of PAH concentrations and fluxes to sediments is expected to show an increasing trend from the early 1900s attributed to the replacement of wood by coal as the largest source of primary energy, and the accelerated economic development after the 2nd World War, followed by a decrease in the latter half of the 20th century due to governmental controls on fuel and coal combustion emissions (Leorri et al., 2014). PCB concentrations are expected to be detectable in the environment from the early 1930s (onset of their industrial production), to show an increasing trend between the 1950s and late 1970s (peak global demand), and to decline rapidly since then, due to the restrictions on PCB use. PBDEs would show detectable levels since the middle 1970s and peak concentrations in the 1990s, in agreement with the beginning of their industrial production and extensive use during the 1980s and early 1990s. Since then, although the trends are found to level off in Europe, they continue to increase in North America up to the early 2000s, owing to differences in the timelines of production and use of technical PBDE products between the two continents (Cheng et al., 2007).

Data from POP monitoring are scarce in Mexico. Most of the studies have been related to air pollution, e.g. by PAHs (Hwang et al., 2003; Calderón-Segura et al., 2004; Velasco et al., 2004; Marr et al., 2006; Amador-Muñoz et al., 2011, 2013), PCBs (Alegria et al., 2008) and PBDEs (Bohlin et al., 2008) in Mexico City, and by PCBs and PBDEs in suburban areas (Shen et al., 2006). A few studies have shown PAH and PCB contamination in various Mexican aquatic environments, where contamination sources were evident (Armenta-Arteaga and Elizalde-González, 2003; Piazza et al., 2008, 2009; Ruiz-Fernández et al., 2012a,b). Other studies have shown the presence of PCBs in maternal plasma (Rodríguez-Dozal et al., 2012) and PBDEs in blood samples of women from an urban area (Lopez et al., 2006) and children from urban-industrial and rural areas (Pérez-Maldonado et al., 2009).

PCB consumption in Mexico started in the 1940s with the use of imported PCB-containing electrical equipment, but PCB imports were banned in 1988. PCBs are included in the Pollutant Release and Transfer Register (PRTR) of Mexico (SEMARNAT, 2012) and efforts have been made to establish a national inventory. Nearly 43,000 t of PCB waste