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## Atmospheric bulk deposition to the Lagoon of Venice Part II. Source apportionment analysis near the industrial zone of Porto Marghera, Italy

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## Abstract

Multivariate statistical analyses were applied to measurements of atmospheric deposition of total particulate (TSP), inorganic elements (Al, Ca, Na, K, Mg, Si, Mn, Fe, Zn, Ni, Cr, Cu, Pb, Cd, As, Hg, V and S) and organic compounds (PAH, PCB, HCB and PCDD/F) collected in four stations, all located in the Lagoon of Venice. Aerosols at the scale of the basin (i.e., within a distance of 20 km) were mainly characterised by two end-members, one natural (composed of mineral particulate and marine spray) and one anthropogenic (with at least two different source components), affecting the sites in various ways. Variability at the two distant (>20 km) sites (Valle Dogà, Valle Figheri) was mainly due to natural components, whereas the other two stations (city of Venice, Dogaletto,  $\sim$ 5 km) were mainly impacted by industrial (and urban) sources. Total annual inputs were compared with the limits recently set by law (maximum allowed discharge=MAD). In the year of study, MAD values were exceeded for total As, Cd, Hg, Pb, dissolved Zn, PAH and PCDD/F.

These results indicate that industrial sources gave rise to a quasi-permanent compositional (background) effect near the industrial area. The risk associated with atmospheric deposition should be quantified within the DSPIR framework to avoid future negative consequences in populations living in the vicinity of Porto Marghera.

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Keywords: Deposition; Trace metals; Organic compounds; Lagoon of Venice; Porto Marghera

## 1. Introduction

This study of atmospheric deposition was initiated for preliminary information on air pollution and consequent deposition to the Lagoon of Venice. Another aim was to shed light on possible natural vs. anthropogenic composition of aerosols (and related deposition).

Based on a recent study carried out by the Provincia di Venezia (2002), major anthropogenic activities having an important influence on air quality in the Venice area may be summarised as follows: (i) oil refining; (ii) metallurgy, now mainly confined to the production of Al; (iii) chloro-soda cycles, discharging dicloroethane (DCE), vinyl chloride monomer (VCM) and polyvinylchloride (PVC); (iv) power generation (oil and coal); (v) urban waste incineration; and (vi) traffic emissions.

Most of these activities take place inside the Porto Marghera industrial zone, which covers almost 12 km<sup>2</sup>, employs more than 10,000 people and produces the following emissions (ARPAV, 2001) (expressed in tons, unless otherwise stated, and averaged on an annual basis): CO=2000;  $SO_x=20,000$ ;  $NO_x=15,000$ ; VOC=800; VCM=7 (dioxins 440 mg TEQ), inorganic Cl compounds=9, chlorine=2,  $NH_4=30$ ; total metals=3 (Pb 0.5, Hg 0.003); PAH=0.6 kg; and PCB=0.1 kg.

Traffic emissions are responsible for half the CO and a quarter of the NO<sub>x</sub> and VOC (ARPAV, 2003).

Some works have already revealed the evident influence of atmospheric deposition in the area. For instance,

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preliminary results from soil and atmospheric deposition studies show clear-cut decreases in some metals in soil with distance, connected with a main source in the industrial zone (Di Domenico et al., 1998). Similar results come from bulk deposition sampling, which shows marked trends in atmospheric fluxes of trace metals with distance from Porto Marghera (Guerzoni et al., 1995; Rossini et al., 2001; Marcomini et al., 1999). Further analysis of these data, which were collected in 1998 and 1999 at air-monitoring stations located in Venice, Porto Marghera and the southernmost and northernmost reaches of the lagoon, indicate average annual loads of approximately 12 g of dioxin (or 400 mg dioxin toxic equivalence (TEQs, using current WHO toxic equivalency factors; Van Den Berg et al., 1998) (Guerzoni et al., 2004). The results of an assessment of PCDD/F levels in soil collected from the industrial zone and elsewhere in the Venetian region also suggest that atmospheric deposition is an important factor in the occurrence of PCDD/F on the soil surface (Della Sala et al., 1999).

Several studies conducted over the past 20–30 years have focused on the potential human health and ecological risks associated with the presence of persistent pollutants such as trace metals (As, Hg), polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) and biphenyls (PCB) in the Lagoon of Venice (Fattore et al., 1997; Di Domenico et al., 1997; Marcomini et al., 1997; Wenning et al., 2000).

This kind of information, only recently available, should be used in describing interactions between society and the environment following the DPSIR method, the causal framework adopted by the European Environment Agency ("Driving forces, Pressures, States, Impacts and Responses," an extension of the PSR model developed by the OECD).

In order to check whether the sampling strategy was useful in deriving management indicators for atmospheric deposition, we used a database simplified from the one described by Rossini et al. (this volume). We discuss here data from a 9-month period of sampling contemporarily in

Table 1

Sampling dates, pH, conductivity values and ionic compositions of the simplified database (36 bulk samples)

Sample	Sampling period		pН	C	Na	K	Ca	Mg	Cl ,	SO <sub>4</sub>	NH <sub>4</sub>	NO <sub>3</sub>
	From	То		$(\mu Sc m^{-1})$	$(mg L^{-1})$	$(mg L^{-1})$	$(\operatorname{mg}^{\circ} \mathrm{L}^{-1})$					
A5	10/11/98	09/12/98	6.9	35.4	2.6	0.38	4.5	1.5	3.3	4.7	0.70	4.5
A6	09/12/98	08/01/99	6.3	42.2	2.1	0.21	1.3	0.48	2.6	5.6	2.4	2.8
A7	08/01/99	08/02/99	6.7	37.1	2.2	0.21	1.8	0.61	3.1	4.5	1.8	3.9
A8	08/02/99	08/03/99	6.3	42.8	2.8	0.29	2.3	0.66	3.3	3.6	1.3	5.6
A9	08/03/99	06/04/99	7.7	53.2	3.7	0.94	7.0	2.3	5.4	4.0	1.1	7.3
A10	06/04/99	04/05/99	5.5	37.9	2.7	0.39	1.1	0.54	3.1	3.3	1.4	5.6
A11	04/05/99	01/06/99	6.7	58.5	3.4	0.83	4.6	1.4	3.3	5.2	1.8	8.5
A12	01/06/99	29/06/99	7.3	33.9	2.2	1.9	1.9	0.58	3.0	3.1	1.4	4.5
A13	29/06/99	27/07/99	6.9	40.1	2.0	0.36	2.2	0.67	3.1	4.1	1.6	6.8
B5	13/11/98	11/12/98	7.3	48.2	1.5	0.66	8.4	2.2	1.4	4.1	1.4	3.4
B6	11/12/98	11/01/99	6.8	33.6	1.4	0.25	0.91	0.28	1.5	3.7	2.0	3.1
B7	11/01/99	09/02/99	7.4	110	4.1	3.3	4.4	1.3	4.9	14.8	10.1	7.1
B8	09/02/99	10/03/99	7.0	68.0	3.0	1.2	3.1	0.92	3.6	7.1	5.4	7.8
B9	10/03/99	08/04/99	6.7	22.7	1.2	0.17	1.4	0.33	1.2	2.9	1.5	4.2
B10	08/04/99	07/05/99	7.6	63.7	3.6	0.46	6.6	1.6	5.3	4.2	2.4	5.4
B11	07/05/99	03/06/99	7.3	72.5	1.9	0.92	4.2	1.0	2.3	7.5	5.7	9.6
B12	03/06/99	02/07/99	6.9	33.9	1.1	0.48	1.7	0.48	1.3	3.5	2.1	5.7
B13	02/07/99	30/07/99	7.2	30.2	1.7	0.82	4.0	1.1	3.2	8.7	3.1	9.1
C5	13/11/98	11/12/98	7.1	102	6.0	0.73	8.3	2.7	11.8	11.4	2.6	8.9
C6	11/12/98	11/01/99	6.9	73.8	3.0	0.41	2.2	0.66	5.9	12.7	4.6	8.8
C7	11/01/99	09/02/99	7.6	66.8	2.8	0.46	3.5	0.71	3.3	8.1	5.4	9.5
C8	09/02/99	10/03/99	6.3	57.4	2.6	0.52	4.7	1.0	3.1	8.9	2.4	17.1
C9	10/03/99	08/04/99	7.1	79.4	6.9	0.71	3.6	1.0	10.4	7.9	2.3	14.5
C10	08/04/99	07/05/99	7.3	69.2	5.5	0.93	4.3	1.3	7.2	7.7	2.6	10.8
C11	07/05/99	03/06/99	6.8	105	5.4	1.1	8.1	1.9	5.4	11.9	3.9	22.9
C12	03/06/99	02/07/99	7.2	69.9	3.9	0.97	3.8	1.2	5.1	6.6	3.2	10.9
C13	02/07/99	30/07/99	6.8	66.5	2.9	0.53	3.8	0.68	3.5	8.9	2.7	12.8
D5	13/11/98	11/12/98	7.3	81.3	2.6	1.1	16.3	3.4	3.3	15.4	2.3	6.5
D6	11/12/98	11/01/99	5.8	36.3	1.5	0.21	1.7	0.52	2.4	6.7	2.0	3.9
D7	11/01/99	09/02/99	7.5	50.6	1.9	0.55	5.0	1.2	1.7	6.8	3.0	5.1
D8	09/02/99	10/03/99	6.8	40.5	1.4	0.39	3.2	0.49	2.1	5.7	2.0	5.1
D9	10/03/99	08/04/99	6.8	34.5	1.1	0.64	2.3	0.42	2.2	5.1	2.4	4.3
D10	08/04/99	07/05/99	6.9	49.5	1.7	0.50	3.1	0.53	1.9	5.6	3.4	4.2
D11	07/05/99	03/06/99	7.1	84.6	1.5	1.3	6.2	1.3	1.3	10.7	6.4	9.6
D12	03/06/99	02/07/99	7.0	38.8	0.75	0.39	1.9	0.32	1.3	4.3	15.6	4.3
D13	02/07/99	30/07/99	7.0	60.3	0.81	0.90	4.5	0.61	1.7	9.8	3.0	8.9

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