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Seasonal evolution of gas-phase PCB concentrations in the Venice Lagoon area

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Abstract

The concentrations of gas-phase PCBs were measured from March 2002 to June 2003 at two sites of the Venice Lagoon and at one site of the Euganei hills. The aims of this study were to evaluate the various gas-phase PCB sources, the spatial and temporal variability of PCB concentrations in the gas-phase that enter the Venice Lagoon atmosphere and the influence of the air temperature on PCB trends. The highest annual average concentration of $\sum$PCBs was observed at the station directly influenced by "urban" sources with values about 3 and 1.5 times higher compared to the concentrations found at the stations where "marine" sources and "not subjected to direct local sources" were respectively sampled from.

The temporal trends of $\sum$PCBs concentrations were similar at the three sampling stations corresponding to seasonal temperature changes. Greater concentrations occurred in the summer and first autumn months while the lower ones occurred in late autumn and winter. The temperature dependences were investigated using plots of the natural logarithm of the $\sum$PCBs concentrations vs. reciprocal mean temperatures.

Keywords: Gas-phase; HRGC-LRMS; Polychlorinated biphenyls; Venice Lagoon

1. Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 compounds that are widely spread in the environment; they are toxic with endocrine-disrupting properties, they bio-accumulate in the food chain and their persistence leads to long-range atmospheric transport. Due to these properties, PCBs have been banned since the end of Seventies in the USA and Europe (Erickson, 2001) and have been included in the priority pollutants lists of the US-EPA and UN-ECE POP Protocol (Lerche et al., 2002).

The PCBs physical–chemical properties are representative of persistent organic pollutants (POPs) (Hornbuckle et al., 1993), so they have been elected as their ideal marker compounds for their global re-distribution (Ockenden et al., 2003). In the last few years several studies have been carried out concerning the

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environmental distribution of PCBs to understand their behaviour and fate.

The atmospheric burden is only a small fraction of the global PCBs inventory, but it has very important environmental implications, because it is subject to rapid turnover and constitutes part of the 'environmentally mobile' fraction (Ockenden et al., 2003). It is known that PCB concentrations in air are higher near urban and industrialized areas (Miller et al., 2001) but, due to their global re-cycling, they have also been found in the atmosphere of remote areas (Stern et al., 1997; Kallenborn et al., 1998; Ockenden et al., 2001; Montone et al., 2003). Once they enter the atmosphere, PCBs redistribute between the gas and particulate phases and are subjected to removal mechanisms such as wet and dry deposition (Wania et al., 1998a). Several processes influence directly or indirectly the transport and environmental fate of PCBs with important consequences for their characteristic travel distances. Diffusion and reaction rates increase with rising temperature, and changes in condensate-gas-phase equilibrium leads to modified deposition rates.

The lagoon of Venice is a transitional ecosystem surrounded both by the Adriatic Sea and the mainland, where several processes contribute substantially to the input of pollutants, such as the atmosphere/water exchange, the exchanges between water and sediments and the fresh water draining from the catchment basins of the lagoon. The Venice Lagoon is located in a highly populated area and is subjected to pollution deriving from agricultural drainage, from industrial inputs (Porto Marghera district), and urban activities (traffic and domestic heating) from the cities of Mestre and Venice. A lot of research on PCBs in different environmental matrices has been conducted in the Venice Lagoon (Maroli et al., 1993; Frignani et al., 2001; Moret et al., 2000) but very little is known about the concentration of PCBs in the atmosphere. Since 2000 the CORILA (Consortium for Coordination of Research Activities concerning the Venice Lagoon System) has supported a research programme on the Venice Lagoon with the aims of providing concrete results to specific queries emerging from policy makers and the public administration. This study is part of the Project "Role of aerosol and secondary pollution in the chemical contamination of the Venice Lagoon" funded by CORILA with the specific aim, among others, of investigating the role and contribution of aerosols to the transport of pollution to the Venice atmosphere.

In this paper the air concentration of PCBs at three different sites near the Venice Lagoon over an entire year are investigated. The objectives of this paper are to assess the spatial and temporal variability of gas-phase PCBs that enter the Venice Lagoon atmosphere and to study the influence of the air temperature on gas-phase PCB concentrations that enter the Venice Lagoon atmosphere.

2. Experimental

2.1. Sampling

To evaluate airborne contamination due to aerosols entering the Venice Lagoon, it has been necessary to adopt a sampling strategy able to differentiate the contributions of the different sources. Due to this reason, the general circulation of wind has been investigated: the analysis of historical series of meteorological data from the Venice Lagoon collected from 1975 to 2002 (EZI, 2003) show that the prevailing wind direction is from the north–east (about 45%), followed by the south-easterly direction (about 18%). As described in previous work (Gambaro et al., 2002), sampling was carried out using high-volume samplers (Tisch Environmental Inc., Village of Cleves, OH) equipped with an anemometer that only sampled when winds blew from fixed directions with a speed greater than 1 m s^{-1}.

Aerosol sampling was performed at two sites of the Venice Lagoon and one site in the Euganei hills (Fig. 1). The first site (St. 1) was located at the Northern inlet of the lagoon (N 45°25′21.8″ E 12°26′12.2″) on the light house, about 15 m high; samples were collected when the wind blew from the southeast which we assume carried predominantly "marine" aerosols. The second sampling site (St. 2) was south of the industrial zone of Porto Marghera and the urban area of Mestre (N 45°25′38.5″ E 12°12′47.6″); samples were collected when the wind blew from the northeast which we hypothesize is dominated by "urban" and "industrial" aerosols. The last site (St. 3) was located on Monte Grande, in the Euganei hills, about 460 m high above sea level and about 50 km from Venice (N 45°21′43.0″ E 11°40′22.4″); samples were collected when the wind blew from the northeast which we suppose carried aerosols from no particular direct local sources.

Samplings were performed every 15-days from March 2002 to June 2003 providing a total of 18 observations for Sts. 1, 11 for Sts. 2 and 14 for St. 3, as shown in Table 1, which reports the averages of collected volumes, temperature and wind speed over each sampling campaign.

Hi-vol samplers were equipped with a quartz fibre filter (QFF) for collecting "particulate" phase compounds and a polyurethane foam plug (PUF) for retaining "gas-phase" compounds. The average operative flux was about 0.34 m^3 min^{-1} but due to different meteorological conditions, collected volumes varied during the study between 50 and 2074 m^3. Every month a calibration was done to check the flow rates.

Results obtained in this and preliminary studies (Gambaro et al., 2004) have shown that "particle-associated" PCBs are negligible in Venice Lagoon aerosol samples because they represent less than the 5% of the total PCB concentration. Due to this reason, only PCB