

# ENVIRONMENTAL TRANSPORT AND FATE

## MONITORING POPS (PCDD/F, PCB, HCB, PAH, DDT) IN ATMOSPHERIC DEPOSITION: SAMPLING AND ANALYTICAL PROBLEMS

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### Introduction

Bulk sampling of atmospheric deposition has been widely used in studies aimed at assessing atmospheric deposition of organic contaminants in industrial, rural and remote sites. Air is the main distribution pathway for organics and their abundance in deposition at a certain site is therefore influenced by different types of emissions, selective transport and atmospheric loss<sup>1</sup>. Horstmann & McLachlan<sup>2</sup> recently found that parallel bulk sampling reproducibility is good (lower than 10%), and also that the diffusive fraction is small with respect to total deposition. Limitations to this sampling method are mainly due to possible under-estimation of fluxes because of the limited collection of dry gases. Advantages are the integration of samples over one month and the possibility of application on a large scale with low-cost equipment. A new sampler has been tested for more than 2 years in marine and coastal sites in the Northern Adriatic (44°Lat N, 12 Long E) and lagoon of Venice, and is derived from that used by Horstmann & McLachlan in a rural environment<sup>2</sup>. It was modified in order to avoid contamination and to make all sampling operations easier. This was due to the consideration that – in spite of the enormous attention paid to analytical procedures - little awareness is often encountered in environmental sampling actions.

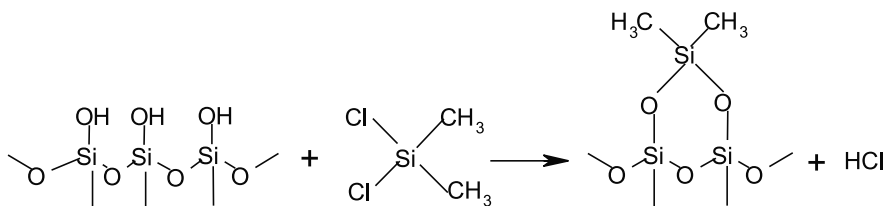
### Materials and methods

The original sampler is composed of a cylinder containing a pyrex bottle, with a funnel on top. We added to the support a protection ring to avoid damage due to birds and other animals, and the structure was fastened by two clamps to a 60-mm diameter post, painted with an inert, organic-free varnish, at a height of 1.5 m above the ground. The sampler was modified in order to avoid contamination both in the structure, made with inert, polymeric material instead of metal, and in the “funnel+bottle” unit. The funnel was 22 cm in diameter, and had a 60-cm vertical wall in order to avoid blow-out of particulate material. Both bottle and funnel had previously been silanized (Fig. 1) with dimethyldichlorosilane 5 % in toluene, thus preventing retention of analytes. Operations for cleaning and silanisation were as follows:

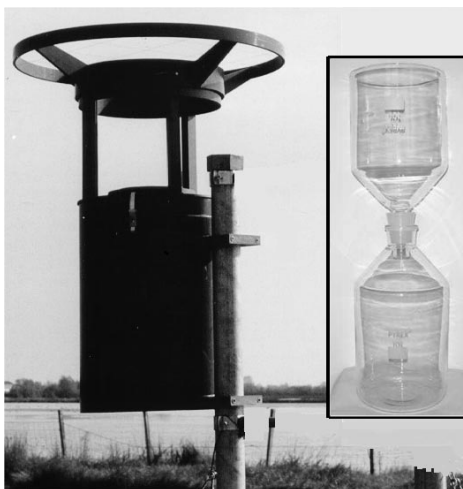
(i) washing with basic detergents and rinsing in water; (ii) treatment with solution of ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (350 g/l of 98 %  $\text{H}_2\text{SO}_4$ ); (iii) rinsing with demineralised, organic residue-free water; (iv) internal and external treatment with acetone RS; (v) silanisation with dimethyldichlorosilane 5 % in toluene; (vi) second rinse with demineralised organic residue-free water; (vii) internal and external drying with RS; (viii) heating at 250 °C for two hours.

Horstmann & McLachlan<sup>2</sup> showed that rinsing the funnel with toluene at the end of one month's sampling was not different from doing it every day for 30 days. On the contrary, daily operations added

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**Figure 1.** Structural modifications of active OH to non-active ( $\text{CH}_3$ ) sites, due to reaction between dimethyldichlorosilane and silica.



**Figure 2.** Bulk deposition sampler (modified from Bergerhoff®) used in the field. Right insert: Pyrex® “funnel-bottle” unit.

some artefacts. They therefore decided to rinse the funnel monthly, thus keeping artefacts due to particle blow-out to 10 %. We avoided blowing up of particles by using a longer funnel wall (60 cm instead of 15) and applied three methods for sample recovery: (i) rinsing the funnel wall with methylene chloride in the field before laboratory analyses (A); (ii) by rinsing the funnel wall with double-distilled water (DDW), in order to avoid dissolution of insects, and then applying methylene chloride (B); (iii) after the water rinse, more intense cleaning of the funnel wall, using glass wool to detach any particles sticking to the wall. Therefore, in the third method, two aliquots of every sample were analysed separately, in order to check possible under-estimation of the previous two methods.

Total atmospheric samples were first spiked with a series of 15  $^{13}\text{C}_{12}$ -labeled 2,3,7,8 PCDD-Fs, 12  $^{13}\text{C}_{12}$ -labeled PCB,  $^{13}\text{C}_{12}$ -HCB substituted isomers, and 5 deuterated PAH (Acenaphthene-D10, Chrysene-D12, Naphtalene-D8, Perylene-D12, Phenanthrene-D10) as internal standards, and then extracted in a separatory funnel with dichloromethane. Extracts were transferred to hexane before clean-up treatment. Sample extracts were first spiked with  $^{37}\text{C}_4$ -labeled 2,3,7,8 PCDD and 3  $^{13}\text{C}_{12}$ -labeled PCB, and then cleaned using an automatic system (Power Prep; Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica and sodium sulphate were used for PAH clean-up. After PAH analysis, extracts were treated with sulphuric acid (98%) and potassium

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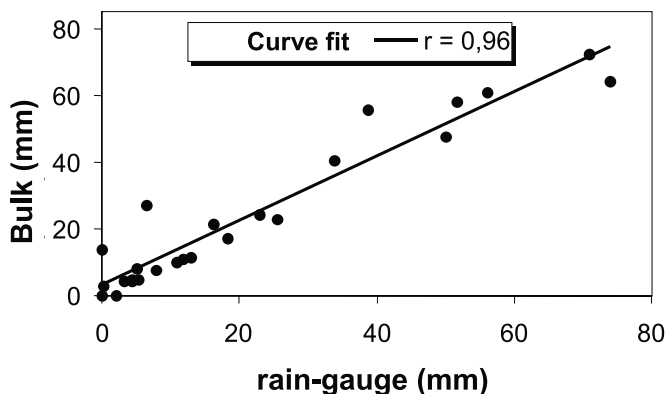
hydroxide (20%) in a 100-mL separatory funnel and then cleaned using the automatic three-column system with pre-packed disposable columns containing multilayer silica, alumina and carbon for PCDD-Fs, PCB and HCB. HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Quantitative determination of PCDD-Fs, PCBs, HCB and PAHs was performed by isotope dilution methods, using relative response factors previously obtained from standard solution injections<sup>3,4</sup>.

All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate) were Picograde<sup>®</sup> reagent grade (Pomochem GmbH, Wesel, Germany). Native and deuterated PAH standards were purchased from Supelco (Belfonte, PA, USA), native and <sup>13</sup>C<sub>12</sub>-labeled PCDD/F, PCB, HCB, Acenaphthylene-D8 and benzo[e]pyrene-D12 standards were purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Recoveries always ranged between 50 % and 110 %. Reproducibility was 15 % for lower values, or better. Laboratory blanks, repeated twice a week, were lower than 9 % with respect to the minimum concentration found.

## Results and Discussion

Fig. 3 compares rain collected by the bulk sampler with data from the rain gauge in the vicinity. Table 1 lists data of the total monthly amount of POPs recovered in the sampler with the first two methods (methylene chloride and water rinses).

Comparisons with rain gauges showed that rain recovery was very good, mainly due to the vertical length of the funnel walls, which also avoided possible loss due to blow-out of particles. The recoveries of the two methods were quite different, the first (methylene chloride) yielding recoveries up to two times higher for PAH and PCDD-Fs and four times for PCB and HCB. Thus, while trying to avoid dissolution of insects and other organic debris by rinsing with DDW, we probably missed particulate attached to the funnel wall.



**Figure 3.** Comparisons between rain recovered by bulk sampler with rain-gauge measurements.

With the third method, recovery clearly improved (20-40%). In this case, on average more than half (range 20-90 %) the total POPs were collected on the funnel surface, as had already been shown for PCDD-Fs by Schröder *et al.* (1997)<sup>5</sup>. At Mediterranean latitudes, it is also possible that, in the case of

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**Table 1.** Total amount of POPs collected in one month in bulk sampler (434 cm<sup>2</sup> surface) with methods A and B respectively (see text for explanation). PCDD-Fs=sum of 17 toxic PCDD/F congeners.

	PAH ng	PCB ng	HCB ng	PCDD-Fs pg
<b>(A)</b>				
mean	1206	14	23	122
min	388	3	1	46
max	3310	31	117	456
<b>(B)</b>				
mean	499	3	6	62
min	10	0.2	0	8
max	1647	9	67	474

large-scale Saharan dust events carrying alkaline particles capable of remaining attached to portions of organics, the role of attachment to the funnel may be even higher.

In conclusion, the tested sampler turned out to be suitable both for rain recovery and for its ability to keep particles inside. The three-step strategy for sample recovery was also more efficient, especially in the case of Saharan dust events, which occur quite often in Mediterranean sampling sites.

## Acknowledgements

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