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Title: Atmospheric deposition of inorganic pollutants close to a steel mill (Aosta, Italy)

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Title: Atmospheric deposition of inorganic pollutants close to a steel mill (Aosta, Italy)

Abstract: Atmospheric depositions were collected monthly by bulk passive samplers in different sites located in Aosta Valley, in the north west of Italy. The town of Aosta has grown around an industrial complex making stainless steel products. The characterization of atmospheric deposition allows to evaluate the impact on pollution caused by airborne metals released by the electrical steel mill and the study of the spatial variability of the atmospheric fall-out, taking also meteoclimatic conditions into accounts. The entire volume gathered was filtered to obtain soluble and insoluble fractions. As, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb and Zn were analysed on both fractions and the total deposition is the sum of the two fractions.

The study identifies Cr, Ni and Mo as typical markers of stainless steel production.

In urban sites, deposition fluxes of typical stainless steel production metals are higher than those measured in the rural site.

The wind direction recorded in the period considered explains the higher correlation values of typical steel production metals in sites located downwind from the plant.

Small differences were observed among urban sites for metal deposition fluxes, confirming the fact that industrial contribution is localized in a restricted area.

Moreover, a comparison with other urban and industrial locations highlights similar data in urban sites for different metal fluxes and important differences between industrial sites, characterized by the presence of typical production markers.

Finally, the characterization of solubility of the entire group of analyzed metals underlines that the percentage of soluble fraction of typical production markers (Cr, Ni and Co) is lower in urban sites than in the rural one.

Keywords: Atmospheric deposition; Heavy metals, Steel mill production; Soluble and insoluble fractions, Bulk deposition, Aosta, Metals.

Abbreviations: PEP: Pépinière industrial site; **CH:** Charvensod urban site distant 0.4 km from the steel mill, out of the main wind direction; **PL:** Plouves urban site distant 0.8 km from the steel mill, out of the main wind direction; **QD:** Quartiere Dora urban site, downwind and distant 1.2 km from the steel mill; **LIC:** Liconi urban site, upwind and distant 2.0 km from the steel mill; **DO:** Donnas rural site distant 50.0 km from the steel mill, out of the main wind direction; **ICP-MS:** inductively coupled plasma mass spectrometry; **ICP-OES:** inductively coupled plasma optical emission spectrometry; **CV:** coefficient of variation.

1 Introduction:

The widespread distribution of metals is a matter of continuous interest because of their role in the biogeochemical cycle and their impact on the environment [1,2]. Metals originate from natural and anthropogenic sources such as soil dust, traffic, combustion, domestic fuel burning, industrial activities [1,3,4]. At the beginning of the 20th Century an electric steel plant was built in Aosta, a small town in the north west of Italy. Today the plant is one of the leading manufacturers of stainless steel products in Europe and, indeed, in the world. Over the years the town of Aosta has grown around the industrial complex which is currently located next to the urban center. The purpose of this study is to evaluate the pollution linked to airborne metals released by the steel mill in Aosta Valley.

2 Materials and methods:

As defined in 2004/107/EC directive [5], total or bulk deposition means the total mass of pollutants which is transferred from the atmosphere to surfaces (e.g. soil, vegetation, water, buildings, etc.) in a given area within a given time. Atmospheric deposition is collected by bulk passive samplers consisting of a polyethylene bottle surmounted by a polyethylene funnel. The system is placed inside a polymeric black cylindrical container on a 1.5 m high tripod [6].

2.1 Sampling network in Aosta

The sampling network was designed on the basis of the dispersion map resulting from air pollution modeling applied to industrial emissions, also considering the topography of the territory. Monitoring sites chosen are (Fig.1 and Fig. 2): one site next to the industrial plant (PEP), three sites in the urban area directly influenced by industrial emissions (CH, PL and QD), one site in the urban area outside the area of direct influence of industrial emissions (LIC) and a rural site far from industrial plant (DO).

In all sites atmospheric depositions were collected monthly from 2013 to 2015.

2.3 Analytical method

The entire volume collected by every sampler was filtered through mixed cellulose esters filters to obtain soluble and insoluble fractions [6]. The determination of metal concentrations was achieved by ICP-MS and ICP-OES techniques. For each metal the total deposition is the sum of depositions resulting from both fractions [7]. The soluble fraction was analyzed without any additional treatment while the insoluble fraction was digested using a mixture of nitric acid and hydrogen peroxide in a microwave digestion unit. Sampling and laboratory blanks were collected and verified periodically and the entire procedure was tested using a certified reference material (Standard Reference Material B4 from Department of Occupational Hygiene National Institute of Occupational Health, Oslo Norway). The percentage recovery of the target value obtained varied from 80% to 97%. The repeatability of the sampling method was assessed exposing two or three bulks in the same site in the same month. The repeatability, estimated as CV% (standard deviation/mean %), changes between 0.3%-23.0% depending on the metal.

3 Results and Discussion:

3.1 Metals deposition fluxes

Deposition samples were analyzed for As, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb and Zn.

Metal concentrations in bulk deposition are shown in table 1. The table shows metal deposition fluxes, expressed as µg $m^{-2}day^{-1}$ and grouped by type of site.

For every metal considered, the ratio between the flux measured in the industrial site and the flux achieved in the rural site are calculated. In the industrial site, concentration values are 2-5 times higher for As, Cd, Fe, Mn, Pb and Zn compared to data from the rural site. As expected [8,9,10] Cr, Ni, Mo and Co fluxes are much higher than those recorded in the rural site (46 times higher for Cr, 34 for Mo, 21 for Ni and 11 for Co).

This confirms that Cr, Ni, Mo and Co can be considered as markers of the stainless steel production, according to scientific literature.

Furthermore, as expected, the study highlights differences between urban sites according to their distance from the industrial zone. All metal deposition fluxes measured are 2-5 times higher in the industrial site compared to the urban sites.

Boxplots in fig. 3, 4 and 5 show Cr, Ni and Mo deposition. The data reveals a less significant presence of these metals in urban sites (CH, PL, QD and LIC) compared to the industrial site (PEP). Moreover metal fluxes in urban sites don't differ significantly one from another, confirming the fact that industrial contribution is localized in a restricted area. In the rural site there is no evidence of a significant deposition of Cr, Ni and Mo.

Cr and Ni are typical metals of stainless steel production and they can also be found in soil in large amounts.

By contrast, Mo has mainly an anthropogenic origin and it is requested by particular manufacturers due to its properties: the metal provided hardness as well as heat and corrosion resistance.

Co can also be found in soils, but its flux has a great variability. This is due to the fact that Co is occasionally used in stainless steel manufacturing to give it specific characteristics.

Zn, Fe and Mn are involved in stainless steel production and they are ubiquitous metals found in all sites due to their terrigenous origin.

In Fig 3,4,5 the size of boxes suggest a great variability for typical stainless steel production markers in the industrial site (PEP) according to the trend of the demand of industrial production.

3.2 Meteoclimatic conditions

The dispersion of pollutants and their deposition are affected by meteoclimatic conditions especially by rainfall and wind. In order to characterize rainfall and wind patterns, during the study period, data from an already existing weather station was used. In table 2 the rain gauge data measured in Aosta is shown. Rain volumes collected in bulk samplers are similar to those measured by rain gauge (correlation coefficient r = 0.91).

In the period considered the main wind direction recorded was eastward during the day and westward during the night (fig.6). This particular wind pattern determines the major fall-out of typical steel production metals observed in sites located downwind from the industrial zone, such as QD site, where the correlation between Cr and Ni is comparable to that found in industrial site (correlation coefficient r= 0.91 in PEP site and r= 0.83 in QD site). The LIC site however, is 2 Km away from the industrial plant and it is upwind. In this site, a weak correlation of Cr and Ni in atmospheric deposition has been detected (correlation coefficient r= 0.43).

3.3 Comparison with other industrial sites

In table 3 the metal fluxes measured in other urban and industrial sites are reported. While in urban sites fluxes are comparable, data collected from industrial sites are characterized by the presence of typical production markers.

As and Cd are very toxic elements for which some European countries provide threshold values [12] and they are typical markers of glass production [13]. In Aosta their concentrations are very low with little difference between industrial, urban and rural sites.

Fe and Mn are comparable in every site, with the exception of Aosta industrial site, where they reach much higher values because they are components of steel.

The data reveals a significant presence of Cr, Ni and Mo in Aosta compared to other sites, not only in industrial site but also in the urban ones, confirming the fact that Cr, Ni and Mo are typical markers of stainless steel production.

Moreover Fe and Mn fluxes are significant, too.

3.4 Soluble and insoluble fractions of heavy metals

The bioavailable fraction of metals is very important because of its interaction with living organisms. The fraction includes the dissolved material in rainwater and the soluble fraction of deposition. In this study metal contents were investigated in their different bioavailable forms and data from soluble and insoluble fraction were collected.

The solubility of metals is due to differences in origin, composition, structure and interaction with inorganic and organic materials.

Metals can be transferred to humans by contact and they can enter the food chain by vegetable consumption. For this reason it is important to monitor metal distribution in both fractions in order to adopt suitable measures for the safeguard of human health.

Some interesting considerations can be inferred by observing element solubility (Fig.7).

The contribution of the soluble fraction to total deposition is usually greater than that of insoluble fraction for all metals, with the exceptions of Cr (mean value: 10%), Co (mean value: 25%) Fe (mean value: 30%) and Ni (mean value: 45%) [8,9,10]. These metals are typical for the production of steel and the production of special steels. In the rural site values referred to the soluble fraction of these metals are similar to those reported in other studies [1]: Cr 40%, Co 55%, Fe 40% and Ni 70%.

4 **Conclusion:**

The present work describes analytical data resulting from metal depositions in Aosta. The samples were collected in order to calculate metal deposition fluxes and to characterize typical markers for stainless steel production in the period considered. The data were used in order to make a comparison with results collected in other industrial locations. A significant presence of Cr, Ni, Mo, Fe and Mn, with expect to other industrial sites, has be found in the urban area of Aosta. Typical and specific correlation between metals were observed and their values were significantly lower moving further away from industrial site.

Meteoclimatic conditions, such as wind direction, are an important element to investigate in order to determine their influence on metal deposition fluxes.

The solubility of metals is also very important because it affects the bioavalaibility and the interactions of metals with living organisms.

Further studies will be carried out to investigate the deposition of metals on the ground. As a matter of fact metals can be transferred to humans by contact and they can enter the food chain by vegetable consumption. It is therefore important to evaluate the impact of dissolved fraction of highly toxic metals on ecosystem health due to their bioavailability.

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Figure 1

Figure 2

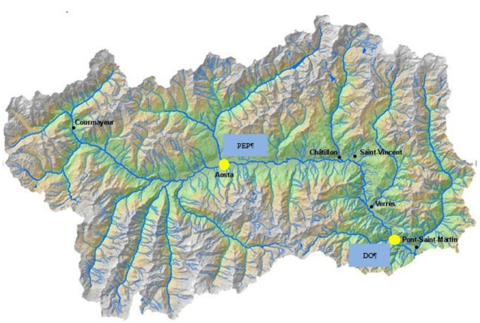

Figure 3

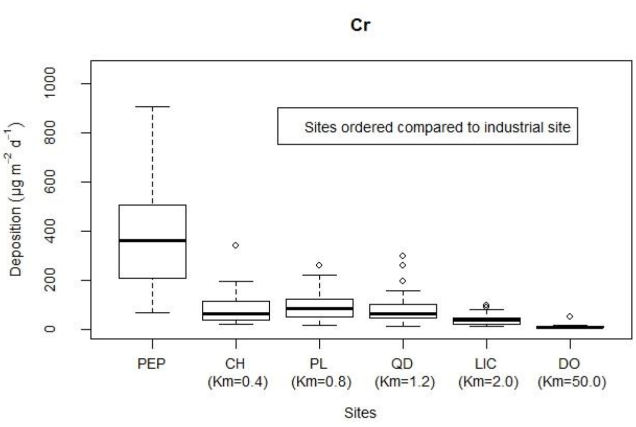

Figure 4

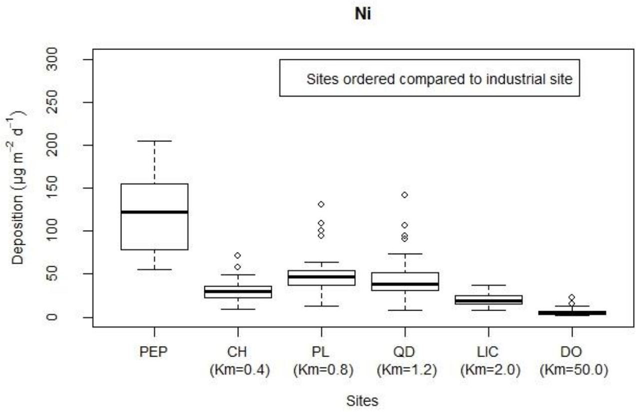

Figure 5

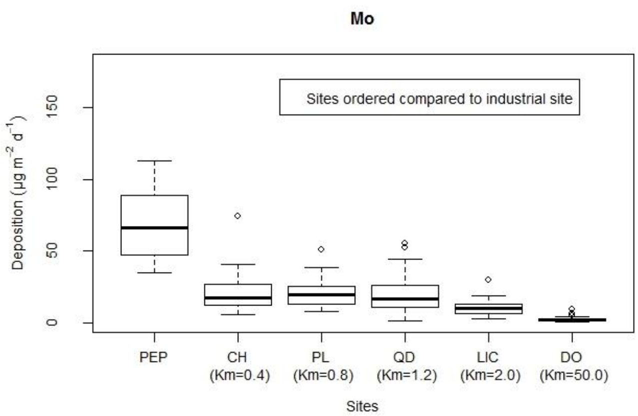

Figure 6

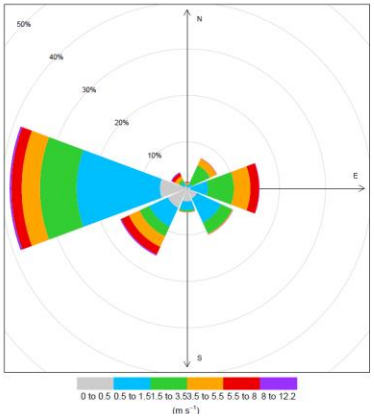

Figure 7

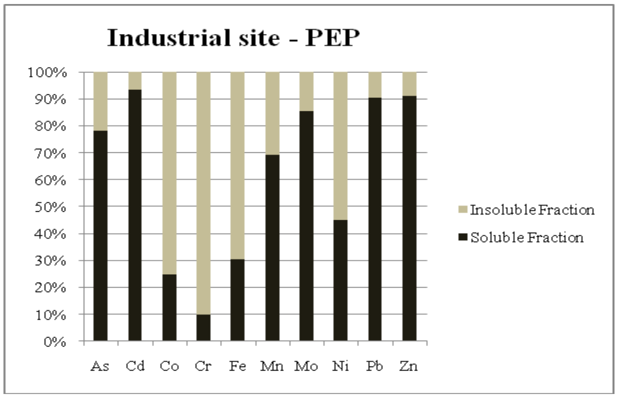

Figure Legend 1: Fig. 1 Sampling sites of different atmospheric deposition in Aosta. The white colored area is the industrial plant.

Figure Legend 2: Fig. 2 Sampling sites of different atmospheric deposition. In particular industrial site (PEP) and rural site (DO).

Figure Legend 3: Fig. 3 Boxplot of Cr in different sites

Figure Legend 4: Fig. 4 Boxplot of Ni in different sites

Figure Legend 5: Fig. 5 Boxplot of Mo in different sites

Figure Legend 6: Fig. 6 Wind rose from studied area (mean values of years 2013-2015)

Figure Legend 7: Fig. 7 Comparison between soluble and insoluble fractions in industrial PEP site

Tables

Table 1: Daily fluxes of metals in bulk deposition in Aosta Valley (unit: µg m^{-2} day^{-1})

		As	Cd	Co	Cr	Fe	Mn	Mo	Ni	Pb	Zn
Industrial site	Mean	1.4	1.2	10.5	403	3518	210	74.9	132	10.9	158
	Median	1.0	0.8	5.3	360	2764	173	66.0	122	8.5	125
Urban sites	Mean	0.9	0.2	4.7	85.0	1855	70.9	20.4	42.2	6.2	106
(Km = 0.8)	Median	0.8	0.1	2.5	69.8	1572	68.1	17.6	38.5	5.7	96.3
Upwind urban site	Mean	0.8	0.2	2.3	37.0	1356	52.7	10.0	21.1	5.3	105
(Km = 2)	Median	0.7	0.1	1.6	34.6	1237	47.8	9.7	19.2	4.2	79.8
Rural site	Mean	0.9	0.2	0.9	8.6	931	49	2.2	6.2	4.4	78.4
(Km = 50)	Median	0.7	0.1	0.6	7.2	652	24	1.8	5.1	3.0	73.4

Table 2: Rain gauge data measured in Aosta (2013-2015)

	Rainfall, mm/month		
Year	Mean	Min	Max
2013	58.38	4	189.4
2014	49.03	12.2	113.8
2015	37.98	0.4	95.2

Table 3: Comparison of different urban and industrial site

		Aosta urban	Venice[a, b]	Urban[d]	Aosta industrial Steel production	Murano[c] Glass production	Porto Tolle[e] Power plant	Corteolona[f] Special wastes incenerator	Industrial[d]	EU limits
As	µg m^{-2} d^{-1}	0.2-2.4	0.2-2.3	0.2-5.0	0.5-9.2	8.2-401	0.3-0.8	0.7-2.4	1.8-708	4 [h]
Cd	µg m^{-2} d^{-1}	0.1-1.1	0.1-6.3	0.2-1.0	0.1-6.5	7.3-105	0.04-0.2	0.2-0.4	0.12-122	0.27-5 [d]
Cr	µg m^{-2} d^{-1}	10.9-96.8	1.4-8.0		67.9-1389	2.3-72	4.8-8.4	6.2-20.8		
Fe	µg m^{-2} d^{-1}	523-4038	160-1841		1270-18893	16.7-5347	939-1686	976-3761		
Mn	µg m^{-2} d^{-1}	23.2-105	4.5-42		79.8-969	11.4-285		60-157		
Ni	µg m^{-2} d^{-1}	8.1-37.5	2.6-14	0.16-3.8	55.3-439	2.4-179	5.2-10.3	6.3-14.6	1.2-129	15 [h]
Pb	µg m^{-2} d^{-1}	1.5-16.6	4.2-28	500 [g]	4.4-53.7	2.3-523	5.4-26.2	43-337	50-8700 [g]	100-3000 [d]
Zn	µg m^{-2} d^{-1}	24.8-308	14-354		46.7-797	148-2833	18.9-36.8	95-128		10-400 [h]

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