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Spatial and temporal distribution of pesticides and PCBs in the atmosphere using XAD-resin based passive samplers: A case study in the Quequén Grande River watershed, Argentina

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ABSTRACT

XAD-resin based passive air samplers were deployed at 10 sites in the Quequén Grande River watershed in Argentina during three periods to evaluate the spatial and temporal variations of pesticides and PCBs in the atmosphere. Endosulfan and chlorpyrifos were the most prevalent pesticide because of their continued usage in Argentina, while DDTs, HCHs, chlordanes, dieldrin and heptachlors registered lower levels, reflecting their use in the past. Atmospheric endosulfan levels were 1–2 orders of magnitude higher during the application period (application: 800–12,000 pg/m^3, pre- and post-application: < 2–350 pg/m^3), suggesting that its use in the area continued even after a ban came into effect. The remaining organochlorine pesticides also reached higher concentrations during this period, which is more likely attributable to temperature controlled air-surface exchange than current applications. The highest concentrations of chlorpyrifos were recorded during the application period, in particular at agricultural sites, where its use is wide-spread on soybean fields. The fungicide chlorothalonil was found predominantly at urban sites and in proximity to Quequén harbor, suggesting that its use might be domestic and as a biocide in antifouling paints. A different temporal pattern was observed for the herbicide trifluralin, suggesting its use in the early stages of the wheat-growing season during winter. Limited spatial variations in PCBs levels indicate a diffuse contamination source in the study area, while their relatively high correlation with temperature suggests re-volatilization from local sources. Relative enrichment of lighter PCBs congeners could be attributed to re-evaporation from secondary sources as well as atmospheric transport from urban sites.

1. Introduction

In the past two decades, Argentina has experienced strong growth in agricultural production, driven mostly by the expansion of soybean cultivation. This process involved a massive increase in the use of pesticides (Villamil Lepori et al., 2013), leading to the occurrence of residues in the environment. Whereas most organochlorine pesticides (OCPs) have been banned in Argentina since approximately 1998, endosulfan continued to be used until July 2013. As recalcitrant compounds, OCPs may persist in the environment, particularly in soils, for many years, even decades after their use has ceased (Aigner et al., 1998). Current-use pesticides (CUPs) include a diverse group of insecticides (organophosphate compounds such as chlorpyrifos), herbicides (triazines, acetanilides and dinitroanilines such us trifluralin) and fungicides (i.e.chlorothalonil), which are deemed to be less bioaccumulative and less persistent than OCPs (Kannan et al., 2006). Nevertheless, some CUPs show evidence of relatively longer lifetime in the environment than predicted (Ruggirello et al., 2010). On the other hand, urban and industrial activities are associated with the release of different classes of pollutants to the environment. In particular, polychlorinated biphenyls (PCBs) were widely used in electrical transformers until they were forbidden in 2010 in Argentina. However, the lack of control of equipment still containing PCBs leads to the presence of point-sources. Unintentional emissions of PCBs are related to open burning events or the incineration of products containing PCBs and constitute also a significant source to the environment (Gouin et al., 2008a).

The occurrence of pesticides in the atmosphere may occur as a result

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of different processes. For banned and persistent pollutants, such as OCPs and PCBs, volatilization and wind erosion from historically contaminated soils are usually the major factors controlling their presence in the atmosphere, while CUPs are preferentially released during application operations as well as a consequence of volatilization (Hayward et al., 2010).

XAD-resin based passive air samplers (XAD-PAS) have been used worldwide to monitor semi volatile organic contaminants (Wania et al., 2003; Shen et al., 2005; Shunthirasingham et al., 2010, 2011; Nasir et al., 2014). The main advantages of this passive sampler are its low cost, simple operation, independence of electrical power and a large uptake capacity (Wania et al., 2003). In Argentina, previous studies have determined air concentrations of polycyclic aromatic hydrocarbons (Wannaz et al., 2013), OCPs (Tombesi et al., 2014; Fillmann et al 2015; Astoviza et al., 2016a), PCBs and polybrominated diphenyl ethers (Pozo et al., 2009; Pegoraro et al., 2016) at urban and agricultural sites using polyurethane foam disks passive air samplers (PUF-PAS). Moreover, as part of the Latin American Atmospheric Passive Sampling Network (LAPAN), the occurrence of POPs has been monitored in different regions of Argentina involving the use of pine needles and XAD-PAS (Miglioranza et al., 2013).

In this study, XAD-PASs were deployed at ten sites in the Quequén Grande River (QGR) watershed during three consecutive periods from 2013 to 2014. The objectives of this work were: (i) to study the temporal variations of pesticides and PCBs in the atmosphere of a typical agricultural watershed in particular with respect to pesticide application periods, and (ii) to asses spatial trends between different land uses.

2. Materials and methods

2.1. Study area

The Quequén Grande River (QGR) basin is located in southern Buenos Aires province, Argentina. With a total area of 9 900 km^{2}it is the largest watershed in the province. Mean annual temperature is 14 °C, and average minimum and maximum temperatures are 7.3 °C and 20 °C in July and January, respectively. Annual precipitation in the catchment is between 700 and 900 mm (Varela and Teruggi, 2002). In the upper QGR basin, agriculture and livestock are the main land uses. The middle basin is characterized by extensive agriculture using direct seeding system. The major crops in the region are soybean, wheat and sunflower. The lower basin includes mostly urban activities, linked to the presence of Necochea (ca. 85,000 residents), the main city of the QGR basin, which is located along the mouth of the river. Moreover, the estuary of the QGRis occupied by a harbor, one of the most important grain exporting ports in Argentina.

2.2. Sampling sites

Ten sampling sites were selected according to land uses (Fig. 1 and Fig. S1). The QGR watershed has three well-defined zones: the upper zone, where agricultural-livestock activities are predominant (sites U1, U2, U3 and U4), the middle zone, in which agriculture is the main activity (sites M1and M2) and the lower zone, which represents an urban area (sites L1, L2, L3 and L4). Coordinates and a description of the sampling sites are given in Table S1 of the Supporting Information.

2.3. Sampling method

At each sampling site, duplicates XAD-PAS of the type described previously in Wania et al. (2003) were securely placed at about 3 m above the ground. The sampling sorbent was pre-cleaned Amberlite XAD-2 resin (Supelco, Supelpak-2, 20/60 mesh). Additional duplicate XAD-PAS were placed approximately 1 m above the ground at sites M1 and M2. This comparatively low deployment height was used in order to monitor the potential emission of pesticides from soils.

2.4. Periods of exposure

Monitoring was conducted during three consecutive periods, covering a full year (2013–2014). XAD-PAS were retrieved and replaced approximately every four to five months. Period 1 was from autumn to early spring (May to September/October; pesticide pre-application period). Period 2 was from early spring to summer/early autumn (September/October to February/April, pesticide application period). Period 3 was from summer/early autumn to winter (February/April to July/September, pesticide post-application period). Details about the sampling schedule are given in Table S1 of the Supporting Information. This first period coincided with the ban on endosulfan use in Argentina (July 2013; SENASA, 2011).

2.5. Extraction and cleanup

After transfer from the mesh cylinder to the Soxhlet extractor, the XAD resin was spiked with 20 ng of PCB #103 as internal standard. Compounds were analyzed with the method by Metcalfe and Metcalfe (1997), with modifications by Miglioranza et al. (2003). After Soxhlet extraction for 6 h with a mixture of hexane-dichloromethane (50:50), extracts were concentrated under vacuum and nitrogen flow to a final volume of 2 ml. Then, samples were purified by elution through activated silica gel, which had been heated to 200 °C for24 h. Extracts were concentrated and kept at −20 °C until analysis.

2.6. Gas chromatographic analyses

OCPs (α-, β-, γ- and δ-HCH, α- and β-endosulfan, endosulfan sulfate, *p,p′*-DDT, *p,p′*-DDE,*p,p′*-DDD, α- and γ-chlordane, *trans*-nonachlor, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide) and PCBs (IUPAC #8,18, 28, 31, 44, 52, 66, 87, 101, 105, 110, 118, 123, 126, 128, 138, 149, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209) were identified and quantified using a Shimadzu gas chromatograph GC-17A with an electron capture detector (ECD), equipped with a fused-silica SPB-5 capillary column (30 m, 0.25 mm i. d., 0.25 mm film thickness, Supelco, Bellefonte, PA, USA). 1 μL was injected in splitless mode at 275 °C and the ECD was at 290 °C. The oven temperature program was: 100 °C held for 1 min, followed by an increase of 5 °C/min to 150 °C, held for 1 min, increase 1.5 °C/min to 240 °C, and then 10 °C/min to 300 °C, held for 10 min. Ultra-high purity helium was used as carrier gas (1.5 mL/min) and nitrogen as make-up gas (Miglioranza et al., 2003).

Chlorpyrifos, chlorothalonil and trifluralin were identified and quantified using an Agilent 7890A GC coupled with an Agilent 7000A triple quadrupole mass spectrometer (MS/MS), equipped with an HP-5MS column (30 m × 0.25 mm i. d., 0.25 μm film thickness, J & W Scientific, Folsom, CA). The GC inlet was operated in splitless mode at 250 °C. Injection volume was 1 μL. Carrier gas helium had a flow rate of 1.2 mL/min. The oven temperature program was 70 °C for 1 min, increase by 50 °C/min to 150 °C, then 6 °C/min to 200 °C, held for 3 min, and 10 °C/min to 300 °C, held for 1 min. The ions are given in Table S2 of the Supporting Information.

2.7. Derivation of volumetric air concentrations

Results are reported in pg/m^3 (C_{air}), generated by dividing the sampler concentration (C_{PAS}; ng/sampler) by the product of the deployment period (t) and the sampling rate (R, m^3/(day·sampler)) (Wania et al., 2003):

$$C_{air} = \frac{C_{PAS}}{R \cdot t}$$

While compound-specific sampling rates compiled from the literature (provided in Table S3) were applied, volumetric concentrations derived from PAS have considerable uncertainties due to sampling rates