### ATMOSPHERIC INPUT OF ORGANIC POLLUTANTS TO THE VENICE LAGOON ECOSYSTEM

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### Introduction

The Venice Lagoon ecosystem is located in a highly populated area and is subjected to pollution from industrial, agricultural and urban sources. Studies<sup>1,2</sup> have been concerned with the pollution level in the Venice Lagoon, the pollution sources and the possible methods of intervention. We know very little about the atmospheric contribution of organic pollutants to the contamination of the Venice Lagoon.

The aim of this study is to investigate the role of aerosols in the organic pollutant contamination of the Venice Lagoon ecosystem. This study was carried out to determine the PCB and PAH concentrations in samples of atmospheric aerosols, in the sea-surface microlayer and in sub-surface water.

#### Materials and methods

Aerosol sampling was performed using a High-Volume air sampler equipped with a quartz filter before the sorbent material, which consisted of polyurethane foam (PUF). This sampler allowed the separate analysis of the particulate and vapour phases of atmospheric aerosol. Figure 1 shows the selected sites for the aerosol sampling. The aerosol sampler at each site was set up to only collect aerosol when the wind blew from defined directions, selected in order to sample from the three main sources (urban and industrial sources, site "a"; no direct source, site "b"; marine sources, site "c").

Filter and PUF samples were analysed separately by Sohxlet apparatus extracting for 24 hours using an aliquot of 480 ml for PUF and 240 ml for the filters respectively, of a mixture of pesticide grade n-pentane and dichloromethane (2:1, v/v),.

The sampling of the sea-surface microlayer (SML) and sub-surface water (SSL) was perfomed in the zone of direct influence of the industrial plants of Porto Marghera. Sea-surface microlayer (10 L) and sub-surface water samples (10 L) were collected simultaneously using a Multiple Use Microlayer Sampler (MUMS) and a teflon membrane pump respectively. For SML sampling a rotating Pyrex glass drum collector, is placed on a floating structure, which samples the sea surface and collects by capillary action a thin layer of water (~ 40  $\mu$ m)<sup>3</sup>. SML and SSL were filtered with glass-fibre filters (0.7  $\mu$ m). In the filtrate water "dissolved" PCBs and PAHs were determined by continuous liquid-liquid extraction for 24 hours with a 2:1 (v/v) *n*-pentane:dichloromethane mixture. For the determination of "particulate" PCBs and PAHs the filtered matter was ultrasonic extracted for 2 hours with the same mixture.

The extract cleanup was done by column chromatography, using a column packed with Florisil and Alumina. The microcontaminants were eluted with n-hexane (30 ml). The eluate was reduced under a gentle stream of nitrogen to 100  $\mu$ l and the PCBs and PAHs were analyzed by gaschromatography-mass spectrometry<sup>4</sup>.



Figure 1. Aerosol sampling sites: site "a", urban and industrial sources; site "b", without direct sources; site "c", marine sources.

Five carbon-13-labeled PCBs and carbon-13-labeled phenantrene were added to the samples before extraction for use as internal standards for the microcontaminants quantification.

### **Results and discussion**

Figure 2 shows the distribution of PCB (expressed as a sum of 56 congeners) and PAH (expressed as sum of 17 compounds) concentrations between the particulate and dissolved phase and the fluxes of PCBs and PAHs in the aerosol samples collected at the investigated sites. It can be observed that:

- the PCB and PAH concentrations were higher at "a" site than at the "b" and "c" sites;

- the PCB and PAH concentrations were higher in the dissolved phase than in the particulate phase at all sites;

- the average daily flux of PCBs and PAHs were higher at the "a" site compared to the flux values at the "b" and "c" sites. The flux values obtained at the "c" site (subjected to marine sources) were comparable with those at the "b" site but was only about three times lower than that at the "a" site.

Figure 3 shows the total concentrations of PCBs and PAHs in the dissolved and particulate phases of the sea-surface microlayer and of the sub-surface water at the considered site. The PCB and PAH concentrations in the microlayer are higher than in sub-surface water but this tendency is more evident in the particulate phase. However the more chlorinated PCBs (5-CB, 6-CB, 7-CB) show a greater enrichment both in the microlayer samples and in the particulate phase (Figure 3).

To our knowledge this is the first study on the microlayer concentration and the atmospheric flux of PCBs and PAHs towards the Venice Lagoon system. However further experimental data in expected from ongoing work will allow a more thorough evaluation of the issue.



**Figure 2.** Distribution of PAHs (1) and PCBs (2) concentrations between particulate ( $\blacksquare$ ) and dissolved phase ( $\Box$ ) in the aerosol samples. Fluxes of PAHs (3) and PCBs (4).

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**Figure 3.** Total concentrations of PCBs (a) and PAH (b) in sub-surface water (SSL, dissolved phase; PSSL, particulate phase) and in sea-surface microlayer (SML, dissolved phase; PSML, particulate phase)