

## HEAVY METALS: SOURCES AND ENVIRONMENTAL PRESENCE

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*Summary. - The Istituto Superiore di Sanità has for many years been involved in the problem of environmental pollution caused by heavy metals. A brief review of the sources of this pollution is first presented which also includes the presence in nature of some heavy metals which are among the most dangerous. Data gathered by the authors is then presented from sampling of the emissions of urban solid waste (USW) incinerators and from environmental monitoring programs in different areas in Italy according to four categories: urban, industrial, rural and mixed.*

*Riassunto (Metalli pesanti: fonti e presenza nell'ambiente). - L'Istituto Superiore di Sanità si occupa da anni del problema dell'inquinamento ambientale dovuto ai metalli pesanti. Dopo una rapida presentazione delle fonti di inquinamento ambientale e della presenza in natura di alcuni metalli pesanti, tra i più pericolosi, vengono riportati i dati rilevati dagli autori sia in emissione da inceneritori di rifiuti solidi urbani (RSU), sia in campagne di monitoraggio ambientale in aree italiane diverse per tipologia (urbana, industriale, rurale e mista).*

### Introduction

Over the last few years the problem of pollution from heavy metals has caused increasing concern.

This applies to both industrialized zones and highly technological populated areas, even though in different ways. In reality, in countries such as Italy, strongly industrialized zones do not really exist, since they are in close contact with populated areas. For this reason highly industrialized mixed areas reflect the real situation much better.

Therefore, the problem of pollution from heavy metals involves the whole population and regards all three receiving compartments, namely air, water and soil.

The principal metal emission sources come from the following industries: petrochemical, extractive, metallurgic

(foundry and metallurgy), mechanic (galvanic processes, painting), chemical (paints, enamels, plastic materials) and ceramic.

Urban pollution is caused by the emissions from solid waste incineration plants, by internal combustion engines running on gasoline containing lead-alkyl compounds (in the next few years the use of additives containing lead will be eliminated) and by combustion processes using coal or oil to produce heat.

In the following sections some of the more dangerous effects of elements present in the environment will be summarized.

### Arsenic

In nature As and its compounds exhibit both metallic and non-metallic properties and can be found almost everywhere. Arsenic in its natural state appears primarily in the form of sulfides in association with those of Ag, Co, Cu, Fe, Pb, Ni and Sb in ores. 40 µg of As per gram of soil is assumed as uncontaminated soil. On the other hand near copper smelters levels of 100-2500 µg/g have been found. Another source of high levels (up to 700 µg/g) may be caused by the use of pesticides, herbicides and defoliants in agricultural soil.

In air, As can be released by natural processes (mostly from volcanic activity) and by man through the use of pesticides, smelting of metals and combustion of fuel (especially low-grade brown coal). Natural emissions are estimated at 7,900 tonnes per year worldwide, while man-made emissions are about 23,600 tonnes per year.

The world production of  $As_2O_3$  is around 40,000-70,000 tonnes per year. In rural areas, representative background levels of As in air are 1-10 ng/m<sup>3</sup>. In urban areas, they can reach several hundred ng/m<sup>3</sup> and can exceed 1000 ng/m<sup>3</sup> near non-ferrous metal smelters and some power plants, depending on the amount of As in combusted coal. Over the 1977-1981 period, annual means in the USA ranged from 2.6 to 11 ng/m<sup>3</sup>.

In air, As is present mostly in particulate form as organic compounds containing the element predominantly in its pentavalent oxidation state [1].

## Cadmium

Cadmium is a soft, light-coloured metal with high vapour pressure causing it to be rapidly oxidized to cadmium oxide in air. While many inorganic Cd compounds are water soluble, CdS and CdO are almost insoluble in water.

In nature, Cd occurs together with Zn at a concentration of about 0.1-1% and is a byproduct of Zn refining, as some Zn ores may contain as much as 5% Cd. Zinc production constitutes the largest source of Cd supply. The world average annual production of Cd was about 12,000 tonnes in 1960-1969 and 15,000-20,000 tonnes in 1980-1985.

Cadmium compounds are used in metal electroplating, as stabilizers or pigments in plastics, in alkaline batteries and in alloys.

In Europe, the major sources of Cd emissions are Zn production, volcanic activity, steel industry and waste incineration, the latter probably being the most troublesome pollution for the near future.

In rural areas, the yearly average ranges from  $< 1$  to  $5 \text{ ng/m}^3$ ; in urban areas from  $5$  to  $15 \text{ ng/m}^3$ ; in industrialized areas from  $15$  to  $50 \text{ ng/m}^3$ , with much higher concentrations in the vicinity of metal processing plants. These concentrations are directly reflected in the precipitation of Cd with yearly deposition values ranging from  $0.007$  to  $0.29 \text{ mg/m}^2$  in rural areas,  $0.15$  to  $11 \text{ mg/m}^2$  in urban areas and  $0.25$  to  $73 \text{ mg/m}^2$  in industrialized areas.

It has been estimated that  $1 \text{ ng/m}^3$  would cause a deposition of  $0.16 \text{ ng/m}^2$  per year [1].

## Chromium

In nature, Cr is found mostly in the trivalent state with hexavalent compounds found in small quantities. The only important ore containing Cr is chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) with its highest grade containing 55%  $\text{Cr}_2\text{O}_3$ .

In Europe, Cr is used in the production of ferrochromium, potassium chromate, sodium chromate and dichromate. The last two are the most important and are used mainly for the manufacturing of chromic acid and Cr pigments, in leather tanning and for corrosion control.

In soil, Cr levels vary considerably with an average ranging from  $14$  to  $70 \text{ mg/kg}$ .

Since it is almost ubiquitous in nature, Cr in air is in part due to wind erosion of soil or to the mining of chromite; the production of Cr compounds probably constitutes the most important source of Cr in air in Europe.

Concentration measurements of Cr in the atmosphere are limited while it should be noted that results coming from studies made over the last 5-10 years are much more reliable.

In 1977-1980, monitoring of urban and rural areas in the USA showed concentrations ranging from  $5.2 \text{ ng/m}^3$  to  $156.8 \text{ ng/m}^3$ . A recent study in Europe showed concentrations for remote areas as high as  $0.3 \text{ ng/m}^3$ ,  $4$  to  $70 \text{ ng/m}^3$  for urban areas and  $5$  to  $200 \text{ ng/m}^3$  for industrialized areas.

Since Cr(VI) compounds are much more dangerous to human health than Cr(III) compounds or other valence states, the two species must be considered separately from a toxicological point of view [1].

## Lead

Lead is a greyish soft metal with a  $327.5^\circ\text{C}$  melting point and a boiling point of  $1740^\circ\text{C}$  at atmospheric pressure. It has four naturally occurring isotopes with ratios depending on the various mineral sources. The usual oxidation state of Pb in inorganic compounds is +2. Most inorganic Pb(II) salts are poorly soluble in water.

Tetraethyl Pb and tetramethyl Pb are organic Pb compounds extensively used as fuel additives which tend to concentrate because of their low volatility during the evaporation of gasoline.

80-90 % of Pb emissions into the atmosphere are caused by the combustion of alkyl Pb additives in motor fuel, but their degree of pollution varies from country to country. Other sources of Pb pollution are mining and smelting of Pb ores, refining and manufacturing of compounds and Pb-containing goods, and refuse incineration.

Lead is also present in coal, so that industries that use coal must also be considered as sources.

The level of Pb present in the atmosphere is much higher in urban areas (current levels in most European cities average annually from  $0.5$  to  $3.0 \mu\text{g/m}^3$ ) than in rural area with ranges from  $0.1$  to  $0.3 \mu\text{g/m}^3$ , even though these values tend to decrease as the Pb content in gasoline is being lowered. Around Pb smelters, concentration values are obviously high.

Most Pb (> 90 %) released from leaded petrol emissions is in the form of inorganic particles (for example  $\text{PbBrCl}$ ) with a mass median equivalent diameter (MMAD) of less than  $1 \text{ nm}$ . Immediately surrounding Pb smelters, larger particles that settle close to the plants can be found. Further away the size of the particles is the same as these found in other urban sites. In general, indoor concentrations of Pb in the air are lower than outdoor concentrations, especially during winter.

Lead is removed from air by dry or wet deposition with varying time of residence. Fallout is mostly limited to the immediate vicinity of the source even though a small part of Pb in air can be carried far away, as shown by the analysis of glacial ice and snow deposits in remote areas. Over the last few decades this has resulted in a long-term global accumulation of Pb [1].

## Manganese

Manganese is a very abundant element, widely distributed in the earth's crust. It does not occur naturally in the native state, the most important Mn-containing minerals

being oxides, silicates and carbonates, while the most common is pyrolusite ( $\text{MnO}_2$ ). Manganese also occurs in most Fe ores, in coal and, in much lower concentrations, in crude oil.

Manganese is used mostly in metallurgical processes, but it is also used in the manufacturing of dry-cell batteries, glass, fertilizers and in the leather and textile industries. Organic carbonyl compounds are used as fuel-oil additives and smoke inhibitors.

Manganese is released into the atmosphere by both natural and anthropogenic processes, mostly in the form of coarse particles, through wind erosion, road dusts, agricultural and building activities and quarry processes. In the form of fine particles it is released into the atmosphere by natural ore smelting and fossil-fuel combustion. Manganese is also emitted by the manufacturing of ferroalloys and other industrial processes.

Since it has a low volatility, Mn settles mostly in the immediate vicinity of its source of release. However, fine particles can be carried far away. In metallurgical processes Mn is emitted mainly in oxide form.

Manganese dioxide can be prepared from manganous sulfate and dithionate and manganese nitrate. In the atmosphere manganese dioxide can be a catalyst for the formation of sulphuric acid from sulfur dioxide.

In air, the natural level of Mn is low with annual mean levels in non-polluted areas ranging from 0.01 to 0.03  $\mu\text{g}/\text{m}^3$ ; in urban and rural non-polluted areas it is present at 0.01-0.07  $\mu\text{g}/\text{m}^3$ . In areas around foundries, it can be found at 0.2-0.3  $\mu\text{g}/\text{m}^3$  and in areas of ferro- and silicomanganese industries, it can exceed 0.5  $\mu\text{g}/\text{m}^3$ .

Most emitted Mn (80%) is found in particle form with an MMAD less than 5  $\mu\text{m}$ , 50% being less than 2  $\mu\text{m}$ ; these particles are transported by air currents and then deposit for the most part spontaneously but also by rainfall.

In the work environment, concentrations of Mn have been reported to be as high as 250  $\text{mg}/\text{m}^3$  or even higher in mines; they are also high in ore-processing plants. In ferromanganese plants and also in dry-cell battery plants the size distribution of Mn aerosols is such that small, respirable particles definitely prevail [1].

## Mercury

There are three oxidation states of this element: Hg (metallic),  $\text{Hg}^+$  (mercurous) and  $\text{Hg}^{2+}$  (mercuric) species. Hg is emitted from land and water surfaces into the atmosphere where it is transmitted on a global scale, possibly converted, and returns to land and water with the ultimate deposition probably occurring in ocean sediments.

Methylmercury enters the human diet through fish; the highest accumulation of methylmercury is found in predatory fish at the top of the aquatic food-chain. Microorganisms can also contribute to the release of Hg into the environment.

Man-made sources of Hg are many and wide-spread. Mercury is also produced in the mining and smelting of cinnabar ore. Mercury is used in industries which produce  $\text{Cl}_2$  and NaOH, paints, electrical equipment, batteries, measuring and control equipments, vacuum apparatuses, chemicals, lamps, explosives, tooth-fillings and fungicides. Mercury is also released by the burning of fossil fuels, smelting, cement manufacture and waste disposal.

In 1985 the total anthropogenic emission of the element to air, water and soil was estimated at around 9300 tonnes, with natural emissions being around 15,800 tonnes. In Europe, the majority of Hg emissions to air are from anthropogenic sources. Background troposphere levels of the northern hemisphere are estimated at 2 ng Hg per  $\text{m}^3$ . The concentrations of total Hg in the atmosphere range from 0.001-6  $\text{ng}/\text{m}^3$  in remote areas; 0.1-5  $\text{ng}/\text{m}^3$  for urban areas and 0.5-20  $\text{ng}/\text{m}^3$  for industrialized areas. Extremely high levels have been found in Japan, where Hg fungicides were used (up to 10,000  $\text{ng}/\text{m}^3$ ), and on busy motorways (up to 18,000  $\text{ng}/\text{m}^3$ ).

Probably the most predominant form of the element in the atmosphere is the vapour of metallic Hg and about 5-10% of total gaseous Hg is water-soluble; particulate Hg makes up for less than 5% of the total element in the atmosphere. The residence time of total Hg, mostly metallic Hg vapours, is 0.4-3 years.

Indoor air pollution of Hg vapours has not been documented although fatalities and severe poisonings have occurred in particular cases [1].

## Nickel

Nickel, a light-coloured hard metal, forms compounds in the oxidation state +2; only the divalent ion is important for both organic and inorganic substances. Adenosine triphosphate, aminoacids, proteins, deoxyribonucleic acid and peptides form complexes with Ni in biological systems.

Nickel is found in the earth's crust in the 58-94  $\text{mg}/\text{kg}$  range, while in water the element background levels are low. The normal level of concentration in soil is around 50  $\text{mg}/\text{kg}$ ; in oil, Ni is present at levels reported to be from 0.29-76.6  $\text{mg}/\text{kg}$ .

More than half of all Ni produced is obtained from pentlandite, a sulfide ore.

In industry, Ni is used in steel production, electroplating, coinage, as a catalyst, ceramics, storage batteries, for dyeing and colouring of glass.

Anthropogenic sources of Ni emissions to the atmosphere are fuel and residual oil burning, mining, refining and municipal waste incineration. Nickel sulfate is the most common form of the element in ambient air and in fly ashes released from boilers and also from coal combustion; coal and oil combustion are the largest sources of Ni emission in the USA.

In global atmospheric emissions, total annual Ni emissions from anthropogenic sources are around 98,000 tonnes and 30,000 tonnes/year from natural sources.

In Europe, the following Ni concentrations were found: 0.1-0.7 ng/m<sup>3</sup> in remote areas; 3-100 ng/m<sup>3</sup> in urban areas; 8-200 ng/m<sup>3</sup> in industrial areas, with daily deposition rates at 0.2-10 ng/m<sup>2</sup>, 2-10 ng/m<sup>2</sup> and 7-70 ng/m<sup>2</sup>, respectively. Nickel concentration varies with the size of particles and more than half of airborne Ni is found in particles smaller than 2-3 µm in diameter, with particles from oil and coal below 1 µm [1].

## Vanadium

Vanadium is a white ductile metal which forms compounds in the +3, +4 and +5 valence state; it is found in the +5 oxidation state in the presence of oxygen and + 4 in presence of reducing agents.

Vanadium is found throughout the earth's crust, with an average concentration of 150 µg/g, reaching high values (up to 400 µg/g) in areas of fly ash pollution. For the most part, geography governs the V concentration in water, with a higher range in freshwater than in seawater.

In 1981, world production of the element was around 35,000 tonnes, mostly used in ferrovanadium which is then used in high-speed and other alloy steel.

Anthropogenic sources of atmospheric emission (about 200,000 tonnes a year as compared to 65,000 tonnes from nature) are metallurgic works and the burning of crude or residual oil and coal. In 1972 in Canada, man's activities resulted in 2065 tonnes of V emissions, of which 94% were from fuel oil combustion and only 1.2% from metallurgic industries.

Vanadium concentrations in ambient air are very low. The range for remote areas is 0.001-3 ng/m<sup>3</sup>; in urban areas 7-200 ng/m<sup>3</sup> and 10-70 µg/m<sup>3</sup> in industrial areas. Probably the greatest source of V pollution in air comes from power stations and heating equipments.

Vanadium is released into the air as fly ashes with a long atmospheric residence time. Most of the particles have a MMAD less than 0.5 µm.

Workers can be exposed to V from different activities, while especially high concentrations were reported in boiler cleaning (17-60 mg/m<sup>3</sup>) [1].

## Conclusions

Over the last few years, the authors have been involved in research concerning heavy metals present both in emissions and in the atmosphere. Through this research it has been possible to assess the range of concentrations reflecting different degrees of exposure in Italy.

As far as industry is concerned, heavy metals were found in the emissions of solid urban waste (SUW) incinerators [2, 3] and, in collaboration with other centers and regions, thus defining the effect these pollutants have on the environment (Tables 1-3).

Table 1. - Concentration ranges of some metals from dust sample at the furnace of SUW incinerators (concentrations are expressed in mg/kg of dust issued)

Metals	Range (mg/kg)
Al	112,736-196,594
As	837-1722
Ba	53-78
Cd	34-819
Co	11-27
Cr	208-658
Cu	1546-2637
Fe	6635-21,157
Hg	1543-3749
Mn	903-3407
Ni	85-364
Pb	662-19,406
Sb	36-142
Sn	32-137
Zn	1449-46,194
V	333-954

Table 2. - Emissions from SUW incinerator plants. Division between particle material and vapour from some metals

Plants	Temperature of emission (°C)	Metal in vapour % (w/w)		
		Cd	Hg	Pb
A	180	49	39	0.14
B	280	9.3	28	0.33
C	290	5.4	69	1.2

Table 3. - Estimate of the emissions of metals at the lower end of abatement system in SUW incinerators. Data calculated from Italian plants (concentrations expressed in g/t of SUW incinerated)

Metal	Technologically traditional plant	Technologically advanced plant
Cd	3.5	0.4
Hg	7.5	0.3
Pb	54	10

Surveys in different industrial areas showed how the emissions of these metals, apart from Pb, are strongly influenced by the plants themselves.

Results regarding metal micropollutants are also summarized. These results refer to a survey made by the Istituto Superiore di Sanità in several industrial and mixed (industrial-urban) areas such as Piombino, Siracusa, Portofino and Lecce.

Table 4 shows the average concentration ranges of heavy metals surveyed in different types of industrialized and urban areas and, for comparison, also in a rural area.



Table 4. - Concentrations of heavy metals in different Italian areas surveyed as part of the Istituto Superiore di Sanità project

Metal	Range ( $\mu\text{g}/\text{m}^3$ )	Areas
Cd	0.0017-0.0194	Rome (urban)
	0.0012-0.223	Venice (urban)
	0.0037-0.0704	Marghera (industrial)
	0.0007-0.794	Portoscuso (industrial)
	0.0001-0.0014	Lecce (mixed)
	0.0003-0.0059	S. Rossore (rural)
Cr	0.001-0.423	Portoscuso (industrial)
	0.003-0.068	S. Rossore (rural)
Cu	0.003-0.118	Portoscuso (industrial)
	0.006-0.279	S. Rossore (rural)
Fe	0.047-4.05	Portoscuso (industrial)
	0.43-41.5	Piombino (industrial)
	0.21-1.26	Lecce (mixed)
	0.064-0.279	S. Rossore (rural)
Pb	1.94-4.02	Rome (city centre)
	0.09-1.03	Venice (urban)
	0.29-9.77	Marghera (industrial)
	0.04-1.19	Siracusa (industrial)
	0.006-6.20	Portoscuso (industrial)
	0.007-0.49	Lecce (mixed)
	0.11-1.48	Piombino (industrial)
	0.002-2.33	S. Rossore (rural)
V	0.012-1.00	Portoscuso (industrial)
	0.007-0.166	Lecce (mixed)
Zn	0.049-16.98	Portoscuso (industrial)
	0.02-1.36	Piombino (industrial)
	0.042-0.871	S. Rossore (rural)

This table demonstrates that the pollution levels of Pb are higher in urban areas with respect to industrialized areas and that, even in the rural area, the concentrations of this metal are in no way negligible [4-10].

The average concentrations of Cd surveyed in different areas show that this metal, in industrial areas, is present at very high concentrations depending on the type of work done in the area (the Portoscuso area has metal industries and natural mining).

The concentrations of Fe is particularly high in the industrial area of Piombino (steel mill).

Contrary to Fe, the concentration of V does not change much from mixed to industrialized areas. This could indicate a fairly important combustion from automobile traffic and heating systems.

Finally, even though the study was limited to only a few areas, it can be clearly observed that the concentrations surveyed are comparable to those found in the rural area of S. Rossore. This locality is about 10 km from the industrial area of Livorno and about 5 km from Pisa.

In future, the study of SUW incinerator emissions will be continued, integrating the research with studies on the impact incinerator plants have on the environment both from the point of view of atmospheric pollution through the storage of industrial wastes.

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#### REFERENCES

1. WORLD HEALTH ORGANIZATION 1987. *Air quality guidelines for Europe*. WHO Regional Publications, European Series no. 23.
2. VIVIANO, G., ZIEMACKI, G. & D'INNOCENZIO, F. 1981. Inquinanti metallici presenti nelle emissioni di inceneritori di rifiuti solidi urbani. *Ann. Ist. Super. Sanità* 17(3): 453-458.
3. BONIFORTI, L., VIVIANO, G., ZAPPONI, G., ZIEMACKI, G., DI GRAZIA, B., MIRABELLA, E., MARINELLI, A. & BONANNI, D. 1982. *L'inceneritore di rifiuti solidi urbani di Lecce: impatto sulla qualità dell'aria*. Roma, Istituto Superiore di Sanità, 1982. (Rapporti ISTISAN 82/28).
4. D'INNOCENZIO, F., CERQUIGLINI MONTERIOLO, S., CECCHETTI, G., BONANNI, D. & ZIEMACKI, G. 1978. Inquinamento atmosferico da piombo in zone urbane ed industriali italiane. *Ann. Ist. Super. Sanità* 14(3): 513-522.
5. CERQUIGLINI MONTERIOLO, S., CECCHETTI, G., ZIEMACKI, G., BERTOLACCINI, M.A., VIVIANO, G. & MUSMECI, L. 1978. Cadmio come inquinante dell'aria. *Ann. Ist. Super. Sanità* 14(3): 503-512.
6. CERQUIGLINI MONTERIOLO, S., FUSELLI, S., OTTAVIANI, M., SANTOMAURO, L., VIVIANO, G., ZIEMACKI, G., DI GRAZIA, B., BONANNI, D., MARINELLI, A., BIANCHI, E. & GUBBIOTTI, P. 1982. *Indagine sullo stato d'inquinamento atmosferico nella fascia costiera da Augusta a Siracusa ed il suo immediato entroterra*. Roma, Istituto Superiore di Sanità, 1982. (Rapporti ISTISAN 82/19).
7. VIVIANO, G., D'INNOCENZIO, F., GUCCI, P.M.B., ZIEMACKI, G., DI GRAZIA, B., MARINELLI, A., BIANCHI, E. & TUROLLA, B. 1981. *Indagine sulla qualità dell'aria nella città di Piombino*. Roma, Istituto Superiore di Sanità, 1981. (Rapporti ISTISAN 81/7).
8. CERQUIGLINI MONTERIOLO, S., VIVIANO, G., ZIEMACKI, G., DI GRAZIA, B., MARINELLI, A., BONANNI, D. & GUBBIOTTI, P. 1984. *Indagine sullo stato di inquinamento atmosferico nella zona di Portoscuso (Cagliari)*. Roma, Istituto Superiore di Sanità, 1984. (Rapporti ISTISAN 84/7).
9. CERQUIGLINI MONTERIOLO, S., FUSELLI, S., OLORI, L., VIVIANO, G., ZIEMACKI, G., DI GRAZIA, B., MARINELLI, A., AMADORI, G., BONANNI, D., GUBBIOTTI, P., GUCCI, P.M.B., BARIS, F., GIORGI, F. & MORGIA, P. 1984. *Risultati del rilevamento della qualità dell'aria nella tenuta presidenziale di S. Rossore*. Roma, Istituto Superiore di Sanità, 1984. (Rapporti ISTISAN 84/23).
10. FUSELLI, S., PACELLI, E., PAOLETTI, L., VIVIANO, G. & ZIEMACKI, G. 1987. Caratterizzazione del materiale particolato atmosferico presente in aree urbane. In: *Inquinamento in ambienti di vita e di lavoro: esperienze e linee di intervento*. Acta Medica Edizioni e Congressi srl.