EXPOSURE ASSESSMENT TO HEAVY METALS IN THE ENVIRONMENT: MEASURES TO ELIMINATE OR REDUCE THE EXPOSURE OF CRITICAL RECEPTORS.

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Abstract. The anthropogenic sources for heavy metals include mining, industrial productions, untreated sewage sludge and combustion by-products produced by coal burning power plants. Atmospheric emissions are probably the most preoccupant to human health and to the environment due to either the great quantity involved, or their widespread dispersion. Mercury, lead and cadmium represent a great issue, mostly due to their ability to travel long distances in the atmosphere before deposition. Exposure assessment to emissions of heavy metals implies to identify and quantify the sources, how heavy metals may be dispersed in the environment and which adverse effects they might cause on human health and on the ecosystem. Heavy metals emissions and releases into the environment are available at the European Pollutant Release and Transfer Register [E-PRTR, 2010]. In this data base main sources from 27 European countries are identified. Data concerning Cd, Hg and Pb were extracted for the year of 2007. This work focuses on the review and analysis of the principal sources of heavy metals emissions into the environment and their role in critical receptors' environmental exposure. The review of the principal sources may give a clearer picture of the situation: the potential regions at risk and the extension of the contamination, essential to the exposure assessment by critical receptors. On the other hand, exposure assessments studies and consequent research allow a better knowledge of heavy metals sources, emissions, pathways and fate in the environment. Therefore both a complete exposure assessment and a consequent risk assessment are needed to establish the identification and implementation of measures to eliminate or to reduce the exposure.

Keywords: Exposure, heavy metals, air emissions, critical receptors, assessment.

1. Introduction

By definition, heavy metals are any metallic chemical element that has a relatively high density (superior to 5 g/cm^3); most of them are toxic or carcinogenic even at low concentrations, such as mercury (Hg), cadmium (Cd), arsenic (As) and chromium (Cr).

Poisoning by exposure to heavy metal is well known to affect central nervous function, damage blood composition, lungs, kidneys, liver and other vital organs. Long-term exposure can cause slower progressing physical, muscular, and neurological degenerative processes. Allergies may also occur and repeated long-term contact with some metals, or their compounds may become carcinogenic.

Heavy metals in the environment may result from many different activities and sources and may enter into the environment by a wide range of processes and pathways; heavy metals are naturally found on earth's crust and have been used in many different applications over decades.

Generic sources of heavy metals include mining and industrial production such as foundries, smelters, oil refineries, petrochemical plants and chemical industry, untreated sewage sludge, disperse sources such as metal piping, traffic and combustion by-production from coal burning power plants. Atmospheric emissions are probably the most harmful to the environment, and consequently, to human health due to either the great quantity involved, or their widespread dispersion which may originate many different exposure pathways. In particular, these three heavy metals (Hg, Pb and Cd) are of great concern to human health and to the environment, mostly due to their ability to travel long distances in the atmosphere before deposition.

Lead is a very soft metal and over decades has been used in many different applications: building materials, pigments for glazing ceramics and pipes for transporting water. It is classified as number 2 in ATSDR's (Agency for Toxic Substances and Disease Registry) top 20 list [ATSDR, 2007]. During the last century, the lead content in fuels was a main source of pollution to the environment and, particularly, the lead released to the atmosphere was especially hazardous to children. Today most of the 25 millions of tons of lead produced every year is used in batteries.

Cadmium is number 7 in ATSDR's top 20 list [ATSDR, 2008]. It is widely used in batteries and in paint pigments. Cadmium is also a by-product of the mining and smelting of lead and zinc. It is a common component of commercial fertilizers used in agriculture (insecticides and fungicides) and is frequently found in agricultural soils. Cigarettes also contain cadmium.

Mercury is naturally generated from volcanoes. It is also a naturally occurring metal used in many man-made products and processes. It may appear in three different forms: i) organic mercury (predominantly methylmercury, ethylmercury and phenylmercuric acetate); ii) non-elemental forms of inorganic mercury (salts such as HgS, HgO, $HgCl_2$); iii) elemental mercury, in the form of a thick liquid at room temperature, mostly familiar by the silver liquid inside mercury thermometers [EPA, 2006]. Mining and paper industry are significant producers of mercury. Mercury is number 3 in ATSDR's top 20 list [ATSDR, 1999]. Until 1990 mercury was commonly added to paint as a fungicide; today it can be found in thermostats and in some medicines (mercurochrome and merthiolate) and also in vaccines. Mercury is still being used in gold mining in some parts of Latin America and Africa.

Heavy metals emissions, sources and quantities from 27 European Member states as well as Iceland, Liechtenstein and Norway, are registered at the European Pollutant Release and Transfer Register website (http://prtr.ec.europa.eu/Home.aspx). In these inventory heavy metals sources or sectors are identified and detailed air emissions are available. Data regarding the heavy metals of concern in this study were extracted from the E-PRTR inventory for the year of 2007. This work focuses on the review and analysis of the principal sources of heavy metals emissions into the environment and their role in critical receptors' environmental exposure. The review of the principal sources may give a clearer picture of the situation, in particular, the potential regions at risk, the extension of the contamination (in particular for Hg, Cd and lead emissions) and the exposure assessment by the critical receptors. Consequently, measures to eliminate or to reduce the exposure may be identified and implemented.

2. Heavy Metals Occurrence and Exposure

2.1. CADMIUM NATURAL AND ANTHROPOGENIC SOURCES

Cadmium is classified as human carcinogenic group I. It occurs naturally in the environment together with Zn, Pb and Cu and is present on the earth's crust between 0,1 and 0,5 ppm, although higher levels may accumulate in sedimentary rocks. Marine phosphates have also been referenced as containing levels up to 500 ppm [Cook and Morrow, 1995], [WHO, 1992]. Cadmium is also present in volcanic activities and forest fires which have been reported as natural sources of cadmium air emissions [Jarup, 2003]. Cadmium releases to the environment may result either from these natural sources, or from anthropogenic sources. Anthropogenic sources of cadmium and their compounds may be grouped in the following sectors [E-PRTR, 2010]: i) Energy sector (mineral oil and gas refineries, thermal power stations and other combustions installations); ii) production and processing of metals; iii) Mineral industry (production of cement clinker or lime rotary kilns or other furnaces, manufacture of glass fibre, manufacture of ceramic products including products tiles, bricks, stoneware or porcelain); iv) Chemical industry (industrial scale production of basic organic and inorganic chemicals, production of phosphorus nitrogen or potassium based fertilizers); v) Waste and waste water treatment (disposal or recovery of hazardous waste, incineration of non-hazardous waste included in Directive 2000/76/EC-waste incineration); vi) Paper and wood production processing; vii) Animal and vegetable products from the food and beverage sector.

Cadmium is not mined but it is a by-product of the smelting of other metals such as zinc, lead, and copper. People living near to any of these types of industry may be exposed to cadmium.

Cadmium is used in fertilizer applications and sewage sludge to farm land. More or less intensively these sources will lead to the contamination of soils, increasing Cd intake by crops and vegetables for human consumption. Food stuffs are the major source of Cd in non-smoking population (it represents more than 90% of human exposure to Cd), its concentration by these pathways is highly variable and the intensity of the exposure depends on dietary habitat [ENHIS, 2007]. Cadmium compounds are used in PVC stabilizers (essential additives in processing PVC resins), colour pigments, several alloys and more commonly in Ni-Cd batteries [Jarup, 2003].

Products containing cadmium are rarely recycled, being usually dumped together with household waste, thereby being dispersed in the environment, especially if the waste is incinerated [Jarup, 2003]. As seen before, the incineration of cadmium products will lead to higher cadmium emissions to the environment, in particular to air. Near industrial areas or hazardous waste sites this will occur more intensively and consequently higher levels of Cd may be present in soil. In addition, car exhaust may contribute to cadmium concentration in soils near roads. Low levels of dissolved cadmium may also be present in surface waters.

Exposure to cadmium may occur through ingestion of terrestrial food, cultivated in contaminated soils or contaminated from atmospheric deposition, contaminated water and from inhalation. Nevertheless, most of the terrestrial food contamination comes from cadmium uptake by plants from fertilizers, sewage sludge and atmospheric deposition.

Exposure at low levels usually does not produce immediate health effects, but may cause severe health problems over long periods. Cadmium is toxic to humans, animals, micro-organisms and plants, however only a small amount of cadmium intake is absorbed by the body and will be stored mainly in bones, liver and, in case of chronic exposure, in kidneys. In the last few years there have been some evidences that relatively low cadmium exposure may give rise to skeletal damage due to low bone mineral density (osteoporosis) and fractures. Animal tests have shown that cadmium may be a risk factor for cardiovascular disease [Jarup, 2003].

For acute exposure, absorbed cadmium can cause symptoms such as salivation, difficulty in breathing, nausea, vomiting, a pain, anemia, kidney failure, and diarrhea. Inhalation of cadmium dust or smoke may cause dryness of the throat, headache, chest pain, coughing, increased uneasiness and bronchial complications [Li-Teh Lu et al., 2007].

2.2. MERCURY (NATURAL AND ANTHROPOGENIC SOURCES)

Mercury occurs naturally in the earth’s crust. Although it may be found in air, water and soil, mercury is mostly present in the atmosphere as a gaseous element. Mercury’s major natural source results from the degassing of the earth’s crust, emissions from volcanoes and evaporation from natural bodies of water. Mining metals also causes indirect mercury discharges to the atmosphere. Due to its long lifetime of approximately of 1 year in the atmosphere, mercury’s dispersion, transport and deposition in the environment will cause harmful effects on ecosystems and human health.

Mercury may be present in the environment in several forms: elemental or metallic mercury, inorganic mercury compounds and organic mercury compounds.

Pure mercury is a volatile liquid metal. It has traditionally been used in products like thermometers, switches, barometers and instruments for measuring blood pressure.

Mercury is naturally present in many rocks including coal. When coal is burned, mercury is released into the environment. For this reason, coal-burning power plants are one of the largest anthropogenic sources of mercury emissions to the air, in addition to all domestic human-caused mercury emissions. Burning hazardous wastes, producing chlorine, breaking mercury products, and spilling mercury, as well as the improper treatment and disposal of products or wastes containing mercury, can also contribute to its release into the environment [EPA, 2009].

Mercury compounds are produced in small quantities for chemical and pharmaceutical applications. In ancient Greece mercury was used as a cosmetic to lighten the skin [Jarup, 2003]: in some sub-Saharan African countries the use of cosmetic products to bleach or to lighten the skin is still frequent. The long-term use of some pharmacologic compounds (hydroquinone, glucocorticoids and mercury) can cause severe health adverse effects [Jarup, 2003]. Large quantities of mercury compounds are still used for amalgamation in illegal gold mining, in some developing countries.

Anthropogenic sources of mercury and their compounds may result basically from the same sources enunciated for Cd. In addition, underground mining, mining quarrying, opencast and, production of phytopharmaceutical products and biocides, pharmaceutical industry, landfills, urban waste treatment plants, industrial waste-water treatment plants, etc. [E-PRTR, 2010].

Exposure to mercury may mainly occur as a consequence of the deposition from air into water or into soil. By natural biological processes certain microorganisms can change mercury into methyl mercury, a highly toxic and stable form that builds up in fish, shellfish and animals that eat fish, accumulating in the food chain. General population is exposed to methyl mercury through the food chain; fish and shellfish are the main source of exposure through the ingestion pathway [EPA, 2009].

Breathing mercury vapor is another possible exposure pathway. This can occur when elemental mercury or products that contain elemental mercury break and release mercury into air, in especial in indoor spaces without enough ventilation. Nevertheless, the main exposure pathway is through food chain and not by inhalation [EPA, 2009].

High level of mercury can cause brain damages, heart, kidneys and affect the immunologic system. Fish consumption does not constitute the main cause of health problems as mercury's quantity is not high. Nevertheless high levels of metylmercure in the bloodstream of little children may affect nervous system, affecting the normal thinking and learning [EPA, 2009].

Mercury's level in European countries has declined in the last few years, but is increasing in countries outside Europe, raising the level in the environment. Emissions are estimated to have declined mainly due to improved controls on mercury cells and their replacement and the generic fall in coal use [EPA, 2009].

2.3. LEAD (NATURAL AND ANTHROPOGENIC SOURCES)

Lead is a naturally occurring heavy metal often used in industry. It may be found in air, water, foodstuff, soil and dust either from natural sources, or from anthropogenic sources. In the past most of the lead emissions to the environment was due to petrol. This decreased in the last few years, in particular in developed countries, mostly due to the introduction of unleaded petrol. Lead can be found in several categories of use: batteries, petrol additives (no longer used in developed countries), rolled and extruded products, alloys and pigments. The most significant anthropogenic lead sources results basically from the same sources as for Cd and Hg (energy sector, production and processing of metals; mineral industry; chemical industry; waste and waste water management; paper and wood production processing and animal and vegetable products from the food and beverage sector [E-PRTR, 2010]:

Lead's exposure can occur from both anthropogenic and natural sources: battery plants, glass industry, and occupational exposure for inorganic lead in mines and smelters and exposure pathways through air near point emissions like coal power plants (combustion). In the environment, lead bio-accumulates in most organisms and is toxic to plants, animals and micro-organisms [UNEP 2008a].

Airborne Pb may be deposited on soil, water and crops and also be transported through the raining containing this metal. Exposure can occur through food chain, drinking water, soil ingestion and dust inhalation. Up to 50% of inhaled inorganic Pb may be absorbed in the lungs. Adults take up 10-15 % of Pb in food, while children may absorb up to 50% through the gastrointestinal tract. Lead elimination is slow and mainly by urine. It is also accumulated in the skeleton and is released from this compartment very slowly. Half-life of Pb in blood is about 1 month and in skeleton about 20-30 years [Jarup, 2003].

Acute exposure to lead's high levels may cause vomiting, diarrhea, convulsions, coma or even death. Chronic exposure, even to small amounts of lead, can be hazardous, especially to children under 6 years old who are particularly vulnerable to lead exposure; low levels of exposure to lead can cause neurodevelopment effects in children. Anemia, brain and nervous system damage are the health consequences of most concern. Other effects to generic exposed receptors include cardiovascular, renal, gastrointestinal, hematological and reproductive effects. In adults inorganic lead does not penetrate the blood-brain barrier but this barrier is less developed in children. A high gastrointestinal uptake and a permeable blood-brain barrier make children critical receptors to lead exposure and consequent severe brain damages [UNEP, 2008a].

Organic lead is able to penetrate body and cell membranes, some forms of organic lead penetrate the skin easily and cross blood-brain barrier in adults and in this way adults can also suffer brain damage related to acute poisoning from organic lead compounds.

Lead in air comes mainly through industrial emissions, smelters and refineries. Dust and soil can be significant exposure pathways resulting either from deposition or from erosion of lead-bearing rocks. Dust may be also originated by lead-based paints or from outside soil. Water may be contaminated by deposition and lead can also enter into the water supply from lead solder in plumbing or lead pipes at homes. Foodstuff may be contaminated by atmospheric deposition of airborne lead or by irrigation with contaminated water [Jarup, 2003].

3. Heavy-metals European emissions

A detailed air emission inventory is available at the European Pollutant Release and Transfer Register. This database provides easily accessible key environmental data from industrial facilities in 27 European Union Member States, including Iceland, Liechtenstein and Norway. The register contains annual data reported by some 24 000 industrial facilities covering 65 economic activities within the following nine industrial sectors: energy, production and processing of metals, mineral industry, chemical industry, waste and waste water management, paper and wood production and processing, intensive livestock production and aquaculture, animal and vegetable products from the food and beverage sector and other activities. Some information on releases from diffuse sources is also available, and intended to be gradually enhanced [E-PRTR, 2010].

For each facility, information is provided concerning the amounts of pollutant releases to air, water and land as well as off-site transfers of waste and of pollutants in waste water from a list of 91 key pollutants including heavy metals, pesticides, greenhouse gases and dioxins. Data provided in the register falls under seven classified groups: greenhouse gases, other gases, heavy metals, pesticides, chlorinated organic substances, other organic substances, inorganic substances [E-PRTR, 2010].

Releases and transfers from European member states must be reported according to the E-PRTR Regulation: EC Nº 166/2006 of the European Parliament Council Directives 91/689/EEC and 96/61/EC. The information to be reported annually by each facility for which the applicable thresholds are exceeded are the following: i) Releases to air, water and land of any of the 91 E-PRTR pollutants; ii) Off-site transfers of any of the 91 E-PRTR pollutants in waste water destined for waste-water treatment outside the facility; iii) Off-site transfers of waste (reported as tones per year) for recovery or disposal.

The reported releases include any introduction of any of the listed pollutants into the environment as a result of any human activity whether deliberate, accidental, routine or non-routine, at the site of the facility. E-PRTR also contains information on releases from diffuse sources into water which will be upgraded and gradually extended [E-PRTR, 2010]. The first report was released in 2009 containing data reporting to the year of 2007. The following report will be released in 2010 covering data from 2008. Registered data is intended to be updated on an annual basis; each report will cover emissions released two years before. As it happened in 2010, the data available in the register will be updated each year in April.

Data of environmental releases from the following countries was extracted: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Germany, Denmark, Estonia, Greece, Spain, Finland, France, Hungary, Ireland, Italy, Latvia, Luxembourg, Netherlands, Poland, Portugal, Romania, Sweden, Slovenia, Slovakia and United Kingdom. The extracted data refers to Cd, Hg, Pb releases into the air, water and soil and are summarized in the following tables. A few appreciations can be done considering environmental emissions reporting to industrial activity.

Production and processing of metals generated about 50% of the total European Cd and compounds emissions (18,66 t) (Table 1). This was followed by thermal power stations and other combustion installations sector (~20%) and mineral industry sector (~10%). Cd and compounds releases into water were mainly due to waste and waste water treatment (~63%) followed by production and processing metals industry (~13%) and paper and wood production processing sector (~6%). Waste and waste water treatment was the major responsible sector for emissions into soil (~72%).

Table 1: Cadmium and compounds emissions into the environment (extracted on March 2010).

Industrial activity - (Cd emissions and compounds)	Facilities	Air	Water	Soil
Energy sector:	142	5,72 t	986 kg	-
Mineral oil and gas refineries	24	992 kg	219 kg	-
Thermal power stations and other combustion facilities	117	3,72 t	743 kg	-
Coke ovens	1	1,01 t	2,41 kg	-
Production and processing metals	132	**9,66 t**	2,21 t	209 kg
Mineral industry	98	1,79 t	934 kg	-
Chemical industry	36	653 kg	991,1 kg	30,2 kg
Waste and waste water treatment	161	218 kg	**10,9 t**	**1,20 t**
Paper and wood production processing	64	509 kg	1,06 t	102 kg
Animal and vegetable products from the food and beverage sector	9	47,8 kg	85 kg	128 kg
Other activities	6	26,3 kg	53,4 kg	-
Total	**648**	**18,66 t**	**17,2 t**	**1,67 t**

Mercury and compounds air emissions were in majority generated in the energy sector (~55%), in particular from thermal power plants and combustion facilities (~51%) (Table 2). This was followed by chemical industry sector (~17%) and production and processing metals industry (~13%). Energy sector (mineral oil and gas refineries industry) was also the major responsible for mercury and mercury compounds releases into water (~44%), followed by waste and waste water treatment industry sector (~32%); this last industry sector was also the great contributor to soil emissions (~79%).

Table 2: Mercury and compounds emissions into the environment (extracted on March 2010).

Industrial activity - (Hg emissions and compounds)	Facilities	Air	Water	Soil
Energy sector:	249	**19,8 t**	**4,65 t**	2,7 kg
Mineral oil and gas refineries	28	940 kg	125 kg	-
Thermal power stations and other combustion facilities	216	18,5 t	4,52 kg	2,7 kg
Coke ovens	2	250 kg	2,29 kg	-
Manufacture of coal products and solid smokeless fuel	3	85,4 kg	-	-
Production and processing metals	91	**4,77 t**	456 kg	9,49 kg
Mineral industry	114	4,00 t	113 kg	-
Chemical industry	78	**6,14 t**	1,85 t	-
Waste and waste water treatment	284	1,22 t	**3,32 t**	**232 kg**
Paper and wood production processing	42	199 kg	1,01 t	27,3 kg
Animal and vegetable products from (food and beverage sector)	4	-	3,58 kg	23,3 kg
Other activities	4	13,0 kg	4,35 kg	-
Total	**866**	**36,1 t**	**10,5 t**	**295 kg**

Production and processing metals generated the majority of lead and lead compounds air emissions (~72%). This was followed by the energy sector (~15%), in particular from thermal power stations and other combustion installations (~11%). Mineral industry generated about 11% of total air emissions. Waste and waste water treatment sector was the major responsible for lead and compounds releases into water (~57%) and into soil (~66%). Mineral industry sector contribute by about 16% to water emissions and production and processing metals sector was responsible with about 26% lead and compounds emissions to soil.

Table 3: Lead and compounds emissions into the environment (extracted on March 2010).

Industrial activity - (Pb emissions and compounds)	**Facilities**	**Air**	**Water**	**Soil**
Energy sector	85	**80,9 t**	21,6 t	-
Mineral oil and gas refineries	14	2,14 t	3,57 t	-
Gasification and liquefaction	1	232 kg	28,0 kg	-
Thermal power stations and other combustion facilities	68	**61,1 t**	18,0 t	-
Coke ovens	2	17,4 t	-	
Production and processing metals	185	**398,3 t**	22,2 t	18,8 t
Mineral industry	86	**60,9 t**	34,8 t	-
Chemical industry	51	2,34 t	9,61 t	749 kg
Waste and waste water treatment	364	5,41 t	**124 t**	**44,7 t**
Paper and wood production processing	59	3,17 t	3,74 t	1,98 t
Animal and vegetable products (food and beverage sector)	10	-	190 kg	1,93 t
Other activities	6	-	421 kg	-
Total	**845**	551,74 t	217 t	68,2 t

In what concerns to country's emissions data was also extracted and is presented in the Table 4. The inventory data refers to those three countries that generated higher heavy metals emissions (Cd, Hg and Pb) either to air, water and soil.

Table 4: Cadmium, Mercury and Lead, and compounds air emissions per country

Cd and compounds					
Air		**Water**		**Soil**	
France	2,96 t	Spain	3,98 t	France	260,64 kg
Spain	2,94 t	Poland	3,28 t	Germany	214,00 kg
Czech Republic	2,76 t	Italy	2,35 t	U. K.	209,00 kg
Hg and compounds					
Germany	7,64 t	Italy	4,18 t	France	104,63 kg
Spain	4,25 t	Poland	2,61 t	Germany	32,90 kg
Poland	3,84 t	Spain	1,01 t	U.K.	18,80 kg
Pb and compounds					
Germany	68,20 t	Poland	99,34 t	U.K.	19,61 t
France	61,86 t	U.K.	32,87 t	France	10,31 t
Belgium	55,70 t	Spain	19,02 t	Germany	8,52 t

The highest cadmium and compounds air emissions was reported by France and Spain (~16% each), followed by Czech Republic (~15%). Spain generated the highest emissions into water (~22%) while France was the highest contributor to soil emissions (~36%).

Germany was responsible to the highest mercury and mercury compounds air emissions (~21%) followed by Spain (~12%) and Poland (~10%). Italy generated the highest mercury and compounds emissions into water (~39%) and France was responsible for the highest slice emissions into soil (~66%).

The highest lead and compounds air emissions were reported by Germany (~13%), followed by France (~11%) and Belgium (~10%). Poland was by far the highest contributor to water emissions (~44%) and U.K. was responsible for the highest soil emissions (~51%).

4. Heavy metals emissions into the environment in Portugal

Data for the Portuguese inventory emissions was also extracted from the E-PRTR database. The following table gives an overview of the industrial sectors emissions to air, water and soil.

Cadmium and cadmium compounds emissions were generated in majority from the paper and wood production processing (~30%) and from energy sector (~33%); in particular, mineral oil and gas refineries are responsible for about 75% of air emissions. Waste and waste water treatment was responsible for about 73% of water emissions and the only register to soil emissions comes from animal and vegetable products (food and beverage sector) industrial sector (Table 5).

Table 5: Cadmium and compounds air emissions in Portugal (extracted on March 2010).

Industrial activity - (Cd emissions and compounds)	Facilities	Air	Water	Soil
Energy sector	6	325 kg	-	-
Mineral oil and gas refineries Thermal power stations and other combustion facilities	2 4	245 kg 80 kg	- -	- -
Production and processing metals	4	280 kg	15,6 kg	
Mineral industry	3	78 kg	-	-
Chemical industry	1	-	94,3 kg	-
Waste and waste water treatment	3	11 kg	536 kg	-
Paper and wood production processing	7	364 kg	6,4 0 kg	-
Animal and vegetable products (food and beverage sector)	3	27 kg	62,7 kg	31,5 kg
Other activities	2	13 kg	15,3 kg	
Total	29	1,10 ton	730 kg	31,5 kg

Energy was the major responsible sector for mercury and mercury compounds air emissions representing ~67% from thermal power plant and other combustion facilities and ~21% from mineral oil and gas refineries. Water and waste water treatment was the main contributor to water emissions (98%). There is no register to mercury and mercury compounds soil emissions (Table 6).

Table 6: Mercury and compounds air emissions in Portugal (extracted on March 2010).

Industrial activity - (Hg emissions and compounds)	Facilities	Air	Water	Soil
Energy sector:	4	432 kg	-	-
Mineral oil and gas refineries	1	138 kg	-	-
Thermal power stations and other combustion facilities	3	294 kg	-	-
Production and processing metals	1	87 kg	-	-
Mineral industry	2	39 kg	-	-
Chemical industry	1		1,8 kg	-
Waste and waste water treatment	3		111 kg	-
Paper and wood production processing	4	73 kg		-
Other activities	1	13 kg	15,3 kg	-
Total	16	644 kg	113 kg	-

Lead and lead compounds emissions were generated in majority from the production and processing metals (~66%) (Table 7). Energy sector and mineral industry were the following contributors representing 17% and 14% respectively of total 2007 air emissions. Chemical industry sector was the main responsible for water emissions (~78%) followed by production and processing metals sector (~14%). There is no register for lead and lead compounds soil emissions.

Table 7: Lead and compounds air emissions in Portugal (extracted on March 2010).

Industrial activity - (Pb emissions and compounds)	Facilities	Air	Water	Soil
Energy sector:	2	1,27 t	-	-
Mineral oil and gas refineries	1	500 kg	-	-
Thermal power stations and other combustion facilities	1	774 kg	-	-
Production and processing metals	4	5 t	288 kg	-
Mineral industry	3	1,06 t	29,1 kg	-
Chemical industry	3	-	1,61 t	-
Waste and waste water treatment	3	250 kg	62,6 kg	-
Paper and wood production processing	1	-	80,4 kg	-
Animal and vegetable products (food and beverage sector)	1	-	80,4 kg	-
Total	16	7,59 t	2,07 t	-

5. General overview of methodologies used on exposure assessment

Exposure assessment relies upon fields of statistics, biochemical toxicology, animal toxicology, atmospheric sciences, analytical chemistry, food sciences, physiology, environmental modeling and others.

The exposure is quantified based on the observed dose-response relationship between the receptor and the contaminant and the assessment includes a description of intensity, frequency and duration of exposure through different exposure compartments, routes of exposure, identification of potential receptors exposed and a prevision of how these factors might change with time and as a consequence of some actions or events. This also requires using monitoring data, exposure modelling techniques and mapping models. Exposure is generally quantified in terms of the predicted environmental concentration, which is calculated on both local and regional spatial scales from monitoring data, when available, or by using realistic worst-case scenarios. If this information is not available, the estimative may result from exposure models. It is necessary to produce a complete description of how, when, and where the exposure occurs or has occurred, by evaluating the sources as well as the releases, the extent and pattern of contaminant contact with humans or ecologically relevant biota [Dinis and Fiúza, 2009].

Most of the times many different sources are present as well as multipathways, and multiple chemicals exposure at the same time. The available assessment guidelines are based on an unrealistic assumption that the releases of chemicals, as well as their effects, are separated from each other; usually the normal procedure is to perform an exposure assessment by calculating the dose resulting for each one of the chemicals.

On the other hand, heavy metals uptake, absorption and subsequent metabolism are determined by chemical speciation of metals and this contributes to the intensity of their toxicity. Also the potential metal toxicity compound depends on the oxidation state of the metal and the solubility of the compound. The chemical speciation of metals to which humans are exposed in ambient air, drinking water or diet is not considered in dose assessment due to the lack of information [Paustenbach, 2000].

Many times specific health effects are associated with a specific exposure route (for instance, lung cancer is related with inhalation), however, most health effects associated with heavy metals exposure affect the whole body and not just a specific route of exposure, although it may influence the systemic dose [Paustenbach, 2000].

The absorption of different metals depends both on the form in which metals are present in the exposure medium and also the route of exposure. Very little investigation of combined metals exposure have been done; it appears that there is, at present, no practical alternative to treating the health impacts of different metals as being additive.

6. Exposure assessment methodology applied to a hypothetical case study

This section describes the methodology applied to assess the potential average daily dose and the lifetime average dose resulting from exposure to chemicals released from an industrial facility during a certain period of time. This approach uses current measures of heavy metals in the environment media where the receptors live, causing exposition during their daily activities.

Air emissions from thermal power plants and other combustion installations were considered to apply the exposure assessment methodology (the main contamination from these facilities comes from air emissions). Coal contains many trace elements that are released during combustion to the surrounding environment. Some of the trace elements present in coal are heavy metals, such as nickel, chromium and those of interest in this study: cadmium, mercury and lead.

Air emissions will generate multipathways exposure assessment which extends the evaluation of the direct inhalation of contaminants, derived from air dispersion and deposition, to consider a variety of indirect pathways that include the deposition of contaminants to soil, water and vegetation, and the subsequent transfer and accumulation in the food-chain. Dermal absorption can also be an exposure pathway from direct contact with contaminated water and soil.

It is well known that the health effects and environmental impacts arising from coal thermal power stations and other combustion installations are originated by the mobilization of toxic elements from ash. The mobilization of these elements into the environment depends on various factors like climate, types of soils, indigenous vegetation and agricultural practices. In this way, the predicted exposure to contaminants resulting from a facility's emissions depends not only upon the levels of the emissions but also on the characteristics of the local land and its uses by the local population. A subsistence farmers (adults and children) scenario was considered for applying the methodology. [Zemba et al., 2002]

Although both children and adults may be exposed to the same pathways, children's rates of exposure to compounds (as expressed per unit body weight) are frequently higher and they may be subject to different types of health risks. Generally children younger than the age of 6 are considered critical receptors as they may easily get exposed by the ingestion of contaminated soil. Infants and children are critical receptors either due to their critical stages of physical and mental development either due to the fact that they receive higher pollutant dose compared to adults as they have lower body weight and higher breathing rate (consume more food per kilogram of body weight than adults). Also, children's developing organs and tissues are more vulnerable to the toxic effects of certain chemicals. With greater exposure and more severe health effects, chemicals in food are more harmful to children than adults. In general, children living in the vicinity of source emissions have the highest health risks. Adults are also at risk mostly from contaminated water and from inhaling dust from source emissions.

For cadmium exposure the health effects on children's are expected to be similar to the effects seen in adults (kidney, lung, and bone damage depending on the route of exposure). However, results from animal studies showed that younger animals absorb more cadmium than adults; younger animals are more predisposed than adults to a loss of bone and decreased bone strength from exposure to cadmium; babies of animals exposed to high levels of cadmium during pregnancy had changes in behavior and learning ability and high enough exposures to cadmium before birth can reduce body weight and affect the skeleton [ASTDR, 2008].

For the farmer subsidence scenario, air, soil, food crops (leafy vegetables); pasture and animal products (meat and milk) were considered as the representative exposure medium. The potential exposure routes were identified: inhalation (dust and soil resuspension from contaminated soil), ingestion (soil ingestion, leafy vegetables, meat and milk ingestion) as represented in Figure 1.

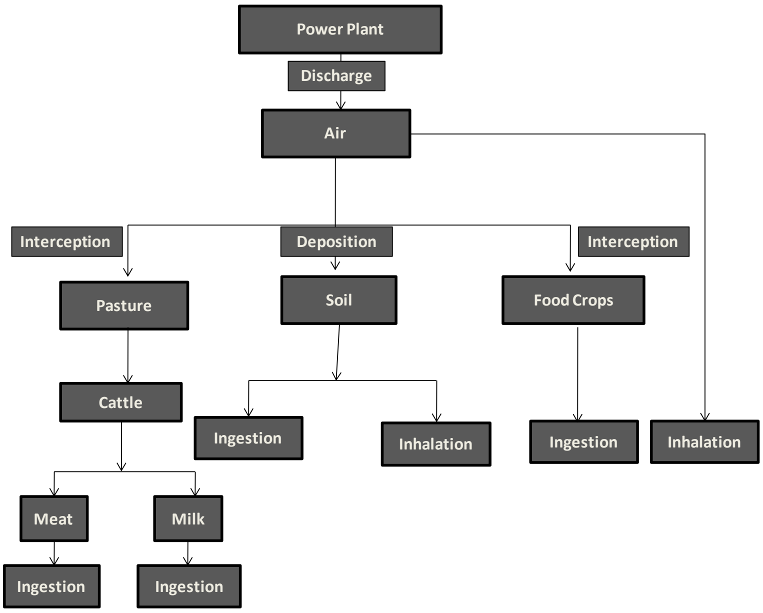

Figure 1: Main exposure pathways considered in the subsidence farmer scenario.

In order to perform dose calculations and exposure assessment the concentration of each chemical/heavy-metal needs to be measured or estimated in air, soil, food crops (leafy vegetables) and animal products (meat and milk). Also a wide range of fate and transport parameters are necessary to conduct the assessment as well as exposure parameters are needed to characterize the scenario. Different default values for exposure parameteres should be considered for children and adults as described in U.S. EPA, Exposure Factors Handbook [EPA; 2007a].

6.1. EXPOSURE ASSESSMENT - DOSE CALCULATIONS

Cadmium is classified as a possible human carcinogenic, in particular due to inhalation [IRIS, 1991]. Lead is also classified as probable human carcinogenic, although quantifying lead's cancer risk involves many uncertainties: age, health, nutritional state, body burden, and exposure duration influence the absorption, release, and excretion of lead. The U.S. Carcinogen Assessment Group recommends that a numerical estimate should not be used to lead [IRIS, 2004]. Mercury (elemental) is not classifiable as human carcinogenic based, however, on inadequate human and animal data [IRIS, 1995].

Cadmium and lead are volatilized on combustion and preferentially get adsorbed on the fly ash. Mercury remains almost entirely in the volatilized state and tends to escape to the atmosphere as vapors. However, mercury species that dominate deposition to soil and surface water are oxidized forms associated with particulate matter. In these conditions mercury deposition rates can be relevant near the source and can effectively influence the amount of mercury that contaminate soil, vegetation and surface waters and ultimately bio-accumulates in local fish populations. The U.S. EPA (1997b) has published fate-and-transport algorithms for predicting the deposition of mercury released from combustion sources.

The herein example focus on the methodology applied to the assessment of the exposure to cadmium emissions in a particle state matter; atmospheric cadmium produced by combustion processes occurs in the form of particulate matter at very small particles sizes. Cadmium oxide is the principal chemical species in the air, nevertheless some cadmium salts (e.g. sodium chloride) can escape to atmosphere, especially during incineration. Both forms are stable and won't suffer significant chemical transformations.

The exposure may occur directly by the inhalation of the cadmium attached to particles and indirectly by their ingestion within food (milk, meat, leafy vegetables and incidental ingestion soil). Drinking water may not be considered if we assume that all ingested water comes from a well that is not contaminated. The calculation of exposure will depend on (1) contaminant concentration in the media relevant to the exposure scenario being considered; (2) the rate at which individual consumes (ingests or inhales) the given medium; (3) the frequency and duration of exposure; (4) the individual's weight. Exposure can be expressed in a generic expression as [Zemba et al., 2002]:

$$\mathrm{I}\left(\frac{\mathrm{mg}}{\mathrm{kg.day}}\right)=\frac{\mathrm{C}\cdot\mathrm{CR}\cdot\mathrm{EF}\cdot\mathrm{ED}}{\mathrm{BW}\cdot\mathrm{AT}} \quad (1)$$

where I is the intake (amount of contaminant, $\mathrm{mg.kg^{-1}.day^{-1}}$); for evaluating exposure to noncarcinogenic contaminants, the intake is refered to as average daily dose, ADD; for evaluating exposure to carcinogenic contaminants the intake is referred to as lifetime average daily dose, LAAD; C is the concentration in media of concern (mg/kg for soil or $\mathrm{mg/m^3}$ for surface water); CR is the consumption rate (kg/day for soil or $\mathrm{m^3/day}$ for water); EF is the exposure frequency (days/year); ED is the exposure duration (years); BW is the body weight (kg) and AT is the averaging time equal to 25 550 days based on a lifetime exposure of 70 years; for noncarcinogens, averaging equals ED (years) multiplied by 365 days per year. The indirect exposure can be calculated by [Zemba et al., 2002]:

$$\mathrm{I_{ind}}\left(\frac{\mathrm{mg}}{\mathrm{kg}\cdot\mathrm{day}}\right)=\mathrm{I_{soil}}+\mathrm{I_{lv}}+\mathrm{I_{milk}}+\mathrm{I_{meat}} \quad (2)$$

where $\mathrm{I_{ind}}$ is the total daily intake of the contaminant by indirect pathways ($\mathrm{mg.kg^{-1}.day^{-1}}$); $\mathrm{I_{soil}}$, $\mathrm{I_{lv}}$, $\mathrm{I_{milk}}$ and $\mathrm{I_{meat}}$ are the daily intake of contaminant from soil, leafy vegetables, milk and meat ($\mathrm{mg.kg^{-1}.day^{-1}}$), respectively. The intake of contaminant due to incidental ingestion of soil is calculated by [Zemba et al., 2002]:

$$\mathrm{I_{soil}}\left(\frac{\mathrm{mg}}{\mathrm{kg}\cdot\mathrm{day}}\right)=\frac{\mathrm{CS}\cdot\mathrm{IR}\cdot\mathrm{FI}}{\mathrm{BW}} \quad (3)$$

where CS is the average soil concentration over exposure duration ($\mathrm{mg.kg^{-1}}$); IR is the consumption rate of soil (kg/day); FI is the fraction of ingested soil that is contaminated (unitless). The intake of contaminant due to the ingestion of leafy vegetables is calculated by [Zemba et al., 2002]:

$$I_{lv}\left(\frac{mg}{kg \cdot day}\right) = \frac{CV \cdot IR \cdot FI}{BW} \quad (4)$$

where CV is the average leafy vegetables concentration over exposure duration (mg.kg^{-1}); IR is the consumption rate of leafy vegetables (kg/day); FI is the fraction of ingested leafy vegetables that is contaminated (unit less). The intake of contaminant due to the ingestion of milk and meat is calculated by [Zemba et al., 2002]:

$$I_{lv}\left(\frac{mg}{kg \cdot day}\right) = \frac{CM \cdot IR \cdot FI}{BW} \quad (5)$$

where CM is the average animal tissue or product (meat or milk) concentration over exposure duration (mg.kg^{-1}); IR is the consumption rate animal tissue or product (meat or milk) (kg/day), FI is the fraction of ingested animal tissue or product (meat or milk) that is contaminated (unitless). The intake of contaminant due to the inhalation is calculated by [Zemba et al., 2002]:

$$ADI\left(\frac{mg}{kg \cdot day}\right) = \frac{CA \cdot IR \cdot ET \cdot EF \cdot ED \cdot 0{,}001}{BW \cdot AT \cdot 365} \quad (6)$$

where ADI is the average daily intake of the contaminant via direct inhalation (mg/kg^{-1}.day^{-1}); CA is the total air concentration over exposure duration (μg/m^3); IR is the inhalation rate (m^3/hr); ET is the exposure time (hr/day); EF is the exposure frequency (day/hr); 0,001 is the units conversion factor (μg/mg) and conversion factor (days/year).

After estimating the average daily intake the next step is the calculation of excess the lifetime cancer risks and non-cancer health hazards resulting from the exposure scenario considered.

Carcinogenic risks are calculated as the product of long-term average dose and the carcinogenic power factor (also known as slope factor). Carcinogenic risks are a conservative estimate of the incremental probability that an individual will develop cancer as a result of a specific exposure to a carcinogenic compound; the estimative is done by multiplying an individual's lifetime average daily dose (LADD) of a compound by the compound's unit risk factor or cancer slope factor (CSF) [IRIS, 2009]. An individual's overall cancer risk is the sum of the cancer risks from all the compounds of concern.

The acceptable risk is generally defined as 10^{-6} for the general public and 10^{-5} for occupational works. This means that an additional one case of cancer is accepted for populations of 1 million or 100 000, respectively. A risk level of 1 in a million, or 1 in one hundred thousand, also implies a likelihood that up to one person out of one million (or 100 000) equally exposed people would contract cancer if exposed continuously (24 hours per day) to a specific radiation dose over 70 years (an assumed average lifetime).

Non-carcinogenic risks are assumed to exhibit a threshold below which no adverse effects are expected to be observed. As such, non-carcinogenic health hazards are evaluated by comparing an individual's exposure to a compound against a reference dose RfD for oral exposures. Reference concentrations and reference doses are used to assess the likehood of chronic toxic health effects from inhalation and oral exposure, respectively. The risk is calculated as a hazard quotient ratio (HQ) of the average daily dose (ADD) to a reference dose response (RfD) both in the units of $mg.kg^{-1}.day^{-1}$.

A total hazard ratio is obtained as the sum of all hazard ratios calculated for individual exposure routes and compounds (Hazard Index - HI) for a particular exposure pathway. The calculated HI value is compared to a benchmark; a HI value of 1,0 or less than 1,0 indicates that no adverse human health effects (noncancer) are expected to occur although values less than 1,0 may not be risk free [IRIS, 2009].

Data to evaluate the chronic toxic effects of Cd may be obtained from the Integrated Risk Information System (IRIS): RfD (Cd in food) = 0,001 $mg.kg^{-1}.day^{-1}$ [IRIS, 1991].

The quantitative risk estimate from inhalation exposure may be presented by a unit risk, being the quantitative estimate in terms of risk per mg/m^3: Cd = 1,8 $(mg/m^3)^{-1}$ or by a slope factor, being the result of the aplication of low dose extrapolation prodecure presented as the risk per $mg.kg^{-1}.day^{-1}$: Cd = 6,10 $(mg/m^3)^{-1}$ [IRIS, 1991].

7. Measures to reduce or to mitigate exposure to heavy metals

In order to reduce or to mitigate exposure to heavy metals, risk analysis should consider not only the direct emissions to the atmosphere but also the impacts of heavy metals deposition, transport and transfer in the food chain and in the drinking water. This is why a complete exposure assessment and a consequent risk assessment are needed. Also a cost-benefit analysis for measures to be taken should be addressed based on the impacts resulting from the exposure [ESPREME, 2004].

At individual level appropriate measures in case of heavy metals exposure include: i) limit the exposure; ii) decrease absorption with dietary suggestions may helpful to inhibit intake and uptake of cadmium, mercury and lead. For instance, Fe reduces uptake of Cd and Pb; Ca reduces the uptake of Cd; high sulfur foods such onions and garlic probably help the body blocking uptake and decreasing retention of many toxic metals, thus decreasing the release of stored metals and protecting the vulnerable tissues [VMICC, 2003]. General population can contribute to heavy metals reduction efforts by purchasing metals free products (for example, Hg free); correctly dispose products that contain heavy metals and reducing demand for products whose production leads to the release of heavy metals into the environment [EPA, 2009].

A European database collected suggested methods and options for reducing the metals occurrence in Europe from industrial facilities [ESPREME, 2004]. The database contains data for every European country. Experts from about twelve countries were involved in the process of the data collection [ESPREME, 2004].

The general Access database contains 483 files for each European country; those refer the processes responsible for emissions to the air, the measures taken for controlling these emissions, the investment and operating costs for each process, the unabated emission factors generated from individual process and the implementation of specific abatement methods.

A short list of several measures for decreasing the emissions originated in industries was extracted. They are classified as primary level and secondary level. Primary measures are considered for emissions from combustion plants (fuel combustion for energy production); fuel supply measures and combustion technology improvements. Primary measures include technical and non-technical actions: i) the first group concerns the minimization of the heavy metals content in fuels and raw materials, as well as technology and fuel switching towards methods generating lower or zero HM emissions and technologic modifications; ii) non-technical actions implies higher surveillance procedures, reducing consumption of heavy metals contain/releasing products and good housekeeping of environment of heavy metals releasing processes [ESPREME, 2004].

Generic secondary measures include i) particulate control techniques (electrostatic precipitators, filters, cyclones, wet scrubbers); ii) absorption techniques to achieve heavy metals emissions reduction, NO_x reduction techniques (aiming the Hg reduction); iii) adsorption methods (activated carbon, impregnated sorbents, etc.) [ESPREME, 2004].

8. Conclusions

Concerning heavy metals sources and emissions into the environment, some statements may be pointed out. In the last few years, the biggest reduction in emissions from European countries has come from industrial processes. Lead and cadmium emissions have both decreased from certain industrial sectors, such as metal refining and smelting activities. This reflects an improved emissions control and, for some countries, the result of economic restructuring and the closure of older and more polluting industrial facilities [EEA, 2010]. Since 1990 the largest mercury reduction (in absolute terms) has been achieved by the energy sector (electric power and heat generation) closely linked to less use of coal, which contains mercury as contaminant. Also, the fuel replacement in many countries from coal to gas and other energy sources, the closure of older inefficient coal-burning plants and the improvement of the processing equipment are responsible for the past decreases in emissions from this sector [EEA, 2010].

For the heavy metals considered of great concern in this study (Cd, Hg and Pb), the main emissions sources in 2007 were from energy-related sources associated with fuel combustion: production of electric energy and heat generating facilities and also from combustion in industrial facilities. Lead emissions from the road transportation sector were greatly reduced since 1990. However, this activity may continue to be an important source of lead: the residual lead in fuel, from engine lubricants and parts, and from tyre and brake wear contribute to the ongoing lead emissions from this sector [EEA, 2010].

The coal combustion is still the major source for the heavy metals focused in this study, except for lead. In general, big power plants are becoming more and more efficiently controlled resulting in developed effort to reduce emissions by mainly changing and improving their technology. Nevertheless, emissions from residential units are still being largely uncontrolled. Waste disposal is underestimated as a source of heavy metals releases to the atmosphere. Alternative renewable energy sources will contribute to reduce emissions from combustion of coal [ESPREME, 2004].

The continuous reduction on heavy metal emissions in Europe for the last 40 years is due mainly to a better knowledge of heavy metals sources, emissions, pathways, transport and fate in the environment. Further progresses have been made in assessing sources and emissions to environment in Europe, at national and regional level. Also, the emission control with more reliable equipment has resulted in more efficient regulatory efforts to reduce heavy metal emissions from anthropogenic sources and it is clear that the most effective way to reduce or to eliminate the exposure to heavy metals in the environment is taking actions at the sources level [EEA, 2010].

Finally, to evaluate the exposure of heavy metals in the environment the procedure still consists in studying isolated contaminants. This means that we still lack adequate data, methods and models to assess multiple exposures and consequently to evaluate the risk to which receptors are exposed [Hinton and Aizawa, 2007].

In 1996 the U.S. EPA started to include mixture of chemicals in its risk assessment for pesticides that have the same mode of action; however, this limitation has again the same additive effect for mixtures [Hinton and Aizawa, 2007]. The recent EPA (2000) guidance for mixtures for human health risk characterization does not suggest any single approach; instead it provides a number of options for consideration [Hinton and Aizawa, 2007]. The ATSDR presented a series of “Interaction Profiles” to characterize the mixtures effects. Due to the lack of data, ATSDR applies an additional safety factor of 10 for mixtures of non-cancerous chemicals and 100 for cancerous chemicals mixtures [Hinton and Aizawa, 2007].

Many agencies have been involved in chemical mixtures exposure assessment (U.S. EPA, NIEHS, ASTDR, U.S. DHHS) and they all recognize the need of substantial research for risk assessment methods applicable to mixtures of heavy metals. In the short term, hazard indices calculations and additive carcinogenic risk calculation is likely to remain the predominant form of assessment for mixtures. A strategic approach involving a multinational, multidisciplinary strategic research methodology is urgently needed. The dispersion of many heavy metals beyond national boundaries implies that solutions must result from a long-term development plan of global research. Collaborative funding calls and joint proposals among several countries will surely allow a more rapid and efficient research on this difficult issue [Hinton and Aizawa, 2007].

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