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Atmospheric pollutants in fog and rain events at the northwestern mountains of the Iberian Peninsula

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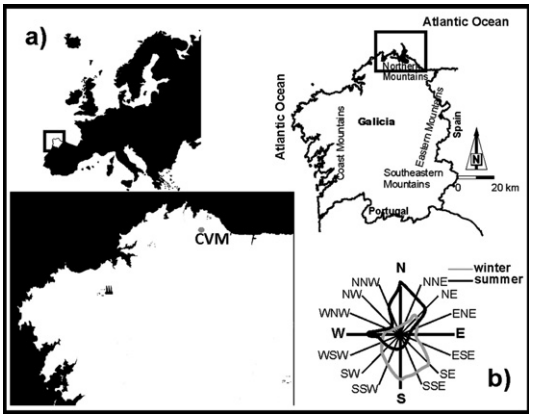
HIGHLIGHTS

- There is no work about both PAHs and PCBs in fog-rain events.
- None of the existing works is about the case of the northwestern mountains of the Iberian Peninsula.
- This is a summary of a 2-year research project drawing conclusions for future approaches.
- It deals with all factors affecting the atmospheric deposition of PAHs and PCBs in fog-rain events.
- It shows input routes and measures to reduce pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) and exist in gas and particle phases, as well as dissolved or suspended in precipitation (fog or rain). While the hydrosphere is the main reservoir for PAHs, the atmosphere serves as the primary route for global transport of PCBs. In this study, fog and rain samples were collected during fourteen events from September 2011 to April 2012 in the Xistral Mountains, a remote range in the NW Iberian Peninsula. PAH compounds [especially of low molecular weight (LMW)] were universally found, but mainly in the fog-water samples. The total PAH concentration in fog-water ranged from non-detected to 216 ng · L^{-1} (mean of 45 ng · L^{-1}), and was much higher in fall than in winter. Total PAH levels in the rain and fog events varied from non-detected to 1272 and 33 ng · L^{-1} for, respectively, LMW and high molecular weight (HMW) PAHs. Diagnostic ratio analysis (LMW PAHs/HMW PAHs) suggested that petroleum combustion was the dominant contributor to PAHs in the area. Total PCB levels in the rain and fog events varied from non-detected to 305 and 91 ng · L^{-1} for, respectively, PCBs with 2–3 Cl atoms and 5–10 Cl atoms. PCBs, especially those with 5–10 Cl atoms, were found linked to rain events. The occurrence of the most volatile PCBs, PCBs with 2–3 Cl atoms, is related to wind transport from far away sources, whereas the occurrence of PCBs with 5–10 Cl atoms seems to be related with the increase of its deposition during rainfall at the end of summer and fall. The

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movement of this fraction of PCBs is facilitated by its binding to air-suspended particles, whose concentrations usually show an increase as the result of a prolonged period of drought in summer.

1. Introduction

Atmospheric deposition occurs when substances are deposited on land or water surfaces from the air. Many forms of atmospheric pollution affect human health and the environment at levels from local to global, especially persistent organic pollutants (POPs). These contaminants are emitted from diverse sources, and their input to ecosystems is mainly the result of human activities (Harvey, 1998). Industrialized nations have made important progress toward controlling some pollutants in recent decades, e.g. in the EEA-32 region, emissions of polycyclic aromatic hydrocarbons (PAHs) have fallen by 52%, polychlorinated biphenyls (PCBs) by 74%, hexachlorobenzene (HCB) by 91%, hexachlorocyclohexane (HCH) by 93%, and dioxins and furans by 83% between 1990 and 2010 (EEA, 2013). Some pollutants, especially PCBs, experiment the so-called grasshopper effect. This is the geochemical process by which POPs are transported from warmer to colder regions of the Earth. This leads to a pattern where a pollutant is emitted from an original source, transported some distance, and deposited. Then, a portion is re-emitted, transported a further distance, and re-deposited. This pattern is indefinitely repeated, although there is evidence that these POPs tend to sorption/desorption processes until they reach northern climates or high elevations. With regard to the background levels of some representative PAHs in the air, there are reports that detected levels of 0.020–1.2 ng · m^{-3} in rural areas and 0.15–19 ng · m^{-3} in urban areas. So, humans may be exposed to PAHs in soil near areas where coal, wood, gasoline, or other products have been burned. Other sources for human exposure to PAHs could also be the soil at or near hazardous waste sites, such as former manufactured-gas factory sites and wood-preserving facilities (ATSDR, 1995). Accurate and complete information on the emissions of POPs are essential for interpreting historical, current, and future pollution levels in ecosystems (Breivik et al., 2006). This information could also be essential to accurately establish the transport and deposition fluxes of these environmental contaminants. Consequently, research needs to be primarily focused on the origin and determination of seasonal variations of atmospheric pollutants.

Normally, the higher precipitation rates are located in mountains. Mountain regions serve as a water supply, both directly and indirectly, through provision of lowland surface water (Daly and Wania, 2005). In high latitudes and altitudes, such deposition is greatly influenced by low temperatures and in particular the phase transition of water at 0 °C. Precipitation occurs in the form of snow rather than rain, which often could be a more efficient scavenger than rain (Lei and Wania, 2004). Fog is also a common feature of mountain regions and ground-based clouds form when a decrease in temperature causes an increase in relative humidity beyond the dew point (Whiteman, 2000). Most relevant are up-slope fogs, whereby moist air is cooled by being lifted up-slope, and radiation fogs, which develop in valleys and mountain basins when outgoing long-wave radiation cools the near-surface air during the night-time and in the winter (Daly and Wania, 2005). Fog droplets are much smaller than rain droplets and have a much higher surface-to-volume ratio. This can lead to significant enrichment of surface-active organic chemicals in fog-water, when compared to the concentration expected from Henry's law (Capel et al., 1991; Goss, 1994; Simcik, 2004; Valsaraj et al., 1993). Therefore, this suggests that fog may be an important mechanism for POP deposition in mountain regions and this fact could explain the differences in POP levels within mountains if the occurrence and frequency of fogs are localized. However, studies on the atmospheric geochemistry of fog, and in particular of the POPs, are scarce.

Two of the most environmentally important POP groups are PCBs and PAHs, which share several characteristics such as origin (mostly anthropogenic), long-distance atmospheric transport capacity, low environmental degradability, and high impact on the health of biota (including humans). Therefore, the aim of this work is to measure the deposition of PCBs and PAHs in rain- and fog-water, and assess possible seasonal patterns of deposition associated with rain and fog events northwest of the Iberian Peninsula. This area has been shown to function as a sink to PAHs associated with its latitudinal position within the context of southern Europe and the properties of soils receiving atmospheric deposition (Pontevedra-Pombal et al., 2012; Rey-Salgueiro et al., 2009a).

2. Methodology

2.1. Sampling strategy

The study area is located in the highest elevations of the Northwestern Iberian Peninsula (Fig. 1). The maximum altitude reached is 1060 m a.s.l., and most of the territory is between 700 and 900 m a.s.l. This area is the best example of wet-fresh environments of southern Europe, with a sharp ombrothermal gradient from the coast to the mountainous areas. At the summit, rainfall is between 1400 and 1800 mm, the effective fog-precipitation exceeds 5000 mm and the mean temperature ranges from 7 to 10 °C. These values define an ombrothermal environment that is cool and very humid. The rainfall gradient is close to 100 mm per 100 m altitude, and the thermometric gradient is of −0.67 °C per 100 m altitude. The seasonal rainfall is very low, the lowest in the Iberian Peninsula. That is, the Northern Mountains are fully in control of mesothermal (not arid) climates, which includes all cold temperate climates, mainly characterized by having an average temperature in the coldest month that is below 6.0 °C. Another defining feature of the climatic conditions of this area is the abundant fogs above 600 m a.s.l. Especially during the summer, under the situations from the north, northeast component, and anticyclonic stability, these reliefs allow flows of oceanic origin generated surface air that allow the development of clouds of stagnation. These, together with the phenomena of radiation fogs, collaborate intensively to increase water input.

Since September 2011, a station of climate monitoring was launched in the vicinity of the Chao de Veiga Mol mire (CVM), a raised bog located in the Northern Mountains (43°32′34,4″ N–7°30′13,41″ W), at 700 m a.s.l. and 15 km south of the Atlantic coast (Fig. 1a). This sector is located over 150 km away from any heavily industrialized and populated city, and is 40, 90, and 130 km away from the three largest coal mines and the largest coal-fired power plant in Spain. Moreover, this sector is located in the direction of the dominant winds coming from an incineration plant (Fig. 1b). This sector was selected because previous research proved useful in identifying temporal accumulation patterns of different atmospheric pollutants on a local, regional, and hemispheric scale (Kylander et al., 2005; Martínez-Cortizas et al., 1999; Pontevedra-Pombal et al., 2012, 2013).

The installation consisted of a meteorological station (rainfall, fog, temperature, humidity, atmospheric pressure, total, and photosynthetically active radiation) and two rain- and fog-water collectors protected from light and solar radiation. This installation was completed with temperature and soil moisture loggers. The rain- and fog-water samples were collected every 15 days, transported refrigerated to the laboratory, filtered (0.45 μm), and distributed in 4 aliquots. The first aliquot was intended for the determination of trace elements, another aliquot to