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Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin

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HIGHLIGHTS

► OCPs, PCBs and PBDEs were found in soils, sediments, SPM, streamwater and macrophytes.
► Pesticides represented 70% of the total pollutants and *pp*′-DDE was the main pesticide found in all matrixes.
► The relation PCBs/PBDEs > 1 agrees with worldwide tendency.
► Macrophytes played a key role in reducing pollutant levels in the river.
► Monitoring critical points of legacy contamination is crucial for watershed management.

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ABSTRACT

This work reports the occurrence and distribution of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in soil, sediment, suspended particle matter (SPM), streamwater and macrophytes, along the Río Negro basin, Argentinean Patagonia. The clear predominance of OCPs among all matrices indicates the impact of agriculture on the watershed. The highest levels were found for *pp*′-DDE which represented up to 95% in agricultural soils (42.0–1.27 x 10^3 ng/g d.w) from the Upper Valley (upstream), where long and historical intensive fruit cultures have been settled and represent a hot spot of legacy pesticides for the environment. The insecticide endosulfan, currently in use, was also found in all matrices. Levels ranged between 0.3 and 708.0 ng/g d.w, being the highest concentrations those of SPM from the Middle Valley, just before the delta area, where pesticides would be retained leading to lower concentrations as was observed downstream. PCB (#153, 138, 110, 101) and PBDE (BDE-47) levels were directly related with the presence of hydroelectric power plants, dams and dumping sites, mainly settled in the Upper Valley (0.8 ng/g and 15.1 ng/g d.w for PBDEs and PCBs, respectively). Although there was a decreasing gradient of these pollutant concentrations through the river flow, downstream urban areas enhanced PCB concentrations in the aquatic environment. More efforts and monitoring programs are highly required to control and reduce soil erosion in order to prevent the availability of forbidden pollutants in the environment.

1. Introduction

The occurrence of persistent organic pollutants (POPs) in environmental compartments has received attention due to their persistence, biomagnification potential, long-range transport capacity and toxicity. The use and production of most of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have been internationally regulated by the Stockholm Convention since 2004. Restrictions for the endosulfan insecticide and the polybrominated diphenyl ethers (PBDEs) were recently implemented (UNEP, 2004, 2011). Particularly, OCPs have been restricted and forbidden in most countries since the late 1970s, while some developing countries are still using them for public health (Wania and MacKay, 1996; Sabljic, 2001; Borghesi et al., 2008). PCBs were banned three decades ago, and PBDEs, used as flame retardants since 1970, have received attention recently due to their persistence and toxic effects (de Wit, 2002; Hites, 2004).

These pollutants can reach the aquatic environment from non-point and punctual sources depending on land use and contaminant delivery, and due to their hydrophobic character they associate to organic matter

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of sediments and/or lipids of organisms. Although the toxicity of weathered organic compounds is generally thought to decline with residence time in the environment (Semple et al., 2003), their long half-lives with their potential for bioaccumulation and biomagnification through food chains, present a significant threat to the environment. Agricultural activities, urban settlements, industries and dams are potential sources of PBDEs, OCPs and PCBs to large basins. To determine pollutant levels and distribution patterns as well as to indentify the sources of these compounds are essential to prevent or mitigate accurately risks to the aquatic environment.

Rio Negro is the most important river with the largest drainage basin (140,000 km^2) and water discharge (600 m^3/s) to the coastal area of Argentinean Patagonia. The basin provides 4% of the worldwide production of apples, pears and peaches concomitantly with an intensive use of pesticides from 50 years ago. Moreover, the settlement of hydroelectric power plants in the upstream zone generates 30% of the electricity consumed in Argentina. In addition, the occurrence of chemical industries and petroleum facilities has been reported by Arribére et al. (2003). Due to the different anthropogenic activities developed in the basin, river discharge could be an important source of contamination to the adjacent costal environment.

This work reports the occurrence and distribution of OCPs, PCBs and PBDEs in several environmental matrices (soil, sediment, suspended particle matter and macrophytes) along the Río Negro basin in relation to land use. Research was sponsored by the United Nations Environment Programme (UNEP), as part of the Project “Argentinean Patagonia Pollution”, which aimed to study the role of Patagonian basins on the POP contamination in the southeastern coast of the Atlantic Ocean.

2. Materials and methods

2.1. Study area

The study was conducted along the Rio Negro basin which is located across the northern region of Argentinean Patagonia (Fig. 1, S 39° 04.9′ 14″; W 67° 02.9′ 59″). The area is included in the Patagonian plateau (east side) characterized by a dry continental climate, low rainfall, good insolation, and a high thermal amplitude with a mean annual temperature between 14 °C and 16 °C (Coronato et al., 2008). Rainfall in most of the plateau is below 200 mm/year, increasing up to 800 mm/year close to the Andes (Coronato et al., 2008). These climate characteristics and the sandy alluvial mollisol type soils (Coronato et al., 2008), allow the cultivation of fruits (e.g. grapes, apples, peaches, plums, pears) and vegetables.

Rio Negro basin transports a great burden of dissolved solids which are delivered into the Patagonian coast (Depetris et al., 2005). Based on land use, the basin is divided in three areas: the upper valley (UV), mostly concerned to fruit production with several dams installed upstream; the middle valley (MV) with animal farming and less intense fruit production, and the lower valley (LV) dedicated mainly to animal farming and has also some natural areas. Moreover, the main urban settlements are concentrated in UV (e.g. Roca, Villa Regina, Cipolletti) and LV (e.g. Viedma, Conesa).

2.2. Sampling

Samples of soil, bottom sediment, streamwater, suspended particulate matter (SPM) and macrophytes were collected along the river basin between February and April 2006, which coincides with the period of the highest pesticide application (Fig. 1).

2.2.1. Soils

Surface soils were sampled covering seven sites according to land use: Hidronor (HN), Villa Regina (VR) and La Josefa (LJ), as representative of agricultural areas; Villarino (VI) and Limay (LI) as development of recreational activities; and Chelforo (CH) and Criadero (CR) as natural soils (Fig. 1). Soil sampling sites were mostly selected to 300–500 mts from river margin. Samples were randomly taken in triplicate from the top soil (0–10 cm). Soils from HN and VR in the UV and VI from LV were also sampled for profile analyses. Soil corers (≤30 cm) were obtained using steel core samplers of 10 cm of diameter and 40 cm of length. Three equidistant samples were obtained for each soil along a 100 m transects and transported to the laboratory. The cores were opened to characterize the profile and subsampled in three or four sections as appropriate from 0–4 to 20–30 cm. Subsamples were placed in aluminum boxes covered with aluminum foil (in order to avoid contamination) and kept at room temperature until they reached constant weight. All samples were sieved (2 mm) to remove coarse organic fragments and homogenized. Subsamples for residue analyses were kept at −20 °C wrapped in aluminum foil until analysis, while subsamples for physicochemical properties were kept at room temperature.

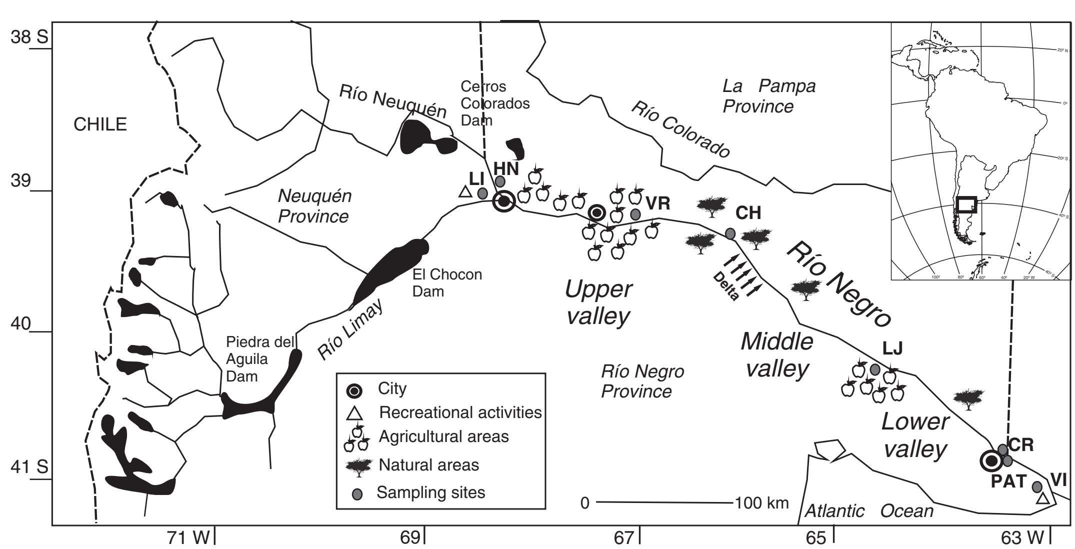

Fig. 1. Study area showing sampling stations of soils, sediments, macrophytes and streamwater (Modified from Isla et al., 2011). Hidronor (HN), Villa Regina (VR) and La Josefa (LJ) = agricultural areas; Villarino (VI) and Limay (LI) = recreational activities; and Chelforo (CH) and Criadero (CR) = natural areas.