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AIR QUALITY DAUGHTER DIRECTIVES

POSITION PAPER ON LEAD

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Generalitat de Catalunya
Environmental Department
General Directorate of Environmental Quality

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Directorate-General XI

NOTE

This document was prepared by the Working Group on Lead. A list of Members can be found on page 73.

This document reflects the opinions of the majority of the members of the Working Group.

It should not be considered as an official statement of the position of the European Commission

Not all experts necessarily share all the views expressed in this document.

POSITION PAPER ON LEAD

The Working Group on Lead is one of the four groups that were established in the meeting of National Experts on Air Quality Group, held in Brussels on 5 July 1995. The aim of this programme is to develop the document that will be used as the basis for the elaboration of the Air Quality Daughter Directive on lead as an atmospheric pollutant.

This position paper reflects the different points of view and recommendations of all the Members States, as it is applicable to the entire territory of the EU.

The points dealt with are the following:

- Introduction.
- Risk assessment.
- Measurement and assessment of concentrations.
- Cost implications.

The Working Group is composed with representatives from Spain as a lead country, Italy and Belgium as a Member States, European Environment Agency, Joint Research Centre and representatives for the Industry, ONG's and DG XI. Furthermore, representatives from WHO and UN ECE have attended the meetings when relevant.

The Working Group has met on four occasions in Barcelona, and the four main points of the general programme were discussed during these meetings.

Background:

The first two European Community programmes of action in the field of the environment gave absolute priority to the fight against pollutants described as category one. In this way the European Commission submitted three proposals to the ministers of the environment of the European Community which were geared towards establishing air quality standards for four substances recognised for their toxicity to man and his environment (SO_2, Pb, NO_2 and particulate matter). Evaluation of the application of these three directives was facilitated by the decision taken by the European Council in 1975 to establish exchange of information between the networks of air pollution observation and control.

The fifth programme of action describes atmospheric pollution control at European level for the next decade. This programme establishes intermediate stages in the form of goals to be reached in the terms established between now and the year 2000 for the substances SO_2, NO_2, lead, particles and black smoke, and establishes the steps geared to achieve these goals. We are dealing with achievements or results that the Community has to foresee in order to take a firm stance in the process of sustainable development.

The general objective of the Community is the constant improvement of the level of well-being of all its citizens. Up till the present, Community programmes of action on the environment were based fundamentally on legislation and control affecting governments and industry. The concept of shared responsibility demands a wider and more active basic involvement of all economic agents, public powers, public and private companies and, principally all persons in their capacity as citizens and consumers.

The air quality objectives foreseen are:

- Effective protection of the population against known health risks caused by air pollution.
- Inclusion of the protection of the environment in the concentration levels of pollutants permitted in the atmosphere.
- Widening the list of polluting substances controlled.

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1. INTRODUCTION

1.1. Lead in the European Union

Lead was already classified as a category one pollutant in the first community programme of action in environmental matters. This pollutant has been the subject of numerous studies and investigations by the Community institutions.

These efforts led, on the 3rd December 1982, to the adoption by the Council of Ministers of the Community of a Directive (82/884/EEC) establishing maximum levels of lead contained in the atmosphere. This maximum level established and currently in force is 2 $\mu g/m^3$ expressed as an average yearly concentration. Its application is intended exclusively to protect human health, as current knowledge did not permit the adoption of maximum levels aimed at protecting the environment. The Directive is not applied to exposure to lead in the workplace or indoors.

The maximum level established in 1982 is now complied with in most Member States. Each state may establish a stricter level at any time.

The Directive obliges Member States to install measuring stations within their territory in places where the population might suffer continuous exposure for long periods. The same applies to places where the member state considers that maximum levels might be exceeded.

The air quality objectives for lead established in the fifth programme of action in the field of the environment are:

- It was proposed that the critical loads should be defined and not surpassed, by means of an emission reduction protocol. The actions proposed are the integrated control of pollution and the revision of current technology.
- As far as vehicles and fuel are concerned, the transfer to unleaded petrol by the year 2000 was proposed.

1.2. The pollutant

Lead is a high density element which is soft, flexible and malleable. It is a poor conductor of electricity but a good insulator of sound, vibrations and radiation. It is highly resistant to corrosion but reacts with nitric acid, and with boiling hydrochloric or sulphuric acids. It is not attacked by pure water although dissolved impurities in water can result in a small amount of corrosion. In the presence of oxygen weak organic acids will attack lead.

Lead does not occur naturally in the metallic state. It has a low abundance (0.002 % of the weight of the earth's crust), but because it is located in extensive mineral deposits, its exploitation is relatively easy.

Lead has a great number of industrial applications, both in its elemental form and in the form of alloys and compounds. The major use of lead is in the manufacture of lead accumulators (responsible for 68% of consumption and growing in parallel with the increase in the number of automobiles), in which it is used both in the metallic form and as lead oxide.

The metal lead has important applications in radiation shielding (in nuclear plants and around X-ray machines), in roofing and for the sheathing of electric power cables. Its corrosion resistance makes it a useful material for tank linings, piping and other equipment used in chemical processes (for example the manufacture of sulphuric acid). Its density makes it suitable for ammunition and for weighting applications (from car wheel weights to yacht keels). Alloyed with tin it is used as a soldering metal.

Lead compounds have a number of important uses. Lead oxide is incorporated into glass to prevent the escape of radiation from cathode ray tubes (for example televisions and computer screens) and for the manufacture of crystal glass. Lead glazes are used for hygienic scratch-free surfaces on ceramic products and organic lead salts are added to PVC as stabilizers to protect it against degradation. The use of lead in paint has virtually disappeared, with lead carbonate and lead sulphate pigments no longer being permitted in paints in the European Union.

Worthy of note is the organometallic compound tetraethyl lead used to prevent knocking in petrol. In 1972 around 400,000 tonnes of tetraethyl lead were consumed throughout the world to improve the octane rating of petrol. Since then this application has declined dramatically because of restrictions imposed thorough environmental legislation. The tetraethyl lead market now accounts for only 1% of lead use, most of which is used in developing countries. In Europe a small amount is still used to provide the leaded petrol requirements of old vehicles, but the application will eventually disappear.

Several of lead's biggest applications lend themselves to recycling. Because it is economically attractive to do so, scrap batteries and scrap metallic lead are widely collected and reprocessed by secondary lead smelters. In most European countries scrap battery collection rates are generally of the order of 90-95% and recycled lead accounts for almost half of Europe's total annual needs. The overall market for lead is growing slowly but this growth is mainly due to increasing requirements for batteries with most other applications either static or declining.

1.2.1. Current tendencies in lead use

The estimated world resources of lead represent a comfortable reserve in the light of expected future consumption. Whereas in the first quarter of the century lead was the first non-ferrous metal in terms of production, it has currently taken second place behind metals such as aluminium, copper and zinc, due to the decrease in its use and the increase in the use of the other metals.

Lead has suffered the loss of some of its most important markets, such as the pigment and water pipe markets, as a result of current legislation reflecting its toxicity and effect on the environment, which has lead to its replacement by plastics and aluminium. These decreases would appear to have become stabilised and have not been disproportionate due to the increase of production of lead batteries for automobiles and transport uses. The lead battery sector constitutes the main use of lead production and recycling.

The industry's main worry has been the drop in price. This reflects the worldwide recession in the industry in the first half of the 80's. The price of lead reached its lowest price of the last few years in 1985, and since then has recovered more than 50%, which has encouraged many producers to modernise out of date foundries with modern technology, which is much better and enables strict legislation to be complied with.

1.2.2. Transport in the environment, transformations and distribution

Transport and distribution of lead both from natural and man-made sources, fixed and mobile, is done mainly through the air. Sources of the lead emitted is deposited near the source of the emission, but most particles may be carried over greater distances. There are many studies within the work carried out by the UN ECE showing that heavy metals can be transported to hundreds and thousands of kilometres away from their sources (*UN ECE, 1994 and 1995*).

A particle size distribution study was carried out by *Degussem et al (1978)*. This study determines the particle size distribution in the vicinity of a metallurgic plant in Hoboken (Belgium) and shows that a maximum is found at a diameter of 2 µm and a second, but smaller maximum, is found between particle sizes of 4 and 8 µm. This maximum decreases fast with increasing the distance from the factory

Lead suspended in the air contributes to human exposure by means of pollution of food, water or by being directly inhaled. Atmospheric conditions and the size of the particles are determining factors of transfer and deposition. Large quantities of lead may be deposited in the ground and water, but because of the low solubility of lead compounds in water the material remains localised.

Lead deposited in water, both from the air and filtered through the earth, quickly separates into a sediment and an aqueous phase. Into what fractions this division occurs will depend on the pH, level of salts and the presence of organic catalysts.

1.2.3. Vehicles and fuel

The first EC Directive establishing emission limits for vehicle exhausts goes back to 1970. Since then emission limits for a number of pollutants have been tightened in successive steps. To that end it is the appearance of the catalytic converter technology that allows us to foresee the possibility of important reductions in pollutants caused by the running of engines.

The following table shows the total number of vehicles in use and the number of persons per vehicle in the different European countries. These data should be borne in mind when the emissions of each country as well as the metal demand for transportation use are considered.

Table 1.1: Vehicles in use in the European Union.

Country	Cars	Persons per car	Commercial vehicles	Total vehicles	Persons per vehicle
Austria	3,593,588	2.2	347,792	3,941,380	2.0
Belgium	4,239,051	2.4	487,337	4,726,388	2.1
Denmark	1,688,240	3.1	342,038	2,030,278	2.6
Finland	1,900,855	2.7	280,384	2,181,239	2.3
France	25,100,000	2.3	5,195,000	30,295,000	1.9
Germany	40,499,442	2.0	3,061,874	43,561,316	1.9
Greece	2,114,097	4.9	847,538	2,961,635	3.5
Ireland	990,384	3.6	155,153	1,145,537	3.1
Italy	30,000,000	1.9	2,806,500	32,806,500	1.7
Luxembourg	224,894	1.8	27,144	252,038	1.6
Portugal	2,560,000	3.9	879,100	3,439,100	2.9
Spain	14,212,259	2.7	2,984,140	17,196,399	2.3
Sweden	3,630,760	2.4	322,286	3,953,046	2.2
The Netherlands	5,632,891	2.7	657,972	6,290,863	2.4
United Kingdom	24,962,263	2.3	3,208,661	28,170,924	2.1
Totals (EU)	161,384,724	2.3	21,602,919	182,951,643	2.0

Source: WAS (1996).

As a result of Directive 94/12/EEC all petrol engined vehicles sold in the European Union since January 1993 are equipped with catalytic converters.

The recent successive reductions of pollution emissions from vehicles could never have been decided if it were not for the important efforts geared towards reducing the harmful effects of different pollutants. Without the general availability of unleaded petrol the introduction of catalytic converters aimed at reducing exhaust fume emission would have been impossible.

In 1978 the Council of Ministers had adopted a Directive (78/611/EEC) limiting the level of lead in petrol to 0.4 g/l. This Directive was superseded and reinforced by the Directive 85/210/EEC which obliged Member States to reduce the level of lead to 0.15 g/l and guarantee the supply and distribution of unleaded petrol (with a maximum lead content of 0.013 g/l) as from the deadline of 1st October of that year.

Details of lead consumption in gasoline in each European Union country during 1995, are presented in the following table:

Table 1.2: Estimated elemental lead use in gasoline in the EU (1995).

Country	Gasoline demand (thousand tonnes)	Leaded (thousand tonnes)	Unleaded (thousand tonnes)	Lead level (g/litre)	% unleaded	Pb use[*] (tonnes)
Austria	2,400	0	2,400	0	100	0
Belgium	2,792	838	1,954	0.15	70	170
Denmark	1,848	0	1,848	0	100	0
Finland	1,838	0	1,838	0	100	0
France	15,494	7,713	7,781	0.15	50	1,562
Germany	29,686	1,781	27,905	0.15	94	361
Greece	2,574	1,751	823	0.15	32	355
Holland	3,960	594	3,366	0.15	85	120
Ireland	1,024	446	578	0.15	56	90
Italy	16,438	9,698	6,740	0.15	41	1,964
Luxembourg	502	95	407	0.15	81	19
Portugal	1,889	1,216	673	0.40	36	657
Spain	8,172	5,802	2,370	0.15	29	1,175
Sweden	4,192	0	4,192	0	100	0
United Kingdom	21,960	8,127	13,833	0.15	63	1,646
Totals	114,769	38,061	76,708	---	67	8,119

[*] Pb use indicates estimate of elemental lead use.

Source: LDA (1996).

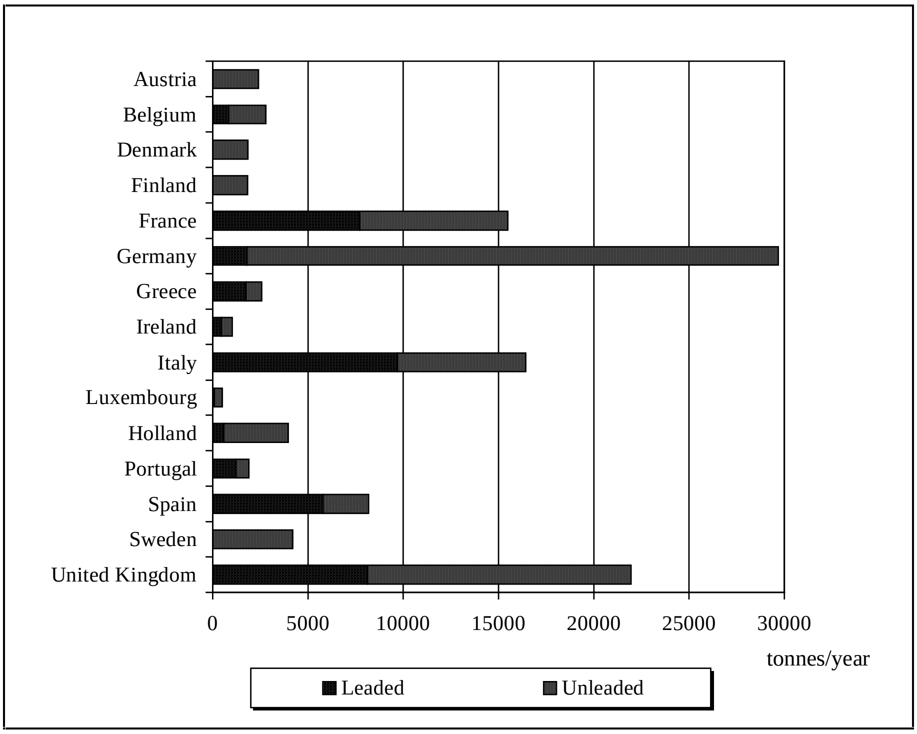

Figure 1.1: Lead use in gasoline in the EU (1995).

1.3. Sources of lead

(a) Natural sources

In the natural cycle, lead is released to the earth's surface through a variety of processes which include weathering of rocks, volcanic activity, and uptake and subsequent release by plants. Other natural sources include sea sprays, windblown dusts, and wild forest fires. The weathering of rocks releases lead to soils and aquatic systems. This process plays a significant role in the global lead cycle, but only rarely results in elevated concentrations in any environmental compartment. Soils derived from carboniferous black shales are an exception, as they can contain up to 200 µg lead/g. Similarly, non-ferrous ore bodies which contain lead can contaminate adjacent water courses and soils.

Background concentrations of lead in the air are between 0.05-0.1 µg/m^3 in rural areas, clean air areas. Natural lead content in the atmosphere is estimated of the order of 0.6 ng/m^3 (*Kühling, 1994*).

(a) Anthropogenic sources

Human activities remove lead from the earth's crust and transfer it to environmental media, where its potential for resulting in both human and ecosystem exposure is greatly increased. While uses of lead have been known since ancient times, industrialization has vastly accelerated its transport into human and environmental exposure pathways. Lead is released into the environment during the mining and smelting of its ores, the production, use, recycling and disposal of lead-containing products, and the burning of fossils fuels and wood.

Estimates of the dispersion of lead emissions into the environment indicate that the atmosphere is the major initial recipient. The development of lead fuel additives and the increasing use of the automobile greatly escalated the rate at which lead was released to the atmosphere. The amount of lead emitted from this source has, of course, now greatly decreased.

Lead also comes, in significant quantities, from certain industrial processes. When discussing industrial emissions, a differentiation must be made between emissions from chimneys, which can be controlled, and fugitive emissions (e.g. from stock piles), which are more difficult to control. The relative importance of industrial emissions (stationary sources) has been increasing due to the decrease of other types (mobile sources). From these emission sources, lead moves through the atmosphere to various compartments of the environment. Its is deposited on soil, surface waters and plants and thus is incorporated into the food chain of animals and man.

Soil and water pollution from car emission fallout is predominantly limited to the immediate urban area. Fallout from the emission of industrial sources, such as smelters, is likewise limited mainly to the immediate vicinity. However, strong evidence indicates that a fraction of airborne lead is transported over long distances. As a result, a long-term global accumulation of lead has occurred in recent decades.

1.3.1. Lead emissions

The main report for the ESQUAD project (*ESQUAD, 1994*) analyzes the impact of atmospheric deposition for three heavy metals (cadmium, copper and lead) and two persistent organic compounds (benzo(a)pyrene and lindane) in the quality of European soil and sea water. This pilot study was drawn up in order to offer a general, systematic view of emissions, concentrations, depositions and load to ecosystems in Europe.

This study includes a list of lead emissions in Europe for 1990. Table 1.3 gives a breakdown of the total emissions for each country and identifies percentages for each type of emission sources for totals per country and for each country within the European total. Figure 1.2 shows a graph of the total emissions. In this case, the relation among total emission values, lead content in gasoline (Table 1.2) and the total number of vehicles (Table 1.1) in each country must be taken into account.

The data of Table 1.3 should be handled with care. They give a general idea on the relative contribution of different source categories, and are obtained by general methodologies. However they only give a rough estimate.

Table 1.3: Lead emissions in the EU (1990).

Country	Totals per country (tonnes/ year)	Relative contribution of source categories to total national emissions (%)					Relative contribution of countries to total EU emission (%)
		Road traffic	Iron and steel	Stationary fuel combustion	Non-ferrous metals	Other	
Austria	292	80.3	17.3	1.0	1.3	0.1	1.6
Belgium	577	50.0	43.8	1.1	2.9	2.3	3.1
Denmark	168	90.6	4.2	1.9	0.0	3.3	0.9
Finland	217	78.8	16.4	1.4	3.1	0.2	1.2
France	2987	83.7	9.3	0.6	4.5	1.8	16.2
Germany	2859	71.2	19.2	1.4	7.8	0.4	15.5
Greece	496	95.5	2.3	2.2	0.0	0.0	2.7
Ireland	133	91.2	2.8	2.6	3.4	0.0	0.7
Italy	2771	83.5	11.5	1.2	3.2	0.6	15.0
Luxembourg	97	51.9	47.7	0.3	0.0	0.1	0.5
Netherlands	377	75.7	15.8	0.9	3.0	4.6	2.0
Portugal	628	96.6	1.5	1.9	0.1	0.0	3.4
Spain	3234	91.1	4.9	1.7	1.7	0.6	17.5
Sweden	448	79.0	12.5	0.7	7.4	0.4	2.4
United Kingdom	3165	85.4	6.9	1.6	5.0	1.1	17.2

Source: ESQUAD (1994).

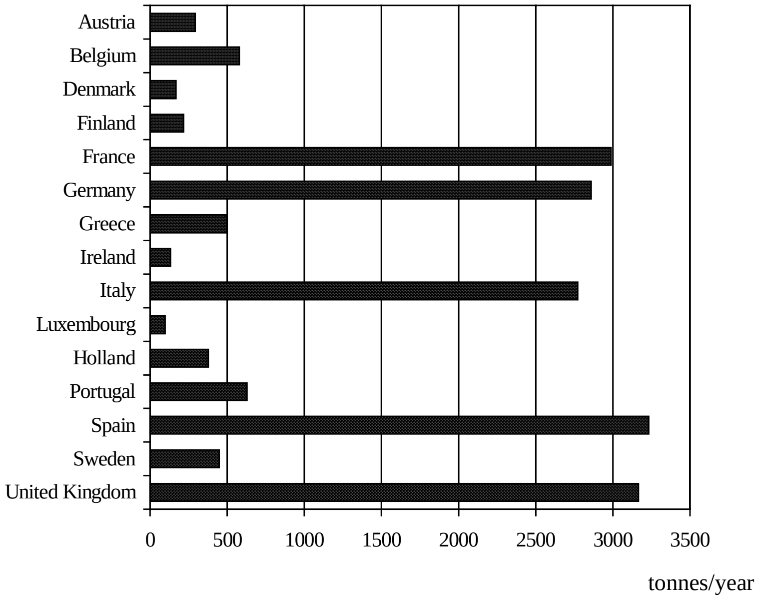

Figure 1.2: Lead emissions in the EU (1990).

From the data presented, it can be stated in general terms that the major contribution to the total of each country is due to the emissions from vehicle traffic.

It is also a fact that these emissions are estimates for the year 1990. Accordingly, one can expect an appreciable reduction of such from 1990 to date because of the reduction of emissions of lead from vehicle traffic. This reduction in the contribution arising from vehicle traffic will cause a clear loss of importance from this source with the corresponding percentage increase of the contribution from other sources, especially of the industrial type.

1.4. Situation of the industry

The intergovernmental organisation *International Lead and Zinc Study Group* edited a publication (*ILZSG, 1995*) in which the main producers of lead were identified, both for primary production from the mineral and for secondary production from fragments and scrap, in various European countries.

A summary of the data presented can be seen in the following table:

Table 1.4: Production of lead in Europe (1995).

Country	Primary smelters		Secondary smelters		Total lead production (thousand tonnes)	Proportion of production from recycling
	Number	Production (thousand tonnes)	Number	Production (thousand tonnes)		
Austria	---	---	6	20	20	100
Belgium	1	84	2	38	122	31
Denmark	---	---	---	---	---	---
Finland	---	---	---	---	---	---
France	2	129	6	165	294	56
Germany	4	151	6	160	311	51
Greece	1	---	1	4	4	100
Holland	---	---	1	22	22	100
Ireland	---	---	1	11	11	100
Italy	2	74	4	98	172	57
Luxembourg	---	---	---	---	---	---
Portugal	---	---	---	13	13	100
Spain	---	---	5	80	80	100
Sweden	1	42	1	41	83	49
United Kingdom	2	150	5	172	322	53
Totals (EU)	13	630	38	824	1,454	57
Poland	1	---	5	---	71	---
Switzerland	---	---	1	5	5	100

Source: ILZSG (1995).

The organisation *Lead Development Association* also has at its disposal a directory (drawn up in 1992) in which all the manufacturing plants of batteries in Europe are identified (*LDA, 1992*).

1.5. Present situation in Europe

Each Member State has been consulted in order to find out the current situation both with regard to the legislation in force and the current levels measured in each country. The information given below has been taken from the reports received.

1.5.1. Member States

1.5.1.1. Austria

In Austria no long-term and area-covering measurements of lead have been conducted. The levels measured are below the European limit value. With regard to the implementation of the European Directive, there is no national legal limit value for lead it is foreseen to fix a yearly average of 0.5 µg/m³.

Austria has reduced the levels of lead in petrol in the last few years. The regulation came into force in March 1992.

1.5.1.2. Belgium

From 1993 Belgium has changed from a unitary state to a federation with three autonomous regions. Most responsibility for the environment has been taken over by the regions. The basis of Belgian legislation regarding maximum levels of lead in the air, is the Royal Decree 1318/84 which establishes the 2 µg/m³ yearly average of the European Directive.

Heavy metal pollution in Belgium is a problem in the places where the non-ferrous metallurgical plants are situated. Pollution from heavy metals in the air has been reduced considerably, especially in urban air, as a result of the reduction of the lead content in petrol.

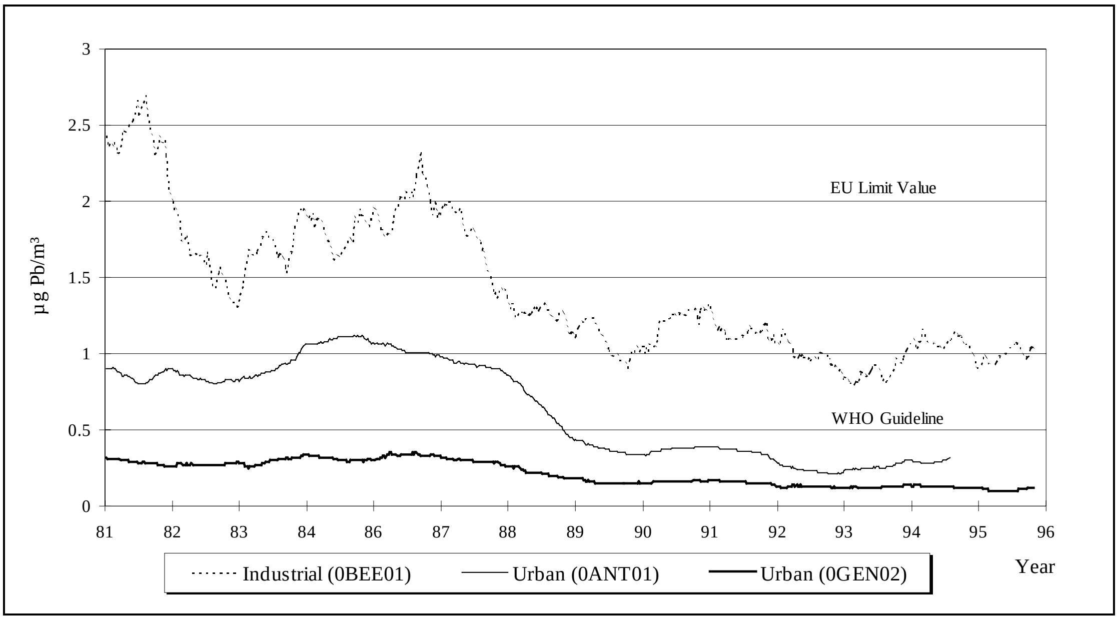

Figure 1.3: Yearly moving average for lead concentration in air, in industrial and in urban zones in Belgium.

Source: FEA (1996).

In all areas measured in the country, lead concentrations have been reduced to below the maximum level of the European Directive. Measurements show that the progressive reduction of the lead content in petrol has had an almost proportional effect on the concentrations of lead in the atmosphere. This reduction tendency is on the point of becoming stabilized since in 1990 use of unleaded petrol became general.

Making abstraction of measuring sites near non-ferrous metallurgic plants, average yearly lead levels are now of the order of 0.1 µg/m³ in the cities and lower than 0.1 µg/m³ in non urban areas.

1.5.1.3. Denmark

The annual mean concentration must not exceed 2 µg/m³. The limit value was laid down when the automobile gasoline was heavily leaded. At present almost all petrol sold in Denmark is lead free and lead pollution has been reduced since 1982.

The Danish Air Quality Monitoring Programme was started in 1982 and comprises an urban monitoring network with stations in three Danish cities. The measured annual averages in 1993 were less than 1/10 of the limit value at the main stations, which are placed on streets with heavy traffic. It is expected that leaded gasoline will not be used at all within a few years. Lead in the atmosphere over Denmark will at that time originate mainly from industrial sources outside the country.

1.5.1.4. Finland

New limit values and guide values for ambient air quality came into force in 1996. The limit value for lead is 0.5 µg/m^3 as an annual average.

Annual average concentrations of lead measured in major cities have fallen from 0.05-1.0 µg/m^3 in 1978-90 to 0.01-0.1 µg/m³ in 1993.

In the transport sector the use of economic incentives has led to the phase-out of leaded petrol. The tax difference between leaded and unleaded petrol is FIM 0.45 per litre. The market share of unleaded petrol has changed from 70% in 1992 to 100% in 1996.

The maximum lead content of unleaded petrol is 0.013 g/l. Typical lead content on the market (e.g. reformulated petrol) is much lower - less than 0.003 g/l.

1.5.1.5. France

In the case of lead, French legislation adopted the European Directive 82/884/EEC.

Lead is measured in 12 districts. Annual averages for values measured in each station in 1993 were between 0.1 and 0.6 µg/m^3. In 1994 they were between 0.1 and 0.5 µg/m^3.

The higher values are due to measurements being taken at stations located in industrial areas. In 1992, 36% of total gasoline sales were of unleaded gasoline.

1.5.1.6. Germany

The Federal Immission Protection law and its technical regulations provide for a yearly average concentration of 2 µg/m^3. That is the same value as in the European Directive. Lead emissions are restricted by an emissions standard of 5 mg/m^3 for facilities with an emission flux ≥25 g/h. In addition, there is an ambient air quality standard for the deposition of lead and its compounds, which must not exceed 250 µg/m^2/day on areas of 1×1 km^2 or 0.5×0.5 km^2, respectively.

The yearly average concentration measured has been going down each year, first with a sharp decline and then more gradually. In the Rhine Ruhr area, for example, the lead concentration fell from 1.3 µg/m^3 in 1974 to 0.07 µg/m^3 in 1994. In the year 1993 yearly averages were below 0,3 µg/m^3 at all stations. In 1994, however, there were particulars points near lead processing facilities with annual averages slightly below or above 0.5 µg/m^3.

1.5.1.7. Ireland

In 1987 a yearly average concentration of 2 µg/m^3 was established as a limit value. Lead concentration has been measured since 1982 especially in areas of heavy traffic density.

Unleaded petrol accounts for approximately 50% of petrol sales (1995)

Since 1977 average yearly concentration levels have been below 1 µg/m^3, with a considerable reduction both in rural and urban areas, and by 1993 they were below 0.2 µg/m^3. The reduction is clear regarding the use of unleaded petrol since 1985.

1.5.1.8. Italy

The basis of Italian legislation regarding maximum levels of lead in the air is the DPR 203/1988 which establishes the 2 µg/m^3 yearly average of the European Directive.

Lead emissions have been reduced considerably as a result of the reduction of the level of lead in gasoline and the more frequent use of unleaded gasoline. Owing to decreases in the lead content of gasoline, there is a trend towards lower air lead values. The limits established in the European Directive are not exceeded, although in some sites the WHO guideline (0.5 µg/m^3) is. The location of sampling sites is prescribed as being such as to represent general population exposure and not over-exposure due to occupational hazard. Typically, when lead is measured in a large city at two sites, one on streets with heavy traffic, annual means ranging from 0.53 to 1.07 µg/m^3 have been measured (Rome, in 1992). Yearly averages were around 0.5 µg/m^3 for the year 1993.

A seasonal variation pattern is generally found in the high traffic sampling station with a maximum from October to January and a flat minimum during spring and summer. On the contrary, no seasonal pattern is generally observed in the station located far from the street.

1.5.1.9. Luxembourg

National legislation implements the existing EC Directives on lead in air and the lead content of petrol. The highest level of lead concentration has been detected in the centre of the city of Luxembourg.

The average monthly concentrations in 1993 were 0.05-0.24 µg/m^3 and in 1994 0.05-0.16 µg/m^3. The maximum monthly average in 1993 was 0.84 µg/m^3 and in 1994 0.92 µg/m^3. Since 1987 the average yearly concentrations have been below 0.5 µg/m^3.

Data since 1980 show a tendency to decrease according to the drop in consumption of leaded petrol.

1.5.1.10. Portugal

Portuguese legislation establishes the same limit as the European Directive in its governmental regulation number 286/93.

A report has been provided on a study of lead and other heavy metals in the atmospheric aerosols of Oporto (*Moura, 1988*). The measurements corresponding to an urban environment with heavy traffic show a daily average of 0.04-0.79 µg/m^3. At times of maximum traffic peak levels of 3.8 µg/m^3 have been recorded in one hour.

The daily averages in the city of Oporto are of the order of 0.2-0.5 µg/m^3 for the year 1994 and the recommendations of the WHO are not exceeded.

1.5.1.11. Spain

The limit under the European Directive was established by Royal Decree 717/1987.

Currently, the figure is at 25% of sales for automobiles with a catalytic converter (1995). This trend is on the increase and runs parallel to the introduction of unleaded petrol. 90% is the forecast for the year 2010.

Regarding concentrations measured in urban stations, annual averages can be considered to be on the order of 0.5 µg/m^3 or less. As an example, Figure 1.4 shows the trend for annual average concentrations in the city of Valencia (typical urban site with a population of around 800,000 inhabitants) for the period between 1980 and 1994. Some stations still record occasional daily maximums on the order of 1.0 µg/m^3.

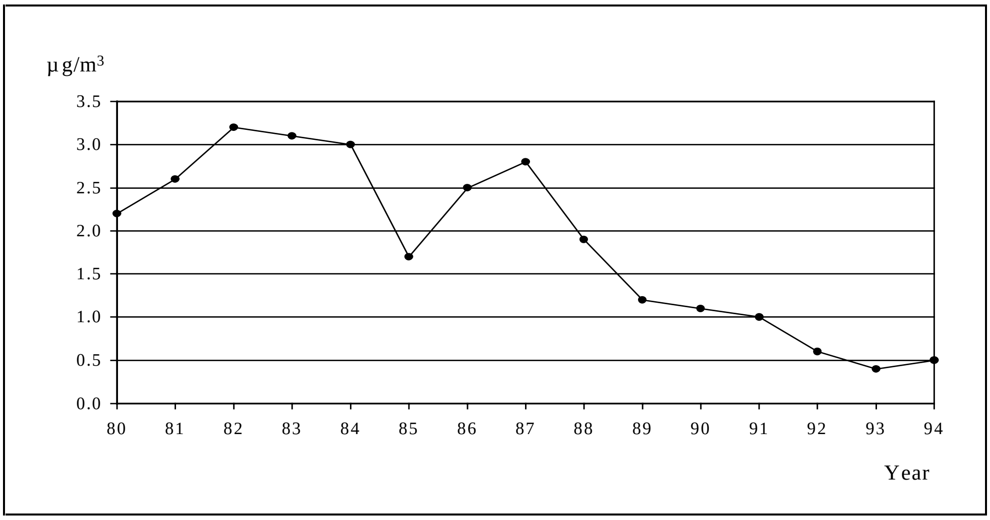

Figure 1.4: Annual averages in the city of Valencia (1980-94).

Source: Ajuntament de Valencia (1995).

Stations located in industrial areas record values superior to previous ones. In 1990, some annual averages were between 3.0 and 4.0 µg/m³. As an example of current concentrations, Figure 1.5 shows the variation of monthly averages and maximum daily concentrations for the period between January, 1994 and August, 1995 at a typical industrial station in Breda (Barcelona). This is a population center of around 3,400 inhabitants, with a concentration of certain ceramics crafts industries, and in this case annual averages were around 0.5-0.6 µg/m³.

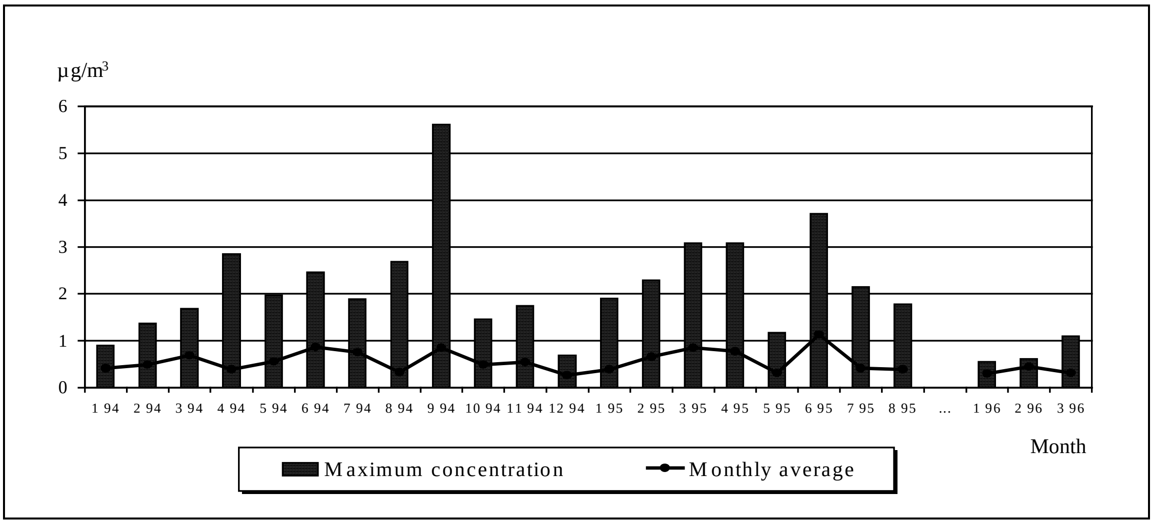

Figure 1.5: Variation of monthly averages and maximum daily concentrations in Breda (Barcelona).

Source: DMA (1995).

1.5.1.12. Sweden

Sweden has as a guideline used the US EPA limit which is 1.5 µg/m³ as an average for three months.

Lead emissions have been reduced considerably as a result of the reduction of the level of lead in petrol and the more and more frequent use of unleaded petrol. At the present time unleaded petrol is available for all vehicles and under a voluntary agreement with the oil companies all petrol sold in Sweden is lead free (additives of sodium/potassium are used). Emissions from industry was reduced by help of the Environmental Protection Law.

Emissions from traffic are minimum. Industrial emissions in 1990 were 90 tonnes/year, much lower than the 950 tonnes/year of 1985 (*SEPA, 1995*).

The average yearly lead concentration does not surpass 0.1 µg/m³. However some ground pollution problems are detected in industrial areas.

1.5.1.13. The Netherlands

The maximum levels provided for by law are a yearly average of 0.5 µg/m³ and a 98 percentile of 2 µg/m³ in 24 hours. Since 1986 the emissions caused by traffic in Holland have been reduced drastically as a consequence of the reduction of the lead level allowed in petrol. In the last few years the WHO guideline value has not been surpassed.

Average yearly levels currently measured are between 0.02-0.04 µg/m³ in non urban areas and 0.05-0.1 µg/m³ in urban areas.

By applying measures such as achieving widespread use of unleaded petrol, it is estimated that it will be possible to bring the whole of Europe to a level below 0.1 µg/m³ yearly average (with the exception of some industrial focal points) by the year 2000.

1.5.1.14. United Kingdom

The air quality regulations follow the European Directives. The main cause of lead pollution is car engine combustion, accounting for 70% of UK lead emissions in 1990 (*UK DOE, 1996*).

In 1985 regulations were applied covering the levels of lead allowed in petrol. A reduction of the average yearly concentration can be observed from 1976/77 to 1992/93 with measurements of 0.82 µg/m³ and 0.11 µg/m³ respectively.

Figure 1.6 offers a graphic example of variation in annual averages for a typical urban station (Central London) contrasted against the increase in the percentage of sales for unleaded petrol.

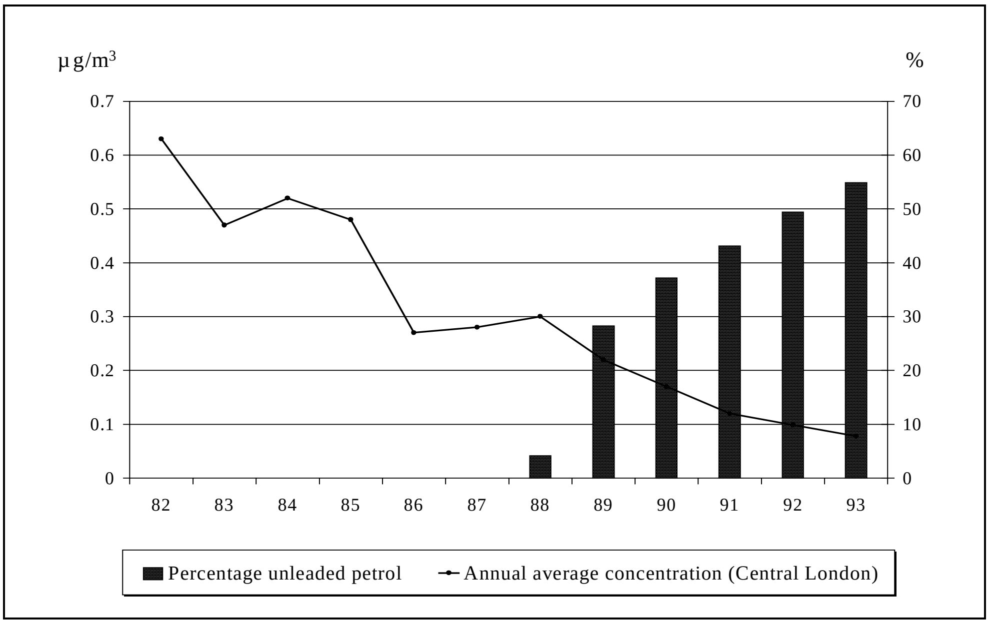

Figure 1.6: Variation in annual averages compared to the percentage of unleaded petrol in London (1982-93).

Source: UK DOE(1995).

The limits established in the European Directive are not surpassed, although in some points the recommendations of the WHO are. The upper limit (1 µg/m^3) was exceeded at one industrial site, and the lower limit (0.5 µg/m^3) at another, both of these monitors are in Walsall.

1.5.2. Other countries consulted

1.5.2.1. Poland

Practically all the lead produced in Poland is concentrated in the province of Katowice. This area registers the highest levels of concentration of lead. In the areas surrounding the industries the maximum level recommended by the WHO is surpassed. In Silesia the values measured are 20 µg/m^3 as a 24 hour average maximum and a range of 0.1-3.2 µg/m^3 for the yearly average (*Poborski, 1993*).

The levels permitted for the air are 1 µg/m^3 (24 hours average) and 0.2 µg/m^3 (yearly average). There are also maximum permitted levels for the soil (100 mg/kg d.m. for heavy soils and 50 mg/kg d.m. for sandy soils), deposition (100 mg/m^2/year) and edible plants.

1.5.2.2. Switzerland

The decrees on control of air pollution are presented. The maximum yearly limit for lead is fixed at 1 µg/m^3. Annual averages in all the stations were below 0.2 µg/m^3 for the year 1994.

The levels of lead in the blood of the Swiss population are currently dropping along with the drop in the level of lead in petrol, the change in life style and environmental factors (*Berode, 1991*).

1.5.3. The state in the UN ECE

At the 13th session of the Executive Body of the Convention on Long-range Transboundary Air Pollution, parties agreed to proceed with the negotiation of a heavy metals protocol. There is no timeframe for completion of such an agreement. However, work is currently underway to develop a comprehensive text for future negotiation of a heavy metals protocol. Only three heavy metals (cadmium, mercury and lead) will be included in the initial protocol. It will limit values for their emissions through reduction in the use of leaded gasoline in vehicles. It may also encompass product-related standards and emission ceilings for each country.

Currently no limit values for critical levels have been agreed upon in the UN ECE framework.

1.5.4. The APIS data base

APIS, *Air Pollution Information System v. 3.04* is a data base of atmospheric pollution. It has been developed by the DG XI/B3 and it is now managed by the European Environment Agency (EEA). This data base gathers together the measurements of concentrations of the main pollutants supplied voluntarily by the Member States in the framework of the Exchange of Information Directive (82/459/EEC).

The data base has been supplied to the Working Group, showing the following situation for the pollutant under consideration (the situation is summarized in the Table 1.5):

- It provides measurements from five Member States.
- The data have not been brought up to date for all the countries in the last few years. As a result there are only trends for Belgium and Denmark, and therefore possible reductions in the lead measured due to the introduction of unleaded petrol cannot be observed.
- There are no exceedances of the EU limit value (2 µg/m^3) in the data available, and since 1988 there are no exceedances of the WHO guideline value (0.5 µg/m^3).

Table 1.5: Situation of the APIS data base regarding lead.

Country	Period covered	Number of towns	Number of stations
Belgium	1982-1994	6	8
Denmark	1982, 1986-1994	8	18
Germany	1988-1989	5	18
Ireland	1982-1987	1	1
Spain	1993	1	4

Source: APIS (1995).

1.5.5. Urban and local lead concentrations

Table 1.6 and Figure 1.7 show 1993 lead mean values for selected stations in some European cities. The levels in these cities are well below the EU limit value and also below the WHO guideline value.

In the preparation of this table the figures used were from the cities that had the highest yearly concentrations for the year 1993 according to the information that the Working Group has. This means that the concentrations shown can be taken as an indication of the maxima but they are not necessarily the absolute maximum concentration in those countries.

Table 1.6: Yearly mean values for selected stations and cities (1993).

Country		City	Station	Yearly mean ($\mu g/m^3$)
Belgium	[a]	Bruxelles	Av. De la Couronne	0.28
	[a]	Liege	Av. Destenay	0.12
Denmark	[a]	Aalborg	Vesterbro	0.14
	[a]	Copenhagen	Jagtvej	0.12
	[a]	Odense	Albanigade	0.10
	[a]	Lille Valby	2090	0.02
Finland	[a]	Helsinki	Valilla	0.02
France	[b]	Paris	Paris	0.28
	[b]	Lille	Lille	0.30
Germany	[a]	Duisburg	Buchholz	0.17
	[a]	Dortmund	Dortmund-mitte	0.16
	[a]	Köln	Riehl	0.13
	[a]	Karlsruhe	Karlsruhe-mitte	0.10
	[a]	Düsseldorf	Düsseldorf-Reisholz	0.09
Italy	[c]	Genova	XX Settembre	0.42
	[a]	Modena	Via Giardini	0.32
Slovakia	[a]	Bratislava	Trnavske myto	0.10
	[a]	Kosice	Galaktika	0.08
Spain	[d]	Barcelona	Pl. Molina	0.38
	[e]	Valencia	Valencia	0.40
Switzerland	[a]	Zurich	Schimmelstrasse	0.22
	[a]	Basel	Feldbergstrasse	0.18
	[a]	Bern	Bern	0.18
	[a]	Lausanne	Lausanne	0.15
UK	[f]	London	Bridge Place	0.10
	[f]	Leeds	Market Building	0.18

Sources: [a] *ETC-AQ (1996),* [b] *BAMET (1995),* [c] *Ministerio dell' Ambiente - Italy (1996),* [d] *DMA (1993),* [e] *Ajuntament de Valencia (1995),* [f] *AEA (1994).*

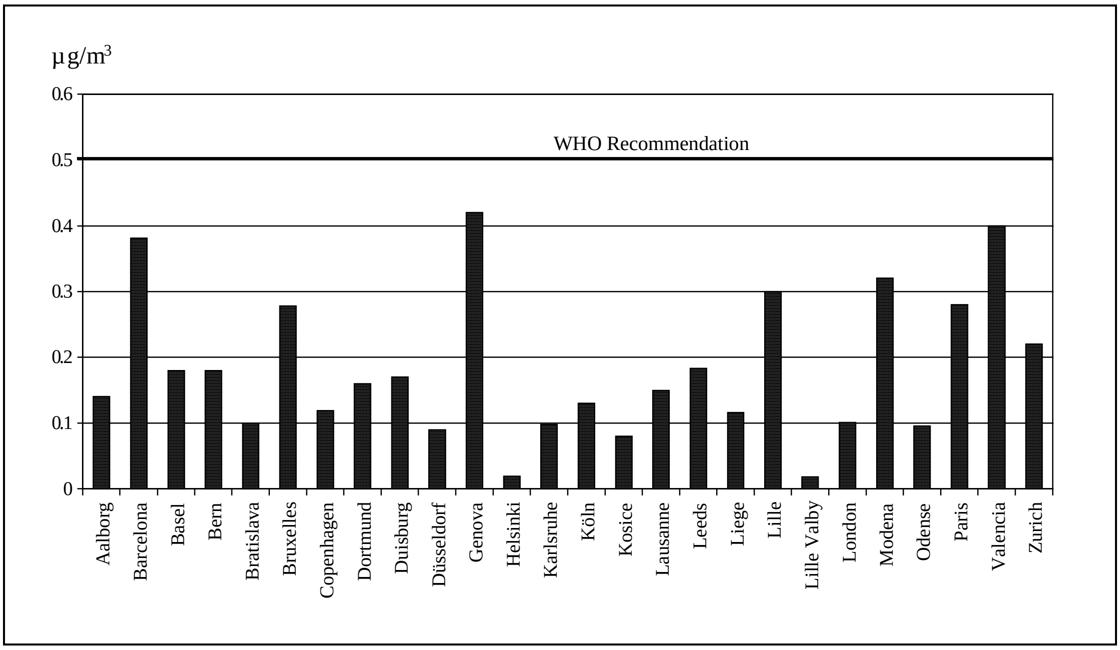

Figure 1.7: Yearly mean values for selected stations and cities (1993).

1.5.6. Summary table

This section offers a general idea of levels in rural and urban areas for each country. High concentrations of lead as recorded in industrial areas or hotspots are not given in this table.

Table 1.7: General levels in the UE.

Country	Yearly averages (µg/m^3)	
	Legislated level	Level measured
Austria	---	<0.5
Belgium	2.0	<0.1 (95)
Denmark	2.0	<0.2 (93)
Finland	0.5	<0.1 (93)
France	2.0	---
Germany	2.0	<0.3 (93)
Greece	n.a.	n.a.
Holland	0.5	<0.1
	2.0 (perc. 98th) daily average	
Ireland	2.0	<0.5 (91)
Italy	2.0	<1.0 (92)
Luxembourg	2.0	<0.5 (92)
Portugal	2.0	<0.5 (94)
Spain	2.0	<0.6 (95)
Sweden	1.5 (quarterly)	<0.1 (95)
United Kingdom	2.0	<0.2 (93)
Switzerland	1.0	---
Poland	1.0 daily average	20 max. (93)
	0.2	0.1-3.2 (93)
US EPA (1978)	1.5 (quarterly)	
WHO	Recommended Guideline 0.5	

1.6. Deposition of lead

Total deposition of lead is a relevant measure of loads to and exposure of soils, ecosystems and surface waters. Total deposition is the result of wet deposition (with precipitation) and dry deposition (all other processes) by the surroundings of industrial installations and sources of coarse particles, total deposition is often assessed by dustfall measurements, using deposition jars.

This section was elaborated using the information available in each country in regard to lead. The purpose is to offer an idea of the current situation in each Member State as regards the values considered under the respective legislations and the levels recorded for each territory. Table 1.8 shows different legislated levels in Europe. Since different sampling strategies and sampling techniques are applied those (legislated) limit values are not mutually comparable. For the same reason the values for lead deposition given in section 1.6.1 are also not mutually comparable.

Table 1.8: Legislated lead deposition limit values in Europe.

Country	Limit value (µg/m^2/day)
Belgium (Flanders)	3000 (limit value) 250 (guide value)
Germany	250
Poland (1990)	274
Switzerland	100

1.6.1. Highest ambient load recorded in some countries

This section deals with the highest data recorded in the Member States with regard to lead deposition, and is complemented with data presented in Annex 1. A description of the measurement methods is given in chapter 3.

Austria: The highest concentrations are recorded in the proximity of industry. In the surroundings of lead works that are closed at Arnoldstein (Carynthia) the annual means achieved were between 300 and 1600 µg/m^2/day. After the reconstruction of this location in 1995, the levels are between 70 and 960 µg/m^2/day showing that the situation is improving (5 sites).

Belgium: Concentrations in the region of Flanders were between 25 and 8,700 µg/m^2/day in the year 1995.

The following table shows yearly mean values of lead deposition for the meteorological year 1993-94 and for the calendar year 1995 in some Belgian stations.

Table 1.9: Deposition in Belgium (1990-95).

Station	Lead deposition (µg/m^2/day)	
	1990-91	1995
Hoboken, non-ferro	1,500 - 21,500	1,500 - 8,700
Beerse, non-ferro	200 - 1,900	200 - 600
Steel industry	100 - 300 [*]	50 - 80
Cities	500 - 700	500 [#]
Background station	25	25

[*] results for the period 1990.
[#] results for the period 1992-1993.

Finland: The following table shows yearly mean values of lead deposition, and corresponding concentrations in precipitation in some Finnish stations. It is related to rural stations for the years 93-94.

Table 1.10: Lead in precipitation and yearly values of lead deposition at rural stations in Finland.

Station	Concentration (µg/l)		Deposition (µg/m²/year)	
	1993	1994	1993	1994
Salla, Värriö (Lappland)	0.7	0.8	400	450
Hailuoto, Marjaniemi (Western coast)	2.3	4.2	890	1130
Kotka, Haapasaari (Southern coast)	3.0	3.4	940	1360
Lieksa, Hietajärvi (Middle Finland)	1.3	1.2	750	750
Lammi, Kotinen (South Finland)	2.4	1.7	1340	940
Kuusamo, Pesosjärvi (Northern Finland)	1.3	0.8	430	380
Utsjoki, Vuoskojärvi (Lappland)	1.0	0.7	250	180

Germany: Highest annual means on areas of 1 km^2 are between 40-1245 µg/m^2/day near lead processing facilities.

The Netherlands: Lead deposition in the Netherlands ranged from 30-100 g/ha/year (≈10-30 µg/m^2/day) (5×5 km) in 1993.

Luxembourg: Highest concentrations of lead are near the old steel works of Esch/Schifflange, Esch/Belval and Differdange (the values are showed in Table 1.11).

They performed more accurate analyses of lead in the environment with the help of biomonitoring. Lead was found in vegetables growing in gardens belonging to persons situated in areas exposed to dustfall with high concentrations of heavy metals especially lead (dust emitted by steelworks).

Table 1.11: Deposition in Luxembourg (1992-95).

Year	Steelworks Esch/Schifflange		Steelworks Esch/Belval	
	Total dustfall (mg/m²/day)	Lead in total dustfall (µg/m²/day)	Total dustfall (mg/m²/day)	Lead in total dustfall (µg/m²/day)
1992	210	219	430	200
1993	250	319	400	226
1994	170	224	360	174
1995	140	100	250	100

Sweden: The highest concentration are recorded in the southern part of Sweden. Yearly means were between 282-2641 µg/m^2/day in 1994, relating to wet deposition in 4 stations

Spain: The measurement of lead deposition is not continuous. Recent data is presented in Annex 1, which refers to local campaigns carried out in various parts of Catalonia for the purpose of categorising these areas with respect to the deposition of this pollutant.

United Kingdom: Lead in dustfall is not monitored on a routine basis in the UK. This is not a requirement of the Directive. Concentrations between 400 and 11,800 µg/m^2/day are achieved near primary lead/zinc smelters. A more detailed explanation of these industrial measurements is presented in Annex 1.

1.6.2. Level of lead allowed on agricultural soil originating in sewage sludge.

Lead may be deposited in soil via routes other than air emissions. For example, sewage sludge deposited on agricultural land contains variable amount of lead, depending on the amount of industrial effluents and waste mixed with the sewage.

Under Directive 86/278/EEC (*CEC, 1986*) the limit value for the amount of lead which may be added to agricultural soil is 15 kg/ha/year, equal to 4110 µg/m^2/day. Air emissions however are the main source of deposition of anthropogenic lead to non-agricultural land.

2. RISK ASSESSMENT

2.1. Sources and pathways of lead in the environment

2.1.1. Lead in the atmosphere

Humans are exposed directly through inhalation of lead emitted into the air. Air also transports lead into other human exposure media, including dust, soil, food and water. Deposited lead can be re-entrained into air with wind-blown dust. Most atmospheric lead is from anthropogenic emissions.

Lead in air can be inhaled or can be deposited in the form of dust on soils, water and food crops. Loading to air can occur from natural emissions and anthropogenic releases such as gasoline combustion, coal burning or industrial emissions.

Automobiles are the primary mobile source of lead in air, reflecting leaded gasoline consumption; although trains, boats, farm vehicles and aeroplanes can also be important mobile sources. The majority of lead emissions occur following the combustion of leaded gasoline in the engine, although some lead is also released with gasoline vapours during refuelling. Current estimates for such emissions would be considerably lower given the reduction in the use of tetraethyl lead that has occurred since 1985.

Air emissions from smelters, processing facilities and solid waste incinerators occur as controlled releases from stacks and fugitive emissions from storage, processing or materials handling. Although worldwide it has been estimated that the non-ferrous metal industry is the second largest lead emitter (see Table 1.3), there are likely to be large regional and natural differences.

Despite declines in general atmospheric concentrations of lead in some countries, areas of higher concentrations still exist due to the presence of local sources.

Industrial lead emissions and the major proportion of automotive emissions are in the form of particles of inorganic compounds of lead. These particles have very small dimensions, but cover a range of sizes which confer different properties upon them.

2.1.2. Lead in water

Lead is a natural, usually very minor constituent of surface and groundwaters. It is considered that the total annual input of lead to aquatic ecosystems has declined since 1985, given the reduction that has occurred in lead emissions from mobile sources. It is important to emphasize that point sources of discharge, although not of great worldwide importance, may have large local impacts. In contrast, the globally important atmospheric deposition is spread over vast areas of ocean and may have little local impact.

Lead deposited from the atmosphere can enter aquatic systems through direct fallout or through erosion of soil particles. Infiltration of rainwater into groundwaters and entry into aquifers normally involve passage through soil. Rainwater can contain appreciable concentrations of lead. These, however, diminish on passage through the soil, as lead binds to soil minerals and humus. Groundwaters therefore normally contain very low concentrations of lead.

Water for potable supplies is normally derived from surface freshwater or groundwater sources. Water treatment prior to distribution does not normally add to the lead content, and usually reduces it (often by as much as 50 %). Plumbing systems may contain lead pipes, lead soldering, and bronze or brass fittings. Corrosions of these materials, aggravated by water with low pH, and subsequent leaching into the drinking water can contribute significant quantities of lead in systems where these materials are used.

Anthropogenic input of lead to aquatic ecosystems can occur from sources such as effluents from mining, smelting, refining and manufacturing processes or the dumping of sewage sludge and atmospheric fallout. Lead deposited from the atmosphere can enter aquatic systems through direct fallout or through erosion of soil particles. In general, there is a little correlation between lead concentrations in rain and snow and concentrations in streams that drain watersheds.

2.1.3. Lead in soil

In rural and remote areas, lead in soil is derived mainly from natural geological sources and lead concentrations reflect those of the underlying bedrock or transported parent material.

As lead accumulates in soil, where it is relatively immobile and has a long residence time, present-day amounts of lead in surface soils largely reflect anthropogenic inputs arising from industrial, urban and agricultural activities. Given the reduction that has occurred in lead emissions from mobile sources, it is considered that the total annual input of lead to soils has declined since 1985, but nevertheless lead is still accumulating in the soil given to the very small amount which is removed from the soil by plants.

A major mechanism of soil and sediment contamination is atmospheric deposition of lead. The concentration of lead in soils near highways is related to traffic density, local meteorological conditions, vegetation and topography. In general, lead concentrations decrease with distance from the highway and with depth in the soil column. Lead soil concentration is greatest within 10 metres of the road and within the top one to five centimetres.

The main components of lead in soil are the soil solution, the absorption surfaces of the clay-humus exchange complex, precipitated forms, secondary iron and manganese oxides and alkaline earth carbonates, the soil humus and silicate lattices. It has been suggested that acidification of the surface environment may influence the chemical species of metals present, their transport pathways and cycling. There is as yet no evidence that acid precipitation is influencing the chemistry and transport of lead in the soil environment.

Although various soil parameters can affect the availability of lead, the total amount of the element present is one of the major factors affecting the lead content of plants. It has been found that there is a positive linear relationship between lead concentrations in plant and soil, and that this relationship exist for a wide range of uncontaminated soils. At higher soil lead levels, however, plant uptake has been found to decline with increasing soil lead concentrations and a curvilinear relationship has been reported. There is general agreement that only a small proportion of lead in soil is available for uptake by plants.

The amount of lead absorbed by plants depends not only on the total lead content of the soil, but also on its chemical form. Other soil factors influencing the bioavailability of lead include cation exchange capacity, organic matter content, soil texture and clay mineralogy, redox potential, and the levels of other elements including the nutrients phosphorus, sulphur and nitrogen and the heavy metal cadmium.

Lead is retained in soil in inorganic complexes or adsorbed to hydrous oxides near the soil surface. The mobility of lead in the soil depends on the soil pH and organic content. In general, lead's relative immobility in soil tends to decrease its bioavailability to humans and other terrestrial life. However, its immobility also increases its residence time in soils.

2.1.4. Lead in dust

The general consensus is that the results from numerous investigations over the past two decades point to the presence of elevated lead concentrations in dust, both external to and within the home. Exposure to lead in dust can occur through ingestion, especially likely in children, or inhalation of resuspended dust.

Dust is found both in the home and in the outdoor environment. There is general agreement that, in many cases, local lead contamination of the outdoor environment, around both primary and secondary lead smelters and lead processing plants, results in enhanced lead concentrations in dusts within the home.

Exposure to lead in dust can occur through ingestion, especially likely in children, or inhalation of resuspended dust. Depositions of airborne lead from leaded gasoline emissions and from stationary sources, such as smelters and coal-powered generating stations, are the major anthropogenic contributors of dust lead in the outdoor environment. An additional major source of lead in dust is the peeling and flaking of lead-based paint. Lead in dust is found primarily as sulphate, along with small amounts of oxide and halide salts. Unlike lead that is incorporated into soils, lead in surface dusts is mobile and is believed to decrease with declining input, precipitation, wind, or street and housecleaning.

2.1.5. Other sources

Lead in paint constitutes a major source of bioavailable lead in the environment. Although many countries have banned or restricted the use of lead in the interior paints, there remains a huge reservoir of contaminated material in existing structures where leaded paints has been used. Children are especially susceptible to exposure to lead in paint.

Occupational exposures to lead have been noted in various industries, such as inorganic pigments manufacturing; primary and secondary lead metal processing; brass, bronze and cooper foundries; battery manufacturing; machinery manufacturing; electronic capacitors manufacturing; auto repair services and garages; bridge, tunnel and elevated highway repairs; stone, glass and clay products manufacturing; munitions manufacturing; and firing ranges. Lead exposures can occur during renovation and abatement of lead-painted homes and other structures. Para-occupational exposures occur when lead in the form of dust is easily carried out of the workplace (on clothing, shoes, etc.) and into worker residences, where spouses and children of lead workers can then be exposed.

2.2. Impact on ecosystems

A publication was edited by UN ECE in which a description of the impact of heavy metals in general on ecosystems (*UN ECE, 1994*) is set out.

The procedure is general to heavy metals, the Working Group has not found other evidence of effects to ecosystems.

(a) Terrestrial ecosystems

Effects caused by the exposure of organisms to heavy metal deposition may be related either to current deposition rates or to accumulated amounts in the ecosystem, many effects certainly being related to both. Metal uptake by plants plays the key role in the entry of metals to terrestrial food chains, because vegetation creates habitats for animals and is eaten alive by herbivores or dead by detrivores. Contaminants may be toxic to plants, diminishing their productivity or biomass, or eliminating some species, and can consequently alter the structure or diversity of a habitat. When plants accumulate metals, these metals can be ingested by animals thus creating the potential for toxic effects at higher trophic levels.

(b) Aquatic ecosystems

Atmospheric deposition of metals may influence the quality of surface waters and groundwater. In addition to qualitative aspects of the water itself (restricted use of water resources for human consumption, livestock watering, recreation etc.) accumulation in aquatic organisms may additionally provoke a series of adverse effects on the food web and, for example, render fish unfit for human consumption.

In general the input of metals to surface waters is related to the input pathways of water. In most cases the major portion of water received by surface waters is supplied from the surrounding watershed or discharge area. The composition of the run off is largely dependent on the hydrological conditions, biochemical processes and geochemistry of the watershed.

2.3. Health effects

2.3.1. Pathways of human exposure

The primary routes of human exposure to lead are inhalation and ingestion (of water, food, air, soil and dust). The relative importance of any single source of exposure is difficult to predict and will vary with geographic location, climate and local geochemistry. Similarly, the intensity of exposure experienced by an individual can vary as a function of age, sex, occupation, socio-economic status, diet and cultural practices. In addition, the amount of lead taken up into the body is believed to vary depending on the concentration and composition (for example, particle size, chemical form) of the lead inhaled or ingested.

Figure 2.1 offers a graphic example of the different routes of human exposure from the main identified sources through the environment.

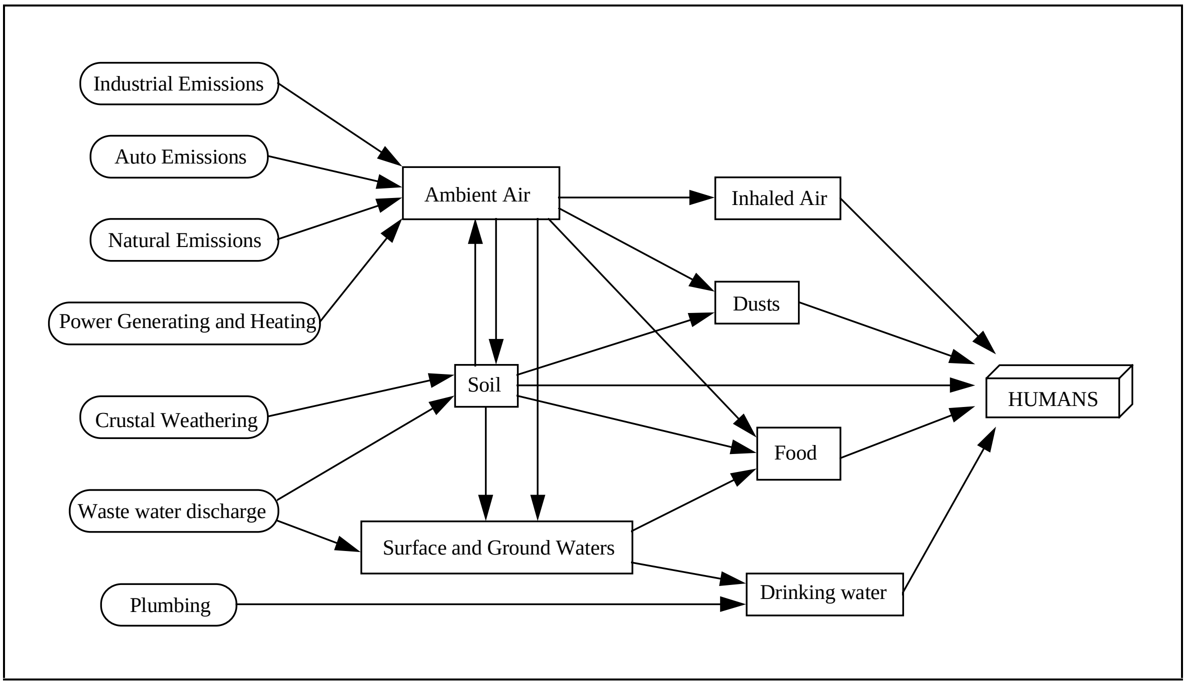

Figure 2.1: Pathways of human exposure.

Air: The health effects of respired lead are dependent upon particle size. A high proportion of inhaled small particles (less than 2.5 µm) is deposited in the deepest alveolar portion of the respiratory system, from which lead is absorbed with almost 100% efficiency into the bloodstream. Particles in the range 2.5 to 10 µm most typically deposit in the tracheobronchial and naso-pharingeal region, from which they are elevated and swallowed. Absorption of lead through the gastrointestinal tract is far less efficient in adults (8 to 10%) but can be up to 50% in children. Thus, a large proportion of lead in these sizes does not enter the bloodstream. Particles of greater than 10 µm enter the nose with only low efficiency and do not represent an appreciable inhalation hazard unless present in very high concentrations. Such particles can, however, contribute to the lead content of surface dusts and soils and can be swallowed by oral intake, especially by smaller children.

Dust: Accidental ingestion of dust or soil (dirt) by hand-to-mouth activity is an important source of lead exposure to young children.

Food: The ingestion of food is a major component of most individuals' total lead uptake, although the relative contribution is a function of one's size, body weight, age and type of diet. The occurrence of lead in the diet may be a result of: natural sources of lead, deposition of airborne lead particles onto crops, forage, feed, soils and water; harvestings, processing, transport, packaging, preparation and storage of food; other sources of lead in foods include leaching from ceramic containers in which lead glazes have been used, uptake of lead from lead-rich urban garden soils into home-grown vegetables crops, and uptake of lead into crops from sewage sludge applied to farmland.

Soil: Children may contact lead-bearing soils during outdoor play, in addition, contaminated soils may be tracked indoors on shoes, clothing, etc. A major mechanism of soil and sediment contamination is atmospheric deposition of lead from gasoline combustion and from stationary sources.

Water: Lead concentrations in drinking water result primarily from lead leaching from water delivery systems, and from previously contaminated drinking water sources.

***Relative significance of different routes of exposure*:**

Exposure to lead from each route can vary significantly for different individuals and population groups. Since the relative contribution of each of these sources can also vary substantially, comprehensive information covering a wide range of circumstances cannot be provided. To give some idea of possible situations, Table 2.1 presents a few simplified calculations (*IPCS, 1995*).

Table 2.1: Estimates of lead absorbed by adults and children from air, dust, food and water at different air lead levels*.

Mean air lead concentration (µg/m³)	Dust intake (mg/day)	Source of lead (µg/day) Air	Dust	Food	Water	Total absorbed (µg/day)
Adults:						
0.3	N.S.	2.4	---	10	2	14.4
0.5	N.S.	4.0	---	10	2	16.0
1.0	N.S.	8.0	---	10	2	20.0
2.0	N.S.	16.0	---	10	2	28.0
Children (1-5 years old):						
0.3	---	0.6	---	25	5	30.6
0.5	---	1.0	---	25	5	31.0
1.0	---	2.0	---	25	5	32.0
2.0	---	4.0	---	25	5	34.0
1.0	25	2	12.5	25	5	44.3
1.0	50	2	25.0	25	5	57.0
1.0	100	2	50.0	25	5	82.0
1.0	200	2	100.0	25	5	132.0
N.S. = Not significant.						

Source: IPCS (1995).

[*] The estimates are based on the following assumptions:

Air:	Respiratory volume in adults is 20 m^3/day and in children 5 m^3/day, the respiratory absorption is 40 %.
Food:	Intake of lead by adults 100 µg/day with 10 % absorption and 50 µg/day for children with 50 % absorption.
Water:	A lead concentration of 20 µg/l, with adult consumption of 1 l/day and 10 % absorption and for children 0.5 l/day with 50 % absorption.
Dust:	Dust concentration of lead was 1000 µg/g and for absorption was 50 %.

2.3.2. Recommendations of the WHO

Source: WHO (1994).

2.3.2.1. Population groups at higher exposure risk

Children up to 6 years of age are a population at increased risk for lead exposure as well as for adverse health effects, for the following reasons:

- Children have a behavioural characteristics (outdoor activity, less concern for hygienic conditions, hand-to-mouth activities or even pica), which increase the risk for lead exposure.
- Children eat and drink more per unit of body weight than adults, so that their relative lead intake is increased.
- Lead absorption in the gastrointestinal tract is substantially higher in children.
- Among children there is greater prevalence of nutritional deficiencies, which enhance absorption of lead from the gastrointestinal tract.
- The blood-brain barrier is not yet fully developed in young children.
- Haematological and neurological effects of lead occur at lower threshold than in adults.

2.3.2.2. Lowest-observed-adverse-effect levels

Table 2.2: Summary of lowest-observed-adverse-effect levels for lead induced health effects in adults.

Lowest-observed-effect Blood-lead-level (µg/l)	Haem synthesis haematological and other effects	Effects on nervous system
1000 - 1200		Encephalopathic signs and symptoms
800	Frank anaemia	
500	Reduced haemoglobin production	Overt subencephalopathic neurological symptoms, cognition impairment
400	Increased urinary ALA and elevated coproporphyrin	
300		Peripherial nerve dysfunction (slowed nerve conduction velocities)
200 - 300	Erythrocyte protoporphyrin elevation in males	
150 - 200	Erythrocyte protoporphyrin elevation in females	

Source: WHO (1994).

Table 2.3: Summary of lowest-observed-effect levels for lead induced health effects in children.

Lowest-observed-effect Blood-lead-levels (µg/l)	Haem synthesis haematological and other effects	Effects on nervous system
800 - 1000		Encephalopathic signs and symptoms
700	Frank anaemia	
400	Increased urinary ALA and elevated coproporphyrin	
250 - 300	Reduced haemoglobin synthesis	
150 - 200	Erythrocyte protoporphyrin elevation	
100 - 150	Vitamin D3 reduction	Cognitive impairment
100	ALAD - inhibition	Hearing impairment

Source: WHO (1994).

2.3.2.3. Basis of WHO guidelines

Guidelines for lead in air will be based on the concentration of lead in blood.

A critical level of lead in blood of 100 µg/l is proposed. It should be stressed that all these values are based on population studies yielding group averages, which apply to the individual child only in a probabilistic manner. Although some lead salts have been found to be carcinogenic in animals the evidence for a carcinogenic potential in humans is inadequate and will, therefore, not be considered here.

- Current measured “baseline” blood lead levels of minimal anthropogenic origin are probably between 10 and 30 µg/l.
- Various international expert groups have determined that the earliest adverse effects of lead in populations of young children begin at 100-150 µg/l. It is assumed to be prudent to derive a guideline value based on the lowest value of this range (100 µg/l).
- Inhalation of airborne lead is a significant route of exposure for adults, but for young children other pathways of exposure (ingested lead) are generally more important than inhaled air lead.
- It appears that 1µg/m^3 in air directly contributes approximately 19 µg/l blood in children and about 16 µg/l blood in adults.
- In order to correct for uptake by other routes, it is assumed that 1 µg/m^3 in air would contribute to 50 µg/l blood.
- It is recommended that efforts should be undertaken to ensure that at least 98% of an exposed population should have blood lead-levels that do not exceed 100 µg/l. In this case, the median blood lead would not exceed 54 µg/l. On this basis, the annual average air lead should not exceed 0.5 µg/m^3 (with the assumption that the upper limit of nonanthropogenic origin in blood is 30 µg/l).
- The air guidelines for lead should be accompanied by other preventive measures. These should specially take the form of monitoring the lead content of dust and soils arising from air lead fallout (some data indicate that lead fallout in excess of 250 µg/m^2/day will increase blood lead levels).

2.4. Limit values for lead

The objective of this proposal is to find a strategy to limit or avoid the harmful effects of lead pollution in the air on human health and ecosystems. This objective will have to be reached within a determined time limit and not exceeded thereafter.

From the information presented in this document it can be seen that lead pollution of the air is basically produced by two clearly differentiated sectors:

- Emissions from vehicles caused by lead present in leaded petrol. In this case the action consists of the total elimination of lead containing fuel.
- Industrial operations. Significant emissions can occur during the production of certain non-ferrous metals and from some processes in which lead is used. Actions to be taken must be tailored to the specific industrial site.

The relative importance of industrial emissions has been increasing due to the decrease in the emissions from traffic.Another factor to take into account is the concrete characteristics of the pollutant. It is considered that it is generally deposited at short distances from the focus of emission and is concentrated in areas near the source, bearing in mind the existing evidences showing that heavy metals (small fraction) can be transported to hundreds and thousands of kilometers away from their sources of transportation of over a long distances (*UN ECE, Executive Body for the Convention on Long-range Transboundary Air Pollution*).

It is proposed the establishment of a model taking into account a tolerance margin in the achievement of the proposed standard. This consideration would only be necessary in hotspot (industrial) areas.

The tolerance margin (Figure 2.2) will be expressed as a percentage of the limit value that could be surpassed in certain cases, during the transition period towards the establishment of the limit value (c_f).

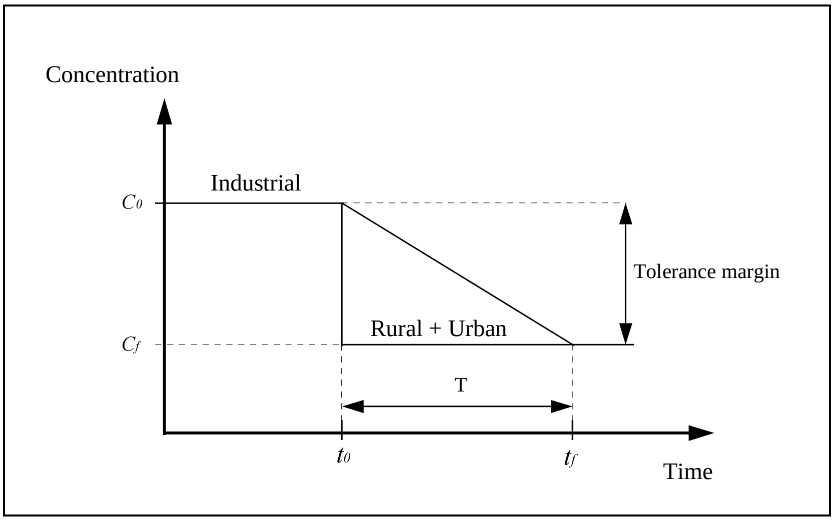

Figure 2.2: Tolerance margin model proposed.

- t_o is the year of application of the Directive
- t_f is the year in which the final limit value will be established in industrial areas (time of compliance).

2.4.1. Recommendations for limit values

It should be borne in mind that the contribution to concentrations of lead in air of natural sources is extremely low. Lead concentrations in areas which are not close to anthropogenic sources are in the region of 0.05 - 0.1 $\mu g/m^3$. Lead once deposited to the soil or to other surfaces is scarcely removed by natural processes, and therefore accumulates. Lead emissions into the environment should be as low as possible in order to avoid further accumulation of lead in the long term. For these reasons the target objective or lead concentrations in the air should also be as low as possible. The WHO guideline of 0.5 $\mu g/m^3$ is a step towards an ojective of reducing lead concentrations as close as possible to natural background concentrations in ambient air.

Recommending limit values is not however straightforward. The percentage of lead absorbed through different sources (direct inhalation, dust, food and water) is different for adults an children. The calculations of ICPS in Table 2.1 show that at ambient air concentrations of lead of 0.5, 1.0 and 2.0 $\mu g/m^3$ adult intake through direct inhalation is respectively 25%, 40% and 57%. Intake through dust ingestion is almost zero.

For children aged 1-5 the daily intake is dominated by dust intake. Daily intake via direct inhalation does not vary with concentrations of 0.5, 1.0 or 2.0 $\mu g/m^3$. Daily intake is dominated by ingestion of dust. This means that for children at risk namely those that are living near industrial plants where high amounts of dust deposited and the levels of lead or dust are also high, the lead intake through dust is much more important than the intake through air. To protect those children at risk, measures should be taken to control the lead levels in dust and by consequence in dustfall or total deposition around industrial plants. Concentrations in air reflect only a small part of the total emissions.

The WHO has recommended a guideline value for lead in air of 0.5 $\mu g/m^3$ measured as an annual average concentration. The Working Group agreed that a limit value set at this level would provide adequate health protection to the general public.

Despite this, serious concerns were expressed about the advisability of recommending a limit value of 0.5 $\mu g/m^3$. Most of these concerned assumptions made by WHO is calculating their guideline value. On the one hand there was a view that the proposals were highly conservative and thus over-estimate the potential contribution of air lead to young children, a view which leads to the conclusion that a lead in air limit higher than 0.5 $\mu g/m^3$ would provide the desired degree of health protection for children. On the other hand there was a view that the proposals were not tight enough and would fail to provide sufficient protection either to the environment or to 100 % of children. This would argue for a lead in air limit lower than 0.5 $\mu g/m^3$.

It was agreed the possibility of establishing a percentile was not appropriate to an annual average and that an alert threshold should not be set. Industry is required to have procedures for dealing with alert conditions internally.

2.4.2. Deposition limit value

On the basis of the information in Table 2.1 the group recommends that a deposition limit value should be developed for protecting health, particularly for young children in the surroundings of industrial plants.

The table indicates that the dominant exposure route in this case is the ingestion of deposited dust. Reducing this exposure will involve two steps:

- Removing the dust (cleaning surfaces, soils, etc.).
- Preventing further dust build-up by reduction of emissions (particularly fugitive emissions).

A direct relation (in the short term) between emissions or air concentration and blood lead levels is not expected, as exposure is mainly arising from dust accumulated from emissions in the past.

However, if cleaning the surroundings is carried out at regular intervals, there will be in the longer term a relation between emissions, concentrations in the air, and exposure, provided that cleaning the environment is carried out regularly.

It is the view of the group that present techniques for measuring air concentrations (PM_{10}, TSP) have limitations in assessing the coarse dust fractions that may contribute most substantially to local deposition. The group has therefore serious doubts whether setting a limit value for air quality alone will provide sufficient health protection for the population most at risk. It is therefore recommended that a deposition limit value should be developed.

WHO has been unable to recommend a deposition guideline value.

Measuring methods for lead deposition have been used, but there are difficulties with these, as they may be doubtfull indicators of deposition to real receptors.

The group recommends that research is set up to:

- Clarify relationships between deposited dust and lead blood levels.
- Provide better relationships between air emissions (chimney and fugitive) and total lead deposition around industrial plants.
- Develop and evaluate adequate measuring techniques for total lead deposition.

The possibility of developing a deposition limit value for lead around industrial installations should be reviewed when further information is available.

The group also recommends that the developing work on long range transport of lead should be reviewed in due course and that the question of whether a deposition limit value should be set to prevent bioaccumulation in ecosystems.

3. MEASUREMENT AND ASSESSMENT OF CONCENTRATIONS

3.1. Current practice in Member States

The information shown in this section has been taken from information received from Member States. In the majority of cases they are shown in the same format as they were received.

3.1.1. Locations of high concentrations near major sources of lead

From the information sent by the Member States to the Working Group it is currently concluded that the principal sources of lead discharge into the atmosphere are those corresponding to localized industrial centres (concentrations of industries or important isolated industries). These industrial emissions are greater than those from vehicle traffic, especially in large cities. This fact has already been mentioned in other sections of this document.

Emissions from industrial centres are the ones that give the greatest relative contribution in the majority of countries. However, the greatest lack of information is from those countries where the use of unleaded gasoline is not yet at the desired level.

Finland: Area around Pori-Harjavalta smelters

Germany: Highest deposition and concentration can be found near lead processing facilities.

Luxembourg: The highest lead concentrations are measured in the centre of Luxembourg-city with estimated emissions of 6 tonnes/year (traffic) for whole Luxembourg in 1995.

Sweden: The major source for lead emission (a smelter) is situated in the northern part of Sweden.

United Kingdom: A number of short term surveys were carried out in the mid 1980’s in a range of industrial areas. As a result of these surveys, 3 areas were identified as having the highest airborne lead concentrations and long term monitoring was continued in these areas: IMI works, Walsall, Brookside works, Walsall and Elswick works, Newcastle-upon-Tyne.

3.1.2. Current state of monitoring in agglomerations

As an example of the current situation regarding this point, tables referring to Spain and the United Kingdom are shown with the list of agglomerations with a population greater than 250,000 inhabitants.

We can conclude that the situation shown is far from that which is being proposed in this document. Just as there are countries where there are no important population concentrations with respect to the number of inhabitants, in others this situation is very different. It is a fact that lead measurement is not carried out over the whole territory and continuously effected. Only sporadic measurements are taken or occasional campaigns made in certain specific areas.

Austria: There are three agglomerations of more than 250,000 inhabitants, in none of which lead measurements have been conducted in recent years.

Spain: The following table shows the situation in Spain. It gives a breakdown of cities with a population greater than 250,000 inhabitants, specificating if lead monitorint is currently undertaken (lead is monitored in 8 of 18 total agglomerations).

Table 3.1: Agglomerations of more than 250,000 inhabitants in Spain.

Province	City	Population	Lead monitoring
Alicante	Alicante	261,255	No
Asturias	Gijón	259,054	Yes
Baleares	Palma de Mallorca	296,754	Yes
Barcelona	Barcelona	1,623,542	Yes
	Hospitalet de Llobregat	269,241	Yes
Córdoba	Córdoba	300,299	No
La Coruña	La Coruña	245,459	No
Granada	Granada	254,034	No
Madrid	Madrid	2,909,792	Yes
Málaga	Málaga	512,136	No
Múrcia	Múrcia	318,838	No
Las Palmas	Las Palmas de G.C.	342,030	No
Pontevedra	Vigo	274,629	No
Sevilla	Sevilla	659,125	No
Valencia	Valencia	752,909	Yes
Valladolid	Valladolid	328,365	No
Vizcaya	Bilbao	368,710	Yes
Zaragoza	Zaragoza	586,219	Yes

Source: MIMAM (1996).

United Kingdom: Table 3.2 shows UK towns and cities with a population greater than 250,000, indicating where lead monitoring is undertaken (lead is monitored in 5 of 18 total agglomerations).

Table 3.2: Agglomerations of more than 250,000 inhabitants in UK.

Urban Areas	Population	Lead Monitoring	Urban Areas	Population	Lead Monitoring
Inner London (North)	4,090,851	Yes	Edinburgh	420,169	No
Inner London (Central)			Leicester	328,835	No
Inner London (West A)			Kingston upon Hull	325,485	No
Birmingham	1,024,118	No	Coventry	322,573	No
Glasgow	765,030	Yes	Belfast	314,000	No
Liverpool	544,861	No	Bradford	295,048	No
Sheffield	477,257	No	Nottingham	277,203	No
Leeds	452,841	Yes	Stoke-on-Trent	275,168	No
Manchester	448,604	Yes	Cardiff	266,267	Yes
Bristol	420,324	No	Wolverhampton	265,631	No

Source: UK DOE (1996).

3.1.3. Measurement methods used in the Member States

3.1.3.1. Lead in suspended dust

Austria: Austria has not monitored lead in the past years but some monitoring stations are under preparation. In 1996 two monitoring stations for lead have started to sample, both of the types urban and kerbside. Five daily samples will be taken by high volume sampling (1000 m^3 per filter) monthly with the aim of calculating an annual mean. The nitrocellulose filters will be analysed by ICP.

Belgium: At the present time air quality monitoring is done by means of a network in each region.

In about fifty stations lead is sampled continuously on a 24 hour basis. The suspended particulate matter is collected on cellulose nitrate filters (0.45 µm) and analyzed with XRF-spectrometry. About 15 m^3 air is sampled during 24 hours. The stations cover agglomerations, rural areas and industrial areas. The sampling station is an own development. It has been tested in wind tunnels and has been compared in real outdoor conditions with PM_{10} samplers used in Great-Britain and France.

There are 29 measuring sites in Flanders of which 2 rural stations, 2 stations situated in agglomerations and 25 situated in industrial zones.

Lead is measured in 7 stations in the Wallonian region.

In the Brussels region 4 measuring points of lead in suspended dust are located, namely 3 in the centre of Brussels and 1 station in the suburban zone which can be considered as a background station.

Finland: Lead is sampled with high volume samplers (TSP and PM_{10} inlet) and impactors.

The method of analysis used to determine the mass concentration of lead in the air is atomic absorbtion spectrometric method described in standard SFS 5008 based on Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air (EPA US Code of Federal Regulations 40 CFR 50 Appendix G. 7 s.). Atmospheric particulates for the analysis are collected according to standard SFS 3863 (determination of suspended particulates in the atmosphere, high volume method).

The site types for lead measurements in Finnish monitoring networks are presented in Table 3.3.

Table 3.3: Site types for lead measurements in Finland.

City/Netw.	Site	Site type	Frequency
Harjavalta	Torttilan koulu	Industrial	24 hours, 2 or 3 per week
Helsinki	Vallila	Urban	24 hours, 2 or 3 per week
Helsinki	Töölö	Urban	24 hours, 2 or 3 per week
Kokkola	Pihlaja	Urban	24 hours, 12-15 per year
Kokkola	Sairaala	Urban	24 hours, 12-15 per year
Kokkola	Tehtaankatu	Urban	24 hours, 12-15 per year
Pori	Itätulli	Urban	24 hours, every 3th day
Pori	Väinölä	Industrial	24 hours, every 3th day
Raahe	Lapaluoto	Suburban	24 hours, 11-19 per year
Raahe	Linja-autoasema	Urban	24 hours, 11-19 per year
Raahe	Pattijoki	Suburban	24 hours, 11-19 per year
Raahe	Ruukki	Suburban	24 hours, 11-19 per year
Raahe	Varikko	Industrial	24 hours, 11-19 per year
Tampere	Keskustori	Urban	24 hours, 1 per week
Valkeakoski	Tietolanharju	Urban	24 hours, every 3th day
Valkeakoski	Yhteistalo	Urban	24 hours, every 3th day

Source: FIN ME (1995).

Germany: Lead concentration is routinely monitored at more than 200 stations; most of them are situated in urban areas but some stations are also monitoring hot spots (e.g. lead smelters or kerbsides) and rural areas. The sampling equipment employed are high (60 m^3/h), medium (15 m^3/h) and low volume samplers (1-3 m^3/h) defined in VDI-Guidelines (e.g. VDI 2463). 104 to 180 daily samples are taken per year and analyzed by AAS or ICP-MS after digestion of the filters (cellulose-nitrate, quartz) with HNO_3 HF/H_2O_2 according to VDI-Guideline 2267. Quality control include, i.a., interlaboratory comparisons and an accreditation for private laboratories issued by the German states.

Ireland: Since 1982 the concentration of lead in air has been monitored by Dublin Corporation at 9 sites representing both city-centre and suburban locations. As road traffic is the primary source of lead emissions, the site locations are determined largely by traffic density.

Italy: Lead is routinely monitored in compliance with the Italian Legislation. The reference method uses a medium volume sampler for sample collection and atomic spectroscopy for analysis. While in the case of industrial sites the location of the samplers is based on prevailing winds and on dispersion modelling predictions, in urban sites the monitoring of lead is performed in sampling stations located in parks, residential areas and in areas characterized by heavy traffic.

Luxembourg: Four measuring stations measuring continuously lead have been working since 1989. Suspended particulate matter in air are collected on filters (24 hour values) and analyzed.

The method of analysis used is X-ray fluorescence spectroscopy. Particulate matter collected on a cellulose nitrate filter (pore size: 0.45 µm). Air sampling at a rate of about 10 l/min. The filters are analyzed in Belgium by the institute ISScP. The usual QA/QC test are performed. The lowest detection limit for lead is 0.05 µg/m^3 24 hour measurements during the whole year in 4 stations (1 rural, 2 urban, 1 urban-industrial).

Spain: In Catalonia autonomous region, with a total area of 32,000 km^2, there is a network of manual stations to measure suspended lead currently with 21 lead samplers (in 1995). These samplers are distributed about the territory, 19 stations in urban locations (5 traffic, 7 industrial, 1 commercial and 6 residential) and 2 in rural locations (1 industrial and 1 residential).

These are high and medium volume samplers which continuously (or every 3-5 days per week) make measurements and give the daily averages. The filters are digested in the laboratory by HCl/HNO_3 diluted and ultrasonication at 100 ºC, and analyzed by AAS according to the US EPA 40 CFR 50 Appendix G.

Sweden: At present Sweden does not measure lead in ambient air in background at their four stations. Their plans are to measure particulate bound heavy metals at the background stations. In cities they have stopped to measure lead depending on the low emissions of lead.

United Kingdom: Sampling of airborne particulate matter is undertaken with the UK “M Type” sampler. The flow rate is controlled to 4.9 l/min and material is collected over a one week period on Millipore Aerosol Field Monitor filters. The filters are analysed by atomic absorption spectroscopy, or inductively coupled plasma atomic emission spectrometry.

The number of monitoring sites and the frequency of monitoring are given in Table 3.4.

Table 3.4: Location of sites and frequency of monitoring in UK.

Survey	Number of stations and type of site	Monitoring frequency
Lead in Petrol	6 (2 urban, 2 rural, 2 kerbside)	Weekly
Multi-Element	5 urban	Weekly/Monthly
Kerbside	1 kerbside	Monthly
Trace and Major Elements	4 rural	Quarterly
EC Directive	9 industrial	Weekly

Source: UK DOE (1996).

The precision of the measuring system is dependent on the stability of the sampling apparatus and the precision of the analytical methods, and has been calculated as ±5%. The accuracy is mainly dependent on the measurement of sample by the gas meter and on the efficiency of sample collection. This has been calculated to be ±5.4%. An intercomparison exercise between AEA and other laboratories involved in analysis has been undertaken and has demonstrated comparable accuracy and precision.

Analytical quality control at AEA Technology, is achieved by calibration of the analytical instrument with standard materials prepared gravimetrically. Calibration is undertaken at zero and two known concentrations. In addition an independent Quality Control standard is used as calibration check and to check for instrumentation drift. The measurement of lead in solution is covered by UK NAMAS accreditation.

For sampling, the main quality check is on the volume of air sampled. All measurements are checked to ensure the flow rate hence volume sampled remains within specified limits (5.4-7.1 m^3 per day). When the flow rate falls outside of these limits, this indicates a fault with the sampling apparatus and the measurements are rejected.

3.1.3.2. Lead in dustfall

In chapter 1 a description of the current situation of the measurement of lead deposition is given in respect to the comparison of the concentrations contemplated in current legislation and the actual concentrations measured. Also, a first idea is given about the locations where the measurement is carried out and about some existing networks. Almost all the concentration values shown correspond to intensive measurement campaigns near to industries or industrial centres liable to give high concentrations of lead in the soil.

This section complements the information already given on this matter. On a general level it highlights the difference between the techniques of concentration evaluation used in the different countries.

Austria: Lead in dustfall is monitored in Austria by the Bergerhoff-method. Lead is analysed by AAS and ICP.

Belgium: The following information is for the measuring points in Flanders:

· Urban and suburban zone: 5 measuring points, of which 3 situated in 2 agglomerations with more than 250,000 inhabitants and 2 in smaller cities.

- Rural zone: 1 measuring point.
- Industrial zone: 28 measuring points (of which 16 measuring points monitoring Union Minière in Hoboken near Antwerp: the factory is situated about 8.7 km from the center of Antwerp).

The Wallonian deposition measurement network at this moment counts 130 stations divided into 20 groups. A group corresponds to a small zone of a few kilometers and generally to the same type of sources. Groups represent 2 to 12 points of measurement. Discussions are going on about the necessity to increase the minimal number of measuring points from 2 to 4. The median of yearly averages is taken into account for each group. The hereby reached value is compared to the German standard (*TA luft, 1986*), being 250 µg/m^2/day. Lead is not measured any more for groups which were showing low values continually.

The last few years, there have not been observed any exceedances of the German standard for Pb. The present groups where lead is being measured are the following (8 groups, 45 stations):

Group	Stations
Nameche (ANDENNE):	10
Sclaigneau Nlvoye (ANDENNE):	4
Vaulx (TOURNAI):	8
ATH:	2
ENGIS - LES AWIRS:	12
JEMELLE:	2
FARCIENNES:	4
TILLY:	3

There are no measuring points in the region of Brussels for lead in deposition.

Deposited dust is sampled in NILU gauges, which contain a half litre of water. Sampling and analysis is done on a monthly basis. Analysis is done with AAS. In the Flemish region a sampling strategy has been retained in the legislation.

Finland: Two methods are used:

- Four bulk samples per month are collected. The collectors are changed on the 1,8,15 and 22 of the month. The samples are analysed by AAS/graphite furnace in 1993 and by ICP-MS in 1994.
- Bulk samples of one month are collected. The collectors are treated with acid. The samples are analysed by AAS/graphite furnace in 1993 and by ICP-MS in 1994.

Germany: Lead in dustfall is sampled monthly by the Bergerhoff method (VDI 2119 B1.2E) and analyzed, after digestion, with AAS (VDI 2267 B1.4). The gauges are arranged in a regular grid with distances of 0.5, 1 or 2 km, depending on the pollution burden. Taking two German Länder as examples, an area of more than 500 km^2 was monitored in recent years in Northrhine-Westphalia, whereas in Baden-Württemberg deposition measurements were carried out at more than 2000 locations.

Luxembourg: Bergerhoff method (standard method). They use glass buckets required by the VDI guideline (VDI 2119, Blatt 2) placed at height of 150 cm to collect dustfall. Heavy metals as lead are determined by Atomic Absorption Spectrometry.

Spain: Lead deposition is sampled with British standard gauges (1 month).

The entire solution is filtered (with Whatman 41 filters). Analysis of soluble and insoluble fraction are ran separately. The filter is digested with diluted HNO_3/HCl (3:1) by ultrasonication at 80ºC and is analyzed by AAS. Soluble fraction contains less than 1% of the total lead.

Sweden: Bulk samplers. Analytical method: ICP-MS. Detection limit: 1 ng/l.

3.1.4. Other assessment methods

From the information available to the Working Group it is inferred that modelling is not used in any of the Member States for the evaluation of lead concentration in suspension or deposition. This technique is not used in Germany, where the Technical Instructions on Air Quality Control (*TA Luft, 1986*) defines computation method for modelling immission, but it is only used in connection with licensing installations, and in the United Kingdom they have studies (*LDA, 1995*) in which specific campaigns were carried out with dispersion models near to smelters in order to check the concentration of estimated immissions of Lead, Zinc and SO_2 as well as the points of maximum collection.

Information was also available from some countries in which studies had been carried out in order to learn about and categorise the deposition values of some heavy metals, amongst them lead, using biomonitoring of mosses (*Nord, 1994* and *Hämekoski, 1995*). In Finland, moss analyses have been used in assessing atmospheric heavy metal deposition, the results of the study indicate elevated lead values in moss samples in relation to background values in the area around Pori-Harjavalta smelters.

3.1.4.1. Air quality modelling

Other techniques to assess ambient air quality, particularly mathematical modelling and objective assessment methods, can be used alone or in complement to measurement techniques to assess air quality according to article 4.3 of the European Directive 96/62/EC (*CEC, 1996*).

Due to the difficulty in describing local circulation systems and turbulent processes in urban areas, air quality management can not be developed on the basis of routinely monitoring networks alone. Air pollution models are required for quantifying the exposure to air pollutants on sensitive targets. The best assessments of air quality is obtained by combining measurements and modelling results.

Model evaluation should be considered as an indispensable part of model development and use. The validity of the modelling results depends on the accuracy of the input data as well as on model performance.

The quality of an air pollution model can be judged in terms of: (1) model consistency (the way in which ‘reality’ is reflected in the simulation results) and (2) model accuracy (which can be estimated in the course of an appropriate model evaluation procedure). Quality criteria for air pollution models have to focus on a well-documented description of the model itself and on the procedure used for model evaluation.

In the particular case of lead modelling, two elements of complexity are added: (1) the dispersion and transport modelling of atmospheric suspended particles is more complex due their granulometric distribution; and (2) the content of lead in the different particles fractions.

Due to the change in the main lead emissions source, from the traffic to the lead industry the models to be considered in the lead case will be dispersion models for fixed point sources considering the temporal aspects as short term and long term, the spatial scale, the terrain complexity and the particular characteristics of this emission source.

3.1.4.2. Estimations based on moss analysis

The report *Atmospheric Heavy Metal Deposition in Europe-estimation based on moss analysis* (*Nord, 1994*) presents a joint moss-survey of Europe made in 1990-1992 with samples from 20 countries. The objectives of the project were to characterize qualitatively and quantitatively the regional atmospheric deposition pattern of arsenic, cadmium, chromium, copper, iron, lead, nickel, vanadium and zinc in background areas in Europe, to indicate the location of important heavy metal pollution sources and to allow retrospective comparisons with similar studies.

The moss technique is based on the fact that mosses, specially the carpet-forming species, obtain most of their supply of chemical substances directly from precipitation and from the impaction and sedimentation of airborne particulates, and in consequence the concentrations of heavy metals in moss are closely correlated to atmospheric deposition.

A summary of the results regarding lead can be seen as follows:

Table 3.5: Number of samples analyses, minimum, maximum, mean and median concentration of lead (µg/g).

Country	No. of samples	Minimum	Maximum	Mean	Median
Austria	38	3.1	33.1	16.4	15.8
Czech Republic	33	9.0	60.0	19.1	16.0
Denmark	76	5.7	61.3	12.1	10.6
Estonia	74	8.4	25.6	14.1	13.2
Finland	821	1.7	31.8	10.7	9.9
Germany	582	5.1	80.5	14.6	12.9
Great Britain	275	0.3	228.0	10.8	6.4
Italy	23	3.5	33.5	16.5	13.9
Latvia	81	5.9	24.8	11.7	11.1
Lithuania	144	0.4	85.0	9.5	7.6
The Netherlands	76	6.9	40.0	15.2	14.0
Norway	505	1.5	78.9	14.0	9.2
Poland	147	8.0	269.0	30.0	21.5
Portugal	179	0.5	173.0	17.4	14.0
Romania	56	9.3	150.0	40.9	35.1
Russia	203	0.2	180.0	10.5	3.4
Slovakia	58	4.7	359.0	60.5	40.8
Spain	12	10.0	84.3	25.1	20.0
Sweden	906	1.9	66.5	13.0	11.3
Switzerland	232	4.2	142.0	18.3	13.6

Source: Nord (1994).

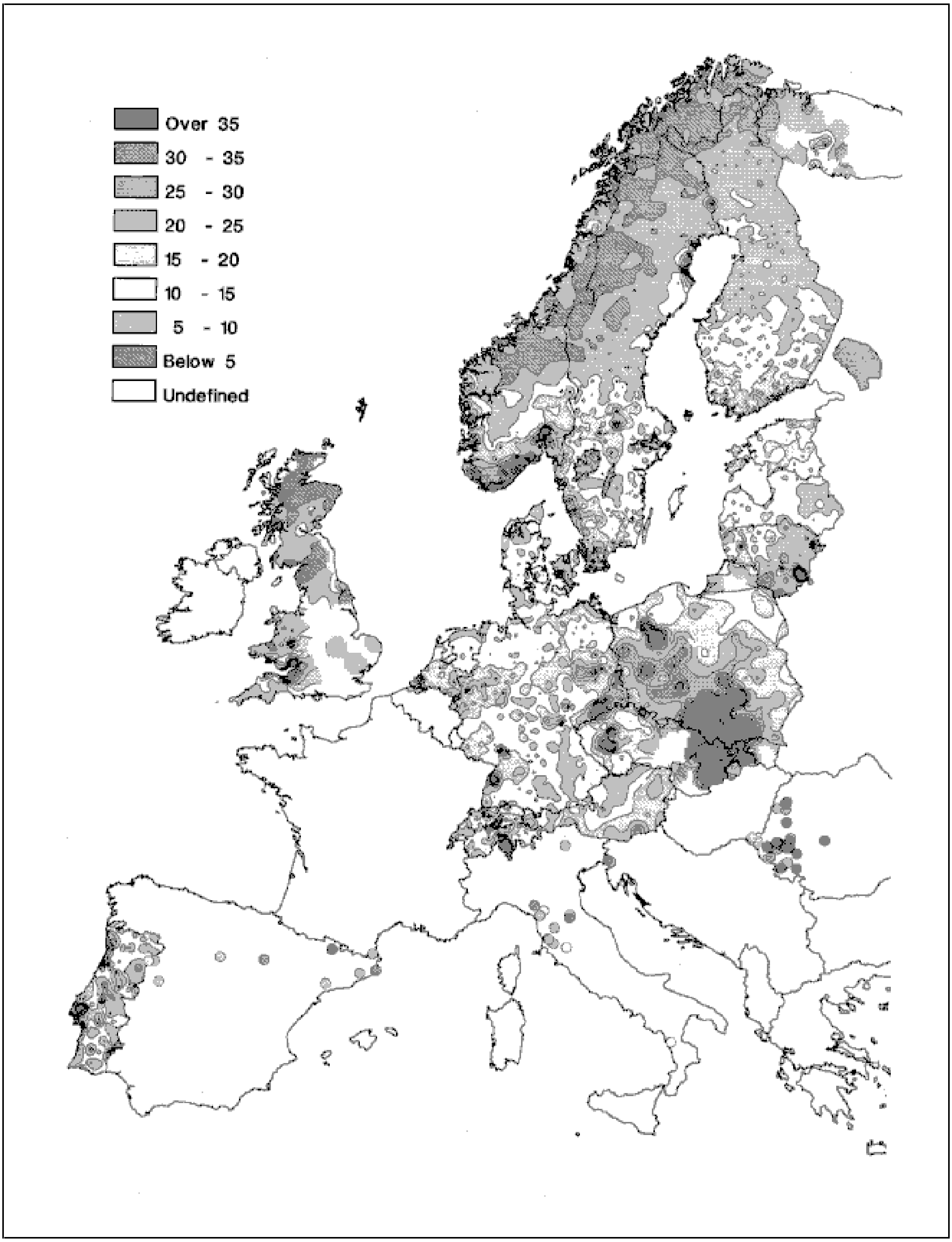

Table 3.6: Contour map of lead concentrations in moss (µg/g).

Source: Nord (1994).

3.2. Reference Measurement Method

3.2.1. Considerations from Directive 82/884/EEC

The current European Directive regarding air quality and lead requires control of human exposure to the lead contained in the atmosphere and ensures that Member States take appropriate measures to guarantee that the levels of lead in the atmosphere do not exceed the limit value.

This will guarantee that measuring stations will be installed and will operate within the territory of Member States to allow verification of compliance with this limit.

The annex of the Directive details guidelines that must be followed in choosing sampling and reference methods for analyzing lead concentrations in the atmosphere.

Rules to be followed in sampling are:

- The filter must collect no less than 99% of all particles with an average aerodynamic diameter of 0.3 µm.
- Sampling efficiency is defined as the relation between the mass concentration of particles in the air collected in the filter and the concentration in the atmosphere. Minimum permissible sampling effectiveness is indicated in the following table:

Table 3.7: Minimum sampling effectiveness as per Directive 82/884/EEC.

Wind speed (m/s)	Aerodynamic diameter of particles	
	5 µm	10 µm
2	95 %	65 %
4	95 %	60 %
6	85 %	40 %

- The aspiration flow rate of sampling must be constant, with a tolerance equal to ±5% of the nominal value throughout a sampling period.
- Sampling sites must be representative of the area in which measurements will be taken.
- Sampling must be continuous. Annual average calculations are only valid if sampling is done for at least 15 working days per month.

Reference method of analysis:

- The reference analysis method consists of atomic absorption spectrometry. Analytical error for determining lead in the particles collected must be less than the value corresponding to an atmospheric concentration of 0.1 µg/m^3 (5% of the 2 µg/m^3 limit value).
- Mention was made of the need to maintain appropriate calibration frequency in order to keep the analytical error within the specified limits.

3.2.2. Measurement method

The measurement of lead can be divided in three separate steps:

- The sampling method.
- The measurement or analysis method.
- The calibration method (when the analysis method is not absolute).

The following tables gives the most current used methods and their main advantages and disadvantages.

Table 3.8: Suspended lead sampling methods.

Methods	Description	Reference	Advantages/Disadvantages
1. WRAC	Wide range aerosol classifier: high volume impactor (100 m^3/h)	CEN	+ excellent classification efficiency - cumbersome and not practicable (only 3 instruments in EU)
2. High volume sampler	Impactor or cyclone sampling head (typically 68 m^3/h)	CEN	+ good classification efficiency - expensive, noisy, indicated for manual and discontinuous operation
3. Medium volume sampler	Impactor or cyclone sampling head (typically 6.8 m^3/h)	---	+ cost effective, indicated for manual or automated network operation
4. Low volume sampler	Impactor or cyclone sampling head (from 1 to 3 m^3/h)	CEN	+ cost effective, indicated for network operation - low collection rate

Source: CEN standard procedure to test equivalence of PM_{10} samplers (document in preparation).

Table 3.9: Lead analysis methods.

Methods	Description	Reference	Advantages/Disadvantages
1. Atomic Absorption Spectrometry (AAS)	Particulate material collected on a filter is digested with acid. The sample solution is analysed by atomic absorption spectrometry	ISO 9855 VDI 2267 Bl.3 EPA*	+ commonly used method, high sensitivity - expensive analyzer
2. Inductively Coupled Plasma (ICP)	Particulate material collected on a filter is digested with acid. The sample solution is analysed by inductively coupled plasma emission spectroscopy	VDI 2267 Bl.5	+ multi element detection possible, high sensitivity - expensive analyzer
3. X-Ray Fluorescence (XRF)	A part of a filter is irradiated with X-rays. Measurement of the emitted X-ray fluorescence	VDI 2267 Bl.2	+ no sample pre-treatment, multi element detection possible - low sensitivity, expensive analyzer
4. Spectrophotometry	Particulate material collected on a filter is digested with acid. A reagent is added to the sample solution and a light absorption can be measured by spectrophotometry	---	+ cost effective - very low sensitivity

*EPA (40 Code of Federal Regulations no. 4, Appendix G)

Table 3.10: Lead calibration methods.

Methods	Description	Reference	Advantages/Disadvantages
1. Lead standard solution	Dilution of a lead standard solution covering the expected concentration range	ISO 9855 (E)	+ easy, cost effective, commercially available
2. Preparation of loaded filters with lead standard solution	Lead solution is carefully dropped on a filter	VDI 2267	+ cost effective, indicated for X-ray fluorescence, cross-check with AAS
3. Preparation of loaded filters with lead salt aerosols	Generating of lead salt aerosol + loading of a filter with this aerosol	---	+ indicated for X-ray fluorescence, cross-check with AAS - aerosol generating

The characteristics of the current method described in Directive 82/884/EEC (see Table 3.7) are very similar to the definition of PM_{10} sampling procedure (sampling efficiency of 50% of particulate matter of 10 µm). For the scope of harmonisation of the lead sampling method with the Daughter Directive for fine particulate matter, it is therefore proposed to select the PM_{10} sampling procedure also for lead.

The reference method of the current Directive is the Atomic Absorption Spectrometry. The calibration of the AAS spectrometer is performed by lead standard solutions. Measurements and calibration method are standarized by ISO 9855 norm. The group has no evidences to think that the current reference method of analysis is not still valid. However, others methods which equivalence can be proved are also allowed.

3.2.3. Dustfall measurement methods

The sample is collected in one of the sedimentable dust collectors described in Table 3.11 below, and probably the NILU gauge should be chosen as a reference method.

Table 3.11: Lead dustfall sampling methods.

Methods	Description	Reference	Advantages/Disadvantages
1. Bergerhoff gauge	Cylindrical pot (Ø 10 cm, height 20 cm) out of glass or plastic	VDI 2119 Bl.2 E	+ cost effective - low collection rate
2. French standard deposit gauge (Horizontal deposit gauge)	Cylindrical pot (Ø 20 cm, height 40 cm)	NF X43-006 ISO-DIS 4222.2	
3. Owen gauge	Funnel (Ø≈20 cm,section 400 cm^2) + collecting bottle	---	
4. British standard deposit gauge	Glass or plastic funnel (Ø 30 cm, height 10 cm) + collecting bottle	---	
5. NILU gauge	Cylindrical plastic pot (Ø 35 cm, height 50 cm), filled with sufficient water to avoid dust losses	EMEP	+ dust prevented from blowing out + high collection rate

After acid digestion of the collected residue, the amount of lead is determined with one of the analytical techniques already described. Although this document describes the use of a variety of techniques used in different countries (as stated in section 3.1.3.2) and even ICP-MS, It would appear that AAS is the most widely used and the most recommendable method.

3.3. Assessment method

Article 6 of the Directive on Ambient Air Quality Assessment and Management (*CEC, 1996*) envisages various possibilities in measurements to be taken in order to carry out the assessment of air quality, once the corresponding limit values have been set. Thus, four cases are defined by delimiting them according to thresholds, and two percentages of the limit value (called *x*% and *y*%) are established as illustrated in the Figure 3.1.

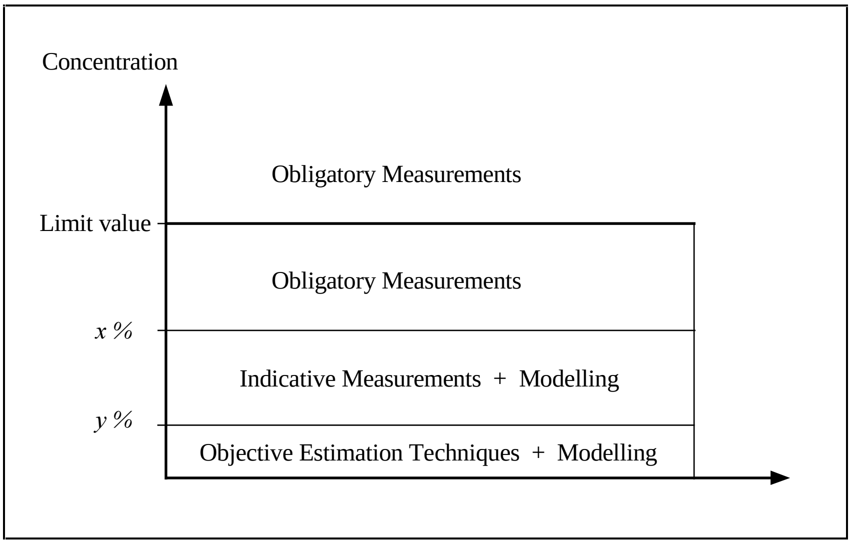

Figure 3.1: Measurements used to assess ambient air quality.

Mandatory measurements must be taken in agglomerations (defined as areas characterized by a population of more than 250,000 inhabitants or, when the population is less than or equal to 250,000, areas with a population density of inhabitants per km^2 that justifies the Member States' evaluating and controlling the air quality) and areas where the limit is exceeded or where the concentration of the pollutant is above the *x*%. For areas of concentration found between values *x*% and *y*%, these measurements may be substituted by modelling and indicative measurements. Below the value of *y*%, measurements only need be taken using modelling or objective estimations.

It was suggested that this value should be based on interannual variability and the accuracy of assessment systems.

Possible values for the constants *x*% and *y*% are presented in Table 3.12. While *x*% was accorded the value of 70, there were differences of opinion regarding the *y*%, with the most reasonable values being between 20 and 50. The proposal is given in Table 3.12 (the column of concentration is calculated with respect to a limit value of 0.5 µg/m^3.

Table 3.12: *x*% and *y*% values.

	Proposal %	Concentration µg/m^3
x	70	0.35
y	20 - 50	0.10 - 0.25

The Working Group has accepted the way in which the two levels have to be calculated, according to the methodology followed for the Daughter Directive on particulate matter. The interannual variability for x, and the accuracy of the assessment systems for y.

3.4. Data quality objectives

Depending on the assessment method that is to be implemented, data quality objectives must be established in order to comply with the monitoring objectives. They will be defined in terms of required precision and accuracy, minimum time coverage and minimum data capture.

Required precision and accuracy (expressed as maximum uncertainty):

- Continuous measurements (24h samples): 25% (target value for individual measurements)
- Indicative measurements: 50% (target value for individual measurements)
- Modelling: 50% (for yearly averages)
- Objective estimation: 100%

Minimum time coverage of the measurements:

- Continuous sampling: 100%
- Indicative sampling: 20% (every fifth day, or 10 weeks evenly distributed over the year, or at random throghout the year)

Minimum data capture:

- Continuous measurements: 90% (breakdown allowed for 36 days per year)
- Indicative measurements: 90% (breakdown allowed during 10% of the time)

Table 3.13: Data quality objectives.

Case	Technique	Time coverage	Uncertainty
1. Agglomerations and areas above *x*% of the limit value	Continuous measurements PM_{10} Supplementary modelling recommended	100 %	25 %
2. Between *x*% and *y*% of the limit value	Indicative measurements + Modelling	20 %	50 %
3. Below *y*% of the limit value	Objective estimations + Modelling	---	100 %

3.5. Quality Assurance and Quality Control of measurements

Quality assurance is a system of procedures that ensures that:

- Measurements are precise and accurate.
- Results are comparable and traceable.
- Data are representative of ambient conditions.
- Optimal use is made of resources.

The major constituents of a quality assurance programme concern:

- Network design: number of stations, siting criteria.
- Measurement technique: sampling, analytical and calibration procedure.
- Equipment evaluation and selection: validation of methods, test of instrument performances.
- Routine site operation: calibration in field conditions, maintenance, management and training.

QA/QC procedures are described in the WHO UNEP GEMS/AIR Methodology Review Handbook Series, UNEP/WHO (1994a) and UNEP/WHO (1994b).

Currently QA/QC programmes only exist in a few monitoring networks of the EU Member States and with a variable degree of efficiency. With the increase of the monitoring networks foreseen with the implementation of the framework Directive, it is expected that a lot of new laboratories, with among them a great number of private companies, will be in charge of the monitoring task. This will require particular measures to assure the quality of the measurements and the capability of the laboratories:

- Accreditation of laboratories: different standarized QA/QC systems have been developed in recent years such as the Good Laboratory Practice (OECD), the ISO 9000 and the EN 45000 laboratory accreditation procedures. The EN 45001 procedure was developed by CEN in collaboration with the Commission and is best adapted for testing laboratories in the field of air pollution measurements. Laboratories asking for accreditation are audited by a national or international accreditation organization. This audit mainly concerns aspects such as laboratory installation and equipment, qualification and training of personnel, proper quality control, technical audit and traceability of the measurements.

The request for laboratory accreditation is the only enforceable way to ensure an effective QA/QC procedure.

- Validation of the measurement methods and standarization at CEN or ISO level.
- Certification of equipment: test of instrument performances (the development of a standarized CEN test procedure is therefore urgently needed).
- Organization of intercomparison at EU level: organization by the Commission of EU wide intercomparison exercises (round robin tests, inter-laboratory exercises, spot checks in the monitoring network) to ensure comparability of the measurements at international level.
- Publication by the Commission of guidance documents, organization of trainings and workshops.

The Group recommends that laboratories involved in monitoring and analysis should be accredited in accordance with the procedures of EN 45001.

3.6. Network design

When the minimum number of sampling points in each of the zones is indicated, two cases are considered:

- The case where measurements are the only source of information (without assessment), the number is related to n_i.
- The case where measurements are supported by other techniques (with full assessment), and the number is related to n_0.

n_0 is the number below which the number of measurements stations may not be reduced. The actual number of measurement stations may be greater than n_0.

3.6.1. Measurements of lead in urban sites

The sampling strategy of lead in urban environments is dictated by the characteristics of this pollutant which is primarily contained in the particulate matter. The sampling strategy encompasses selection of representative sites, choice of devices for sampling and choice of the method to assure preservation of the sample integrity. The determination of airborne lead in urban sites is strictly linked to the determination of PM_{10}. In this regard, it is known that the collection characteristics of high volume samplers are strongly affected by wind speed, wind direction and inlet size. However, since most lead particles have a mass median aerodynamic diameter in the range of 0.25-1.4 μm, the PM_{10} samples should represent reasonably good estimates of ambient lead.

The number of the sampling stations should depend on population density, structure of the residential areas, presence of specific pollutant sources, orographic and meteorological situation and the number of inhabitants.

Measurements are obligatory according to the Directive (96/62/EEC):

- In zones where levels exceed x% or y% of the limit value. In this type of zones at least one station per zone is needed.
- In agglomerations with more than 250,000 inhabitants. In this type of zones the minimum number of stations is as described in Table 3.14.

  Table 3.14 shows the minimum number of stations to be considered in designing the system, according to the number of inhabitants. Both cases provided in the Directive are differentiated: (1) with assessment, when a good information is available (monitoring is supported by other techniques). And (2) without assessment, when there are no information in the zone (sole tools is monitoring). In cases of increases in these quantities, the number of stations will increase according to the number of inhabitants in excess of the quantities in the table).

Table 3.14: Minimum number of stations in urban sites.

Population	Minimum number of stations	
	Without assessment (n_i)	With full assessment (n_0)
250,000	2	2
+ 250,000 (incr.)	+ 1	---
1,500,000	7	2
+ 500,000 (incr.)	+ 1	---

The minimum number of stations should be n_i where no information is available and may be lower than n_i where justified on the basis of supporting information, but never lower than n_0 (even in the simplest case).

3.6.1.1. Location of the stations

For the case of n_0, the location of the sampling points, should be in heavy traffic streets where people spend a significant amount of time.

And for the case of n_i, the structure of urban sampling sites should be planned on the basis of monitoring stations of 4 categories (A to D).

The characteristics of the defined sampling stations are:

Category A: Sampling stations located in urban areas not directly affected by urban emissions (e.g. parks, traffic restricted areas).

Category B: Sampling stations located in areas characterized by high population density (residential area).

Category C: Sampling stations located in areas characterized by high traffic. The concentration values measured in these sampling stations can be associated in a spatial scale of representativeness to a microscale level (i.e. limited to a range of few meters from the source).

Category D: Sampling stations located in suburban or rural areas.

While in the case of industrial sites the location of the samplers should be based on prevailing winds and on dispersion modelling predictions, in urban sites priority should be given to stations of category C, followed by B and followed by A. Table 3.15 presents the station categories and the typical site classified by its priority:

Table 3.15: Stations type in urban sites.

Station Type	Site
C	Heavy traffic (kerbside)
B	Residential
A	Urban parks
D	Outskirts (rural)

At least, measurements of lead in one station o category C should be recommended for a large city. In consideration of the fact that pollution due to lead should behave as a total suspended particulate matter or as PM_{10} and that the concentration of these species are strongly related to atmospheric stability conditions, the results from sampling stations of category A and B will be used, in combination with the meteorological data to the assessment of the general levels in a city. The measurements in the sampling station of category C will be used at the level of neighbourhood scale for the assessment of lead exposure in conditions of high traffic and pollution density.

With respect to the siting of monitors for lead, valid criteria should be established in connection with the other monitoring activities. In consideration of the fact that in urban areas (in particular in urban areas of the category C) distance from the source whether vertical or horizontal, can be the primary determining factor for changes in air lead concentration, standards for elevation of the monitoring above ground level, setback from roadways, and setback from obstacles should also be established.

3.6.2. Measuring strategy of lead in suspended dust near industrial sites

3.6.2.1. Introduction

The Directive on Ambient Air Quality Assessment and Management (96/62/EEC) requires measurement in zones where concentrations are high. Industrial throughput provides an indication of likely concentrations. Monitoring may be indicated where factories have an estimated and controlled high emission of lead (an emission through stacks).

Important stock-piles of raw ore or raw material with a high lead content, or process related emissions at low height, that can give rise to lead emissions (fugitive emissions) may also indicate a need for monitoring.

A description of a general measuring network design to determine the lead concentrations in suspended dust near industrial sites is given. In absence of measured data of the lead concentration, a description is given for a preliminary investigation to determine the necessity of the installation of the network. Also a yearly evaluation of the network is given.

Figure 3.3 shows the flow chart resultant in the application of the proposed strategy.

3.6.2.2. Development of a measuring network to determine lead in suspended dust

A general strategy is proposed for a network design around important industrial installations. However in all cases the distances of the sampling stations with the border of the installation of their exact location may be modified taking into account:

- The exact location of the sources in the installation.

- The distances where the maximum impact of the emission of the installation on the yearly average ambient air concentration in the neighbourhood of the installation can be expected (see Table 3.16 as an example for stack emissions).
- The places where people are living.
- The meteorological characteristics (e.g. mean wind rose) of the area.
- The topographical characteristics

Table 3.16: Maximum impact of the emissions of an industrial installation.

Chimney height (m)*	Nearest distance (m)	Farthest distance (m)
10	10	80
20	25	200
30	50	350
40	70	550
50	100	750
60	125	1000
70	150	1200
80	180	1400
90	220	1700
100	250	2000
150	450	3500
200	700	5000

[*] Chimney height is the effective height.

In all cases, the diagrams established are presented in Figure 3.2, and the values for variables *a*, *b* and *c* are found in Table 3.17.

(a) Point sources < 30 m or surface sources:

If there are only point sources with an altitude of < 30 m or surface sources:

- Four sampling stations are placed around the installation with mutual differing angles of 90° and a distance of 50 m from the border of the installation. If in a certain direction nobody is living at a distance less than 100 m of the place where the station should be installed, the station can be omitted. However at least one station should remain installed.
- A fifth station is placed along the axis of the most important source of lead or the centre of the factory with one of the above mentioned stations, namely the one where the highest yearly average ambient air concentration is to be expected, at a distance of 200 m from the border of the installation. In cases where the mean wind rose has a dominant wind direction, this axis will be equal to the predominant wind direction.

(b) Point sources > 30 m:

If there are only point sources with an altitude of > 30 m:

- Four sampling stations are placed around the installation with mutual differing angles of 90º and a distance of 200 m from the border of the installation. If in a certain direction nobody is living at a distance less than 100 m of the place where the station should be installed, the station can be omitted. However at least one station should remain installed.
- A fifth station is placed along the axis of the most important source of lead or the centre of the factory with one of the above mentioned stations, namely the one where the highest year average ambient air concentration is to be expected, at a distance of 1000 m from the border of the installation. In cases where the mean wind rose has a dominant wind direction, this axis will be equal to the predominant wind direction.

(c) Point sources > 30 m and point sources < 30 m or surface sources:

If there are point sources with an altitude of > 30 m and point sources with an altitude < 30 m or surface sources:

- Four sampling stations are placed around the installation with mutual differing angles of 90º and a distance of 50 m from the border of the installation. If in a certain direction nobody is living at a distance less than 100 m of the place where the station should be installed, the station can be omitted. However at least one station should remain installed.
- A fifth and a sixth station is placed along the axis of the most important source of lead or centre of the factory with one of the above mentioned stations, namely the one where the highest yearly average ambient air concentration is to be expected, at a distance of 200 m and 1000 m from the border of the installation. In cases where the mean wind rose has a dominant wind direction, this axis will be equal to the predominant wind direction.

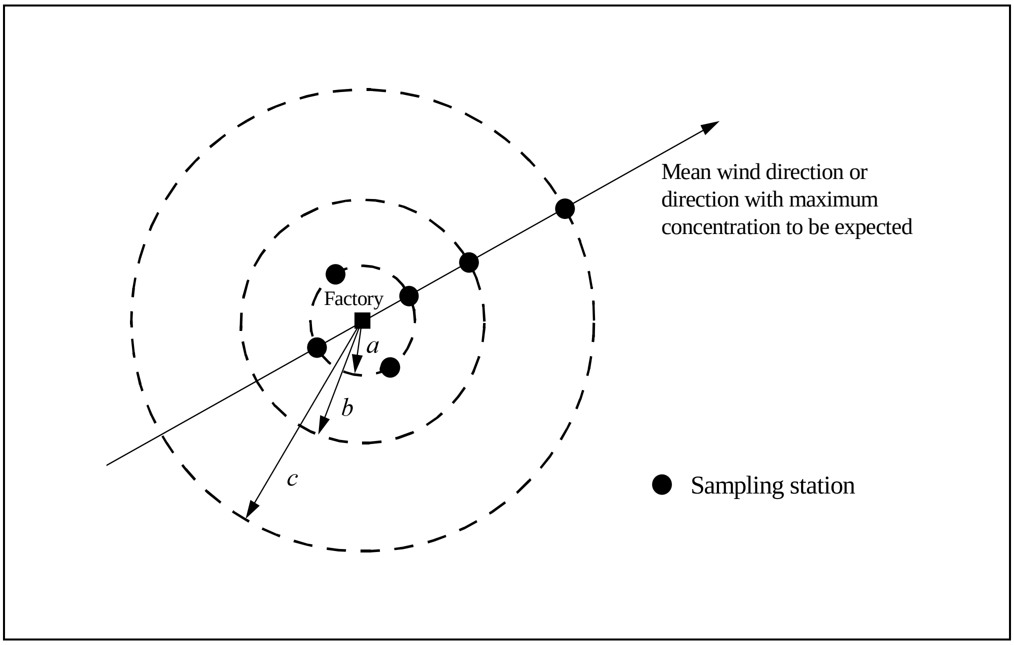

Figure 3.2: Measuring strategy of lead near industrial sites.

Table 3.17: Distances for siting the stations near industrial sites.

Case	*a*	*b*	*c*
Point sources < 30 m or surface source	50 m	200 m	---
Point sources > 30 m	200 m	1000 m	---
Point sources > 30 m and point sources < 30 m or surface sources	50 m	200 m	1000 m

3.6.2.3. Preliminary Investigation

In absence of measured data a preliminary investigation is to be done.

Three cases can be distinguished:

(a) Surface sources or equivalent (fugitive emissions)

A measurement station should be installed under the dominant wind direction on a distance, related to the border of the facility, of five times the height of the constructional obstacle located inside this border. If required, e.g. nearer buildings, the mentioned distance may be consequently adapted. The distance from the border of the facility may be lower if people are leaving nearer to the facility and higher concentrations are expected near the place where they are living.

At this station, according a code of good practice, a 24-hours mean value of PM_{10} should be taken and the lead content measured to obtain the lead concentration ($\mu g/m^3$). The yearly average of those measurements is i_{Pb}.

(b) Point sources only (controlled emissions)

At least 80% of the totality of the yearly lead emissions should be inventorised on a measurement basis and/or on a calculation basis (e.g. emission factors). The ambient air concentration should be calculated by a recognized dispersion model. If several sources are present the different concentrations obtained by the dispersion model should be added together, in the case the model takes only in account one source. The obtained result is i_{Pb}.

(c) Both point sources and surfaces sources

If these types of sources are simultaneously present at the facility, the concentrations should be determined as stated in paragraphs *a)* and *b)*. The highest of both values is the representative ambient air concentration.

Measurement programme:

- $i_{Pb} \leq y/2$: no measurement or estimation has to be done.
- $y/2 < i_{Pb} \leq y$: no measurement has to be done, lead concentrations may be assessed by objective estimation techniques and modelling.
- $y < i_{Pb} \leq x$: no complete network has to be installed, indicative measurements should be combined by modelling, to obtain the lead concentrations.
- $x < i_{Pb} \leq LV$ (air quality limit value) : a network of three to four stations has to be installed. In this case the four sampling stations placed around the installation, with mutual

differing angles of 90° can be reduced by two sampling stations placed around the installation with a mutual differing angle of 90 to 180°.

- $LV < i_{Pb}$: a complete measurement network should be installed. Measures should be taken to reduce the air pollution.

No measurements or estimation should be done in the case $i_{Pb} < y/2$ and the same management remains on the facilities. In the latter case and if the management is significantly changed, with as consequence an important increase of the lead emissions, the preliminary investigation should be done again.

3.6.2.4. Yearly evaluation of the network

A yearly evaluation of the network should be done. The first time it should be done in the basis of data from the most recent three years of measurements.

An evaluation is done based on i'_{Pb}. The value of i'_{Pb} is taken as the highest measured or calculated yearly average value, chosen from all the measured or calculated values of the last three year period.

- $i'_{Pb} \leq y/2$: the measurement or estimation programme can be stopped.
- $y/2 < i'_{Pb} \leq y$: the measurement can be replaced by objective estimation techniques and modelling.
- $y < i'_{Pb} \leq x$: the measurements can be replaced by indicative measurements and modelling.
- $x < i'_{Pb} \leq LV$ (air quality limit value) : a network of three to four stations has to be installed or has to be retained in duty. In this case the four sampling stations placed around the installation, with mutual differing angles of 90° can be reduced by two sampling stations placed around the installation with a mutual differing angle of 90 to 180°.
- $LV < i'_{Pb}$: a complete measurement network should be installed or should remain in duty. Measures should be taken to improve the air quality.

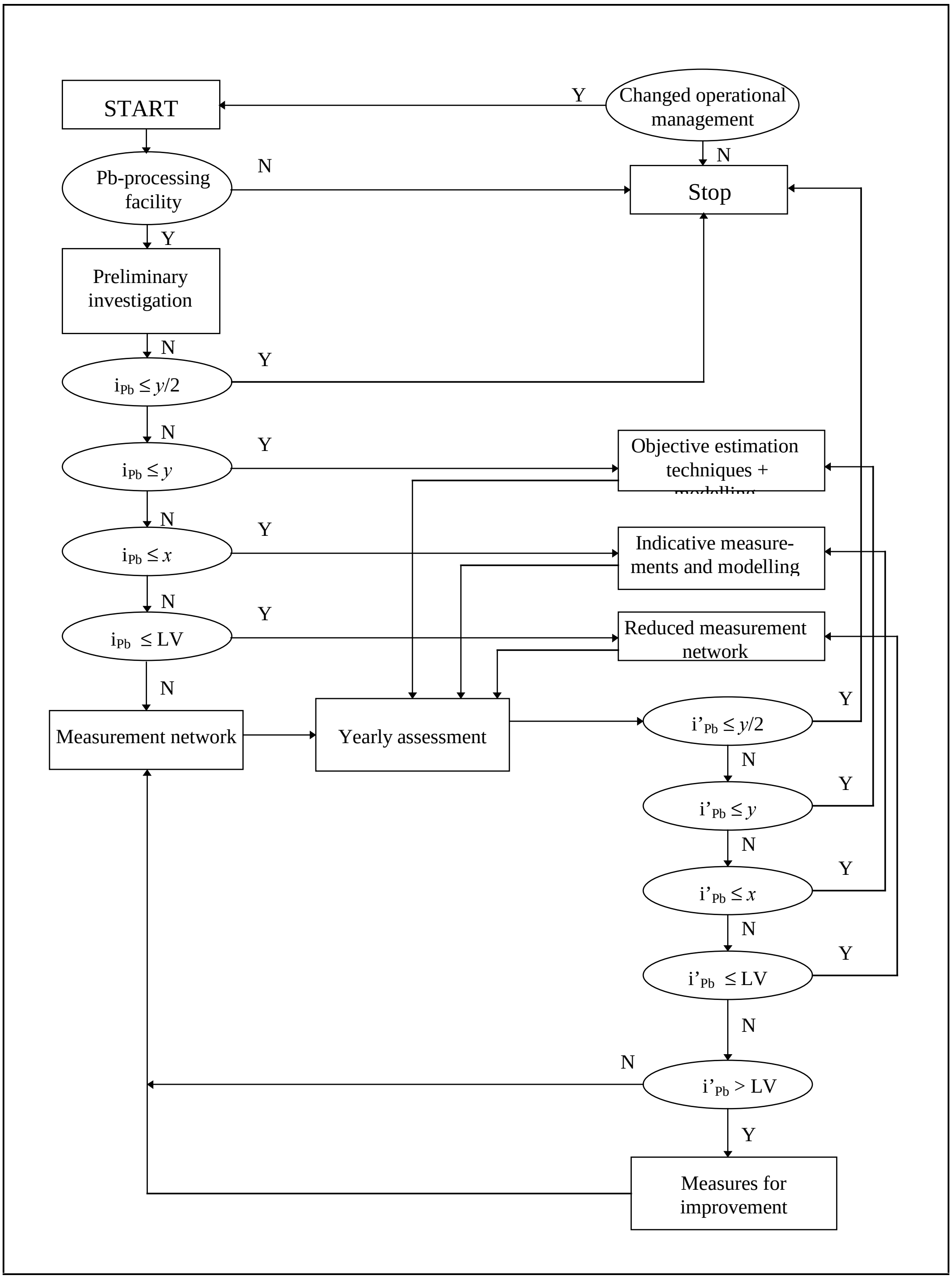

Figure 3.3: Measurement strategy for lead in suspended particles near lead processing industrial sites - proposed flow chart.

3.6.3. Utilization of mathematical models in monitoring network design

Results of mathematical model simulations can be used to predict pollutant dispersion or deposition patterns, and thus help in site selection or monitoring station, complementary to measurement to assess ambient air quality.

When these techniques are used in complement to measurement strategy, the number of monitoring stations may be reduced; and also used to define their location.

Specially, to take in consideration, for site selection, the following factors:

- Monitoring objectives.
- Sources and emissions in area.
- Meteorology and topography.
- Existing air quality data (background level).
- Demographic/health/land use data.

Modelling can be used to assess patterns as an aid to network design and to estimate concentrations in zones without measurement stations; as an exploratory assessments, in absence other kind of measures; and as an essential tool for related air quality concentration to emission sources and sectors as input information for exploring and planning solutions, and predicting the result of action plans.

4. COST IMPLICATIONS

In Chapter 1, the automobile and industrial sectors are identified as prime sectors contributing to the current measured levels of lead. In accordance with this information, and taking into account the identification of receptors exposed to impact by the pollutant offered in Chapter 2, identification has been made of the benefits that would be achieved in complying with the recommendations, and the costs due to lack of action, in accordance with the current trend that measured concentrations are following. This identification must lead to recommendations regarding the final deadline for compliance with limit values and regarding recommendations for the permitted margin of exceedance.

Table 4.1 shows a summary of the qualitative factors identified by the group.

Table 4.1: Qualitative identification of factors on cost-benefit implications.

BENEFITS:

- Emissions reduction.
- Better human health conditions, specially for children (better air quality).
- Increase of environmental quality (better air quality).
- Increase of material welfare (better air quality, indirect benefit, through reduction of the particle load).
- Better data and information (monitoring).
- Social-economic welfare (cleaner industry).
- Environmental industry development (need for equipment).

COSTS:

- Increase the industry costs (investment and operation):
  - Adopted control air pollution equipment:
    - focal point emissions from primary and secondary smelter/batteries/...
    - fugitive emissions.
  - Adopted analysis measures.
  - Adopted good practices for a better environmental management (training, procedures, etc.).
- Increase the public monitoring costs.

As an example of the amount of children at risk, living near an industrial plant in Hoboken (Belgium), which causes a high amount of lead containing dustfall. About 300 children beneath the age of 12 are living in the neighbourhood of the factory and can be considered as children at risk (*FEA, 1996c*).

4.1. Monitoring costs in the Member States

Belgium: An estimation of the cost of a network heavy metals in suspended dust.

Measuring network of 30 stations distributed over a geographical area of 15,000 km^2. Analytical technique: XRF

• Investment cost (10 years)	
– 30 stations (own development) 2,000 ECU × 30:	60,000 ECU
– XRF + aerosolgenerator:	310,000 ECU

Total: 370,000 ECU or *yearly 37,000 ECU*

If one will be obliged to buy commercial stations (e.g. with PM_{10} head) the investment cost can be much higher.

• Working costs (*yearly cost*) filtermaterial, entretien XRF and sampling stations, electricity sampling (travel costs)	60,000 ECU
• Costs for personnel (*yearly cost*) 1 university degree, 1 ind. eng, 1 laborant	135,000 ECU
Total yearly cost:	232,000 ECU

Note:

1.- The cost estimation does not include general costs as: housing, secretariat, general administration and organization costs, etc.

2.- The applied method gives also the results for several other metals (Cd, Zn, Pb, Cu, As) without extra cost.

3.- The cost estimation is related to the monitoring costs in one region of Belgium. Total cost of the monitoring of heavy metals in suspended dust in Belgium, will be nearly the double.

Source: FEA (1996).

Luxembourg: Current cost of monitoring. One person + equipment: 20,000 ECU.

Spain: In the case of Catalonia there are internal financial studies available which calculate the total cost of the final measurement of suspended lead (corresponding to the 1995 network structure described in chapter 3). This shows a cost of 1680 ptas per final data (11 ECU) for a network with 21 stations measuring continuously and generating a daily average in each one of the stations. The result is a final yearly amount of about 4000 ECU/station (*DMA, 1996*).

Sweden: The current costs for sampling and analyses of heavy metals at the four background stations are about 100,000 SKR (10,000 ECU).

Switzerland: The costs of monitoring are about 5000.- Swiss francs per station.

United Kingdom: The total cost of monitoring lead and other elements in the UK is approximately £100,000 (130,000 ECU).

4.2. Abatement techniques

Emissions reduction measures can be oriented towards process techniques as well as towards off-gas cleaning. In the first case, the generation of dust or gases containing heavy metals is reduced. In the second, the content of heavy metals in an air or gas flow is reduced.

The following major sources can be identified for lead: combustion of leaded gasoline, primary and secondary non-ferrous metal production and the use of products (*UN ECE, 1994*). In the European Union there are 11 primary lead smelters and over 30 secondary lead plants.

4.2.1. Primary non-ferrous metal industry

Production of lead using conventional sintering-smelting-refining technology should in the first step be carried out by sintering in up-draught machines. The sulphur should be fixed in a double contact plant, preceded by thorough dedusting and mercury removal. The shaft furnace has a closed top construction or efficient off-gas hood collection and efficient dust evacuation from tapholes and covered launders. All gases are cleaned in fabric filters to < 5 mg/Nm^3. If softening of the lead bullion is carried out in reverberatory furnaces, the operation should be continuos. Oxygen softening reduces the off-gas generation.

Lead production in some new processes is carried out without sintering of the concentrates. This greatly reduces the risk for fugitive emissions, and represents BAT for the new plants.

4.2.2. Secondary non-ferrous metal industry

The main constituents in scrap to secondary lead smelters are used car and truck batteries. Two different kinds of strategy in process route are available. In one, a distinct separation is done to reuse all of the materials (paste and organics as well as metals) in battery scrap. In the other process route undismantled battery scrap is direct charged in the smelting furnace. Here, the organic content is used as fuel for the melting operation which means less energy demands. On the other hand, these processes demand and afterburning and sometimes an aircooler which result in an extra energy need. In Europe, short rotary furnaces are used for the melting. Raw materials, fluxes and reductants are charged in the furnace and lead bullion is tapped in the end of the cycle. In USA it is common to use a two step furnace treatment to produce lead bullion. BAT should include one melting operation in short rotatory furnace or shaft furnace. For energy input oxy-fuel burners should be used which can reduce waste gas volume and flue dust production by 60%.

4.2.3. Fugitive emissions

Actions to be made to eliminate or reduce fugitive emissions from stock piles, transports, and handling of material giving off dust are discussed as well as ways to minimize uncontrolled escape of dust-laden air from process steps.

The following, and combinations thereof, should be considered as BAT:

- Encapsulation of dust-creating units or use of efficient dust-collecting facilities.
- Storages should be located indoor or covered to avoid wind-blow emissions. Where that is not practicable sprinkling of stockpiles or use of chemicals should be adopted.
- Raw material should be received in sealed containers or in closed vehicles.
- Unloading to stockpiles can be made through chutes equipped with wet suppression system or with dust suction to filter.

- Reclamation or raw materials from stockpiles should be done by closed or enclosed conveyors.
- Roads should be hard-surfaced and properly cleaned.
- A comprehensive system for wheel wash or vacuum cleaning.

4.3. Industrial sector and associated costs

As for point sources in Finland (*MEF, 1995*), heavy metals like lead are generally removed from flue gases primarily by reducing emissions of other components, usually particles. The costs associated with heavy metal emissions have been examined using case studies. Because treatment measures are not generally targeted directly at lead or other heavy metals, the costs associated with these are difficult to assess. The acquisition costs of bag filters, which are almost always able to reduce the overall concentration of the most harmful heavy metals in particulate phase to well below 1 mg/m^3, are FIM 50-100/m^3/h. The acquisition costs of electrical filters, which are generally able to reduce the concentrations to 1 mg/m^3 or below, vary between FIM 30,000-80,000/MW, depending on the capacity of the energy production plant.

Effectiveness and cost of applying pollution reduction methods in Luxembourg (*AEL, 1996*): In applying new technologies (modern electric steel works) the cost would be the same than modernizing the old conventional steel works. The cost foreseen for filter equipment for dust and gases in the three steel works substituted by new electric steel works is $25.3 \cdot 10^6$ ECU. In this case, the emissions of lead before the substitution programme by new steel works (electric) are 48,800 kg/year, and after the substitution are 4,800 kg/year. Emission reduction of 90%.

4.3.1. Primary plant

Heavy metals emitted by primary non-ferrous smelters can be controlled by cleaning the off-gas before its discharge to the atmosphere.

As an illustration of the possible magnitude of such costs, in 1986 the US Bureau of Mines published a paper which examined how emissions from four domestic primary lead producing plants could be reduced to the lowest theoretical levels and calculated the costs associated with such measures. Given the ambient air lead levels from which the plants were starting (some at least well in excess of 2.0 µg/m^3) and the fact that mass emissions could be expected to reduce by between 50 and 75% it is unlikely that any of the plants would be able to meet a 0.5 µg/m^3 standard despite adopting the most effective techniques that can be envisaged.

In each case the ultimate technique for containment consisted of building structural enclosures and baghouses to capture and filter all fugitive emissions from the sites. Table 4.2 summarize the anticipated improvements and associated costs. Broadly speaking for plants of between 90,000 and 225,000 tonnes capacity, emission reductions of between 50 and 75% were estimated to cost between US $37m and 97m (at 1986 prices). This equates to between $267 and $882 per tonne of capacity, or an average of $490 per tonne of capacity. At 1996 prices, these costs would undoubtedly be very much higher.

Table 4.2: Costs of lead reduction in ambient air at four US primary lead plants.

Plant	Capacity (short tonnes)	Cost of improvements (in 1985 US$)		Efficiency improvement (%)		Emission reduction (kg/day)		
		Capital costs	Running costs	1985	Future	1985	Future	% reduction
Buick	135,000	55m	3.5m	97.7	98.8	637	297	53%
Glover	110,000	97m	7.8m	98.8	99.6	400	149	63%
Herculaneum	225,000	60m	4.5m	97.9	99.5	807	197	76%
East Helena	92,000	37m	2.7m	---	---	---	---	---

Source: US Bureau of Mines (1986).

As already stated, there would be no guarantee that measures such as these would enable a 0.5 µg/m^3 ambient air lead standard to be met but they would represent the optimum techniques which could be adopted for primary lead smelters (11 in the European Union). Costs would probably be lower for secondary lead plants (of which there are over 30 in the European Union plus a further eight plants which have refineries only) but still very significant.

4.3.2. Secondary plant

Information of an UK and a Canadian secondary lead plant is presented.

Table 4.3 shows very roughly total controlled stack emissions and ambient air quality in the vicinity of a UK secondary lead plant (which invested heavily in new plant in 1986) over a number of years. The stack emissions are actual measured quantities. The air quality data are the averages of six monitoring stations, of which four are close to the plant and two are about 0.5-1.0 km downwind.

Table 4.3: Stack emissions and ambient air quality in the vicinity of a UK secondary plant.

Years	Stack emissions (kg/week)	Air quality (µg/m^3)
1980 - 83	300 - 400	1.3 - 2.0
1984 - 86	150 - 200	1.0 - 1.5
1987 - 90	40 - 60	0.5 - 1.0

Source: LDA (1996).

As can be seen, emissions and air levels declined steadily in the earlier years as a result of various engineering improvements. The major investment phase which was completed in 1986 resulted in a reduction of about 75% in stack emissions but a much smaller reduction in air lead levels. This is not surprising since fugitive emissions are unlikely to have been reduced by such a large margin. The new plant cost £12m of which £5.5m was invested for environmental reasons.

Further reductions would be much more difficult to achieve and would undoubtedly cost far greater sums of money.

In *UN ECE (1994)* is identified the average capital cost of applying BAT to meet Canadian regulations on secondary lead emissions. These was in the range of 2 to 3 MCAD (1991). That included the control of emissions as well as good operation practices for a 10,000 tonnes/year secondary smelter.

Table 4.4: Costs of applying reduction techniques on a Canadian secondary lead smelter.

Process:	Secondary Lead Smelter Emission: 10,000 tonnes/year
Abatement:	Air Pollution control: Fabric filter Exhaust vent Fug. dust Emission: < 10 mg/Nm^3 Emission reduction: 15.2 kt/year
Total investment:	2-3 MCAD
Total operating cost:	61 CAD/tonne Pb/year
Total cost per kg abated:	137 CAD

Source: UN ECE (1994).

4.4. Issues to be addressed

4.4.1. Practicability

As far as the practicability of a recommended 0.5 µg/m^3 annual average lead in air limit was concerned, it was agreed that there should be no problem in attaining the level in rural and urban areas. Many industrial plants should also be technically capable of meeting the value within five years from implementation of the Directive. There are, however, some types of plants for which industry cannot envisage a future BAT which would enable the limit value to be reached in the immediate vicinity. The problem with such plants is fugitive emissions which are very difficult and relatively expensive to control than stack emissions.

4.4.2. Timetable and margin of exceedance

The question of the timetable for meeting limit values should be addressed in the light of further information on costs.

The group considers that a diminishing margin of exceedance should not be necessary for urban and most other areas, given the decline in the use of leaded petrol. As already stated a margin of tolerance is likely to be necessary for industrial areas. The level of the margin should also be examined in the light of further information on costs and practicability.

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Annex 1: Dustfall measurements

A summary of a collection of lead measurements in dustfall is given in this annex. It can be a complement of the description in Chapter 1.

In the first part it has been presented the deposition in three stations located in the region of Catalonia, Spain. These are urban and background/industrial stations. Details of its characteristics are given in Table 6.1.

The second part of the annex presents the deposition values in three stations of a heavily industrialized area of Bristol, UK. Results of these stations can be representative of the emissions originating in primary lead and zinc smelters.

Table 6.1: Characterization of the stations in the Spanish locations.

Station	Type of station	Type of zone	Characterization of zone	Observations
Barcelona - Pça Molina	Traffic	Urban	Residential Commercial	Urban centre near heavy traffic streets
Breda	Industrial Background	Suburban Rural	Industrial	Background station in an industrial zone
Terrassa - ITEMA	Industrial Background	Suburban	Industrial	Suburban / Country

Lead in dustfall was sampled with standard deposit gauges, and analyzed after an acid digestion by AAS .

. ***Results***

The following tables show the concentrations of lead in dustfall and the total deposition in the first three locations.

Table 6.2: Station: Barcelona - Plaça Molina.

Period	Days	Total dustfall (mg/m^2/day)	Lead in total dustfall (µg/m^2/day)
30.12.95 - 18.1.96	19	230	166
19.1.96 - 18.2.96	30	340	328
19.2.96 - 11.4.96	22	286	209
12.4.96 - 20.5.96	38	169	165
21.5.96 - 13.6.96	23	331	184
14.6.96 - 19.7.96	35	356	171
20.7.96 - 16.8.96	27	333	---
17.8.96 - 13.9.96	26	195	174
14.9.96 - 10.10.96	27	269	224
11.10.96 - 15.11.96	35	86	119
1.12.96 - 30.12.96	30	359	237

Table 6.3: Station: Breda.

Period	Days	Total dustfall (mg/m^2/day)	Lead in total dustfall (µg/m^2/day)
9.4.96 - 7.5.96	28	534	252
1.5.96 - 1.6.96	31	455	157
4.6.96 - 1.7.96	27	575	271
2.7.96 - 1.8.96	30	701	190
2.8.96 - 1.9.96	30	867	293
2.9.96 - 1.10.96	29	498	200
2.10.96 - 1.11.96	30	460	138
2.11.96 - 1.12.96	29	238	163

Table 6.4: Station: Terrassa - ITEMA.

Period	Days	Total dustfall (mg/m^2/day)	Lead in total dustfall (µg/m^2/day)	
			Soluble	Insoluble
1.3.96 - 14.3.96	44	146	< 9	37
15.3.96 - 15.4.96	31	242	< 9	34
18.4.96 - 18.5.96	30	140	< 10	28
21.5.96 - 20.6.96	30	135	< 9	44
22.6.96 - 23.7.96	31	124	< 9	39
31.7.96 - 2.9.96	33	111	< 10	41
4.9.96 - 4.10.96	30	81	< 9	26
29.10.96 - 29.11.96	31	135	< 6	31
10.12.96 - 9.1.96	30	78	< 6	11

Total dustfall and lead in the soluble and insoluble fraction corresponding to near primary lead and zinc smelters in the second locations are presented in the following tables. Figure 6.1 represents the moving concentrations in the three stations.

Table 6.5: Station: 6 Borewell, Kings Weston Lane.

Period	Days	pH	Concentration in mg/m^2/day		
			Total deposited matter	Lead in soluble matter	Lead in insoluble matter
25.5.94 - 5.8.94	72	5.9	208	4.4	7.0
5.8.94 - 21.9.94	47	5.2	227	7.4	5.7
21.9.94 - 10.11.94	50	5.7	178	3.1	4.1
10.11.94 - 28.12.94	48	5.3	257	7.7	5.6
28.12.94 - 30.1.95	33	5.1	309	11.8	2.5
30.1.95 - 8.3.95	37	5.4	302	7.7	6.5
8.3.95 - 19.7.95	133	5.6	217	2.1	8.5

Table 6.6: Station: Poplar Farm, Lawrence Weston Lane.

Period	Days	pH	Concentration in mg/m^2/day		
			Total deposited matter	Lead in soluble matter	Lead in insoluble matter
25.5.94 - 5.8.94	72	5.9	238	0.4	4.1
5.8.94 - 21.9.94	47	5.5	278	1.2	4.2
21.9.94 - 10.11.94	50	5.8	236	1.0	2.0
10.11.94 - 28.12.94	48	5.7	209	---	2.2
28.12.94 - 30.1.95	33	5.4	264	5.6	1.7
30.1.95 - 8.3.95	37	5.4	214	2.5	1.9
8.3.95 - 19.7.95	133	5.7	171	0.7	2.8

Table 6.7: Station: Hallen Village.

Period	Days	pH	Concentration in mg/m^2/day		
			Total deposited matter	Lead in soluble matter	Lead in insoluble matter
25.5.94 - 5.8.94	72	6.0	132	0.4	1.8
5.8.94 - 21.9.94	47	5.3	154	0.9	1.7
21.9.94 - 10.11.94	50	6.3	636	0.5	1.1
10.11.94 - 28.12.94	48	5.3	160	---	1.2
28.12.94 - 30.1.95	33	5.3	245	2.1	1.7
30.1.95 - 8.3.95	37	5.6	285	1.5	2.0
8.3.95 - 19.7.95	133	5.6	145	0.4	1.7

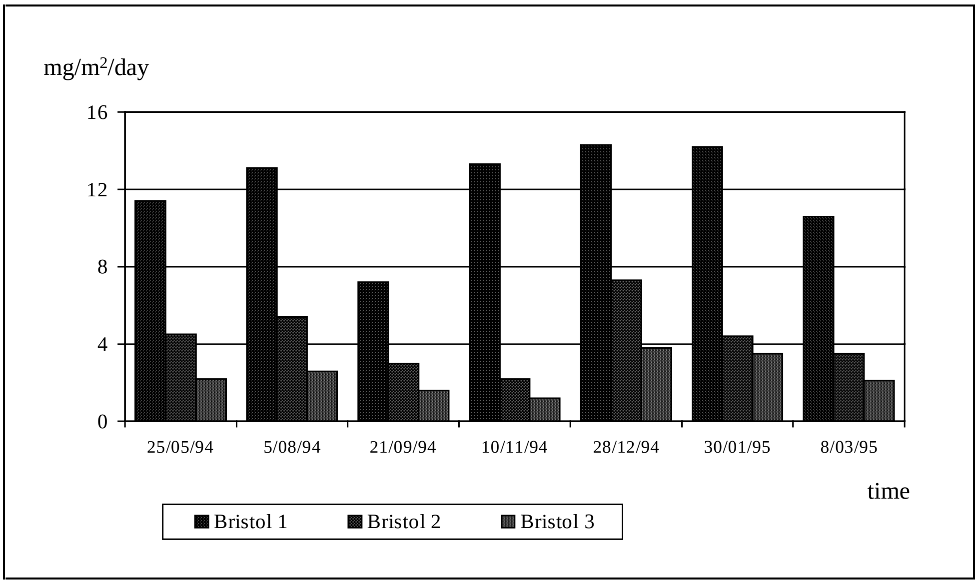

Figure 6.1: Moving concentrations in the three industrial stations.

Annex 2: Climatological Modelling of Lead Particles Dispersion from Typical Primary and Secondary Lead Smelters

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. *Main goal*

This work is devoted to assess the atmospheric impact of particles containing lead (Pb) that are released by typical primary and secondary lead smelters. Special attention is focused on the fulfilment of the WHO guideline value that has been proposed for lead (0.5 µg/m^3, annual mean). Spatial distribution of air quality levels is shown for several cases, depending on emission source, meteorology and terrain.

. *Methodology*

The methodology used in this work is based on a modelling approach. Since the air quality level is given for an annual mean (i.e. chronic pollution), we have simulated the long term average concentrations by using a climatological model. Specifically, the model used is EMITEMA-AIR (*Baldasano et al., 1990; Rovira et al., 1991*). EMITEMA-AIR is a model based upon the climatological expression of the Gaussian model. The model optionally allows to consider the interaction between the plume and terrain. The model also includes plume rise calculations and a deposition mechanism. The meteorology is taken into account by means of the so-called dispersion matrix, that is, a climatological summary that accounts for wind velocity and direction, and atmospheric stability.

Two emission scenarios are considered: lead particles released by a primary smelter that obtains lead from mineral), and lead particles released by a secondary smelter (i.e. it obtains lead from recycling batteries, for example). Two "typical" smelters are defined, after analyzing data from some 50 lead European smelters, and with the assessment of three experts from three European countries. The characteristics of these two sources are given in Table 6.8.

Table 6.8: Simulation conditions for defined sources.

	Primary lead smelting	Secondary lead smelting
Capacity (t/year)	90,000	25,000
Air pollution control system	Fabric Filter	Fabric Filter
Emission factor (kg Pb/t Pb prod.)	0.1	0.05
Emission concent. (mg Pb/m^3)	2	2
TSP speciation	$PbSO_4$, PbS, PbO	$PbSO_4$, PbS, PbO
Emission temperature (°C)	100	100
Exhaust gases velocity (m/s)	18	18
Emission height (m)	50	40
Flow (Nm^3/h)	562,000	130,000

Besides, *two geographic locations are considered*: one in North Europe and other in the South Europe. Terrain in the Northern site is assumed flat, while the meteorological data correspond to real data measured in Kastrup (Copenhaguen, Denmark). For the Southern site, both the topography and the meteorology correspond to Martorell (Catalunya, Spain); terrain, as shown in Figure 6.2, is quite complex at this site.

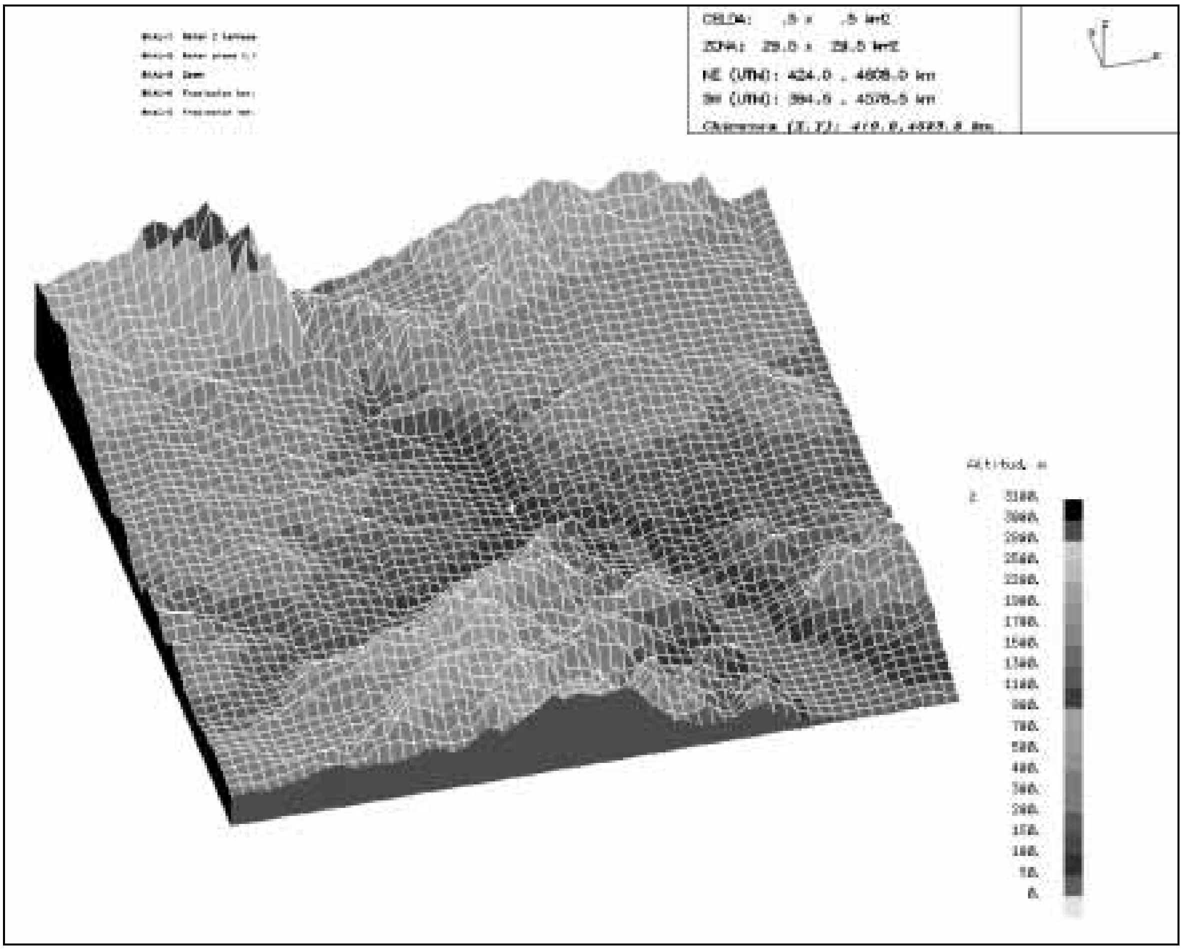

Figure 6.2: Digital topographic map of Martorell (Spain).

Comparison between meteorology at the two sites can be done by looking at Figure 6.3, Table 6.9 and Table 6.10. The wind rose obtained for Kastrup after 1 year of hourly data is shown in Figure 6.3-*a*; any wind direction is almost equally probable, although West shows higher frequency than other sectors. The wind rose obtained for Martorell after 4 years of hourly data is shown in Figure 6.3-*b*; this rose is clearly more asymmetrical, showing high frequencies in the NW-SE axis (i.e. in the direction of the valley). Wind speed distributions are also very different (Table 6.9). In Martorell, 60% of time the wind is lower than 2.5 m/s, while in Kastrup 60% of time is higher that 2.5 m/s. Something similar happens regarding atmospheric stability Table 6.10): in Kastrup, 90% of cases are neutral or stable, while in Martorell, 45% correspond to unstable.

Table 6.9: Wind velocity distributions (%) at Kastrup and Martorell.

	South Europe (*Martorell, SP*)	North Europe (*Kastrup, DK*)
Calm	30.3	0.9
0.5 - 2.5 m/s	30.6	21.6
2.5 - 4.5 m/s	20.5	24.4
4.5 - 6.5 m/s	12.3	26.7
6.5 - 9.5 m/s	5.7	21.7
> 9.5 m/s	0.6	4.7

Table 6.10: Atmospheric stability distribution (%) at Kastrup and Martorell.

	South Europe (*Martorell, SP*)	North Europe (*Kastrup, DK*)
Terrain	complex	flat
Annual mean temp. (°C)	15	10
A: very unstable	6	3
B: unstable	21	3
C: slightly unstable	17	7
D: neutral	13	49
E: slightly stable	11	15
F: stable	32	23

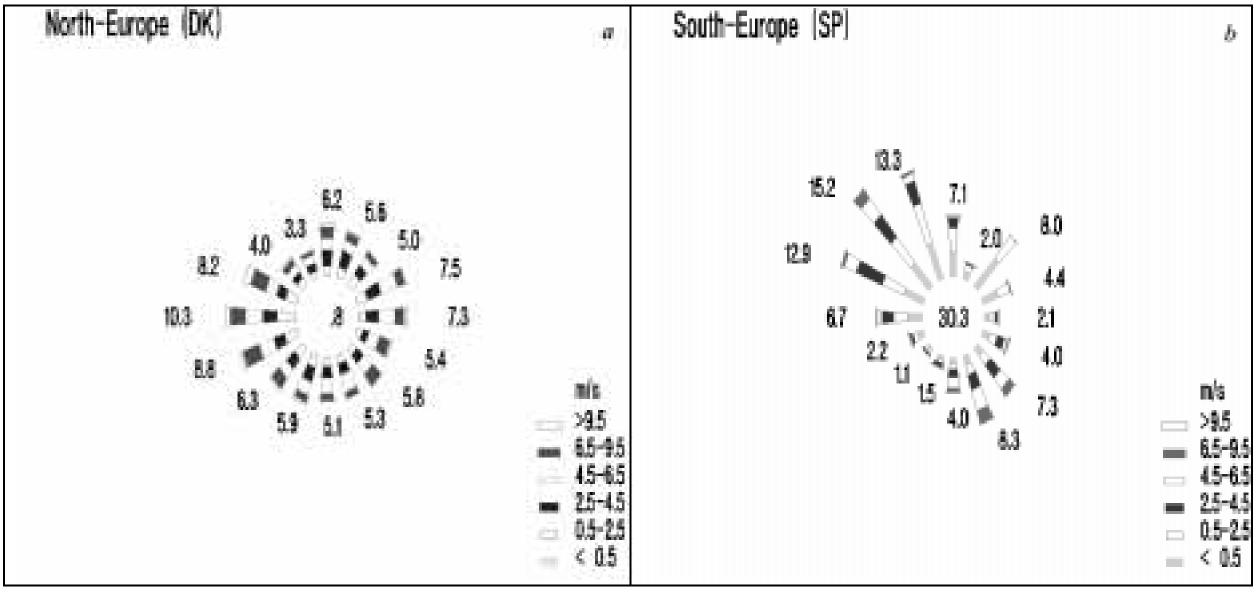

Figure 6.3: Wind roses for Kastrup (Denmark) and Martorell (Spain).

. *Results*

By combining the two defined sources and the two sites and meteorology, four cases are simulated. The spatial distribution of ambient air concentrations obtained for every case is shown in Figure 6.4. Since both topography and dispersion matrix are more symmetrical at the Northern site, ambient air concentration spatial pattern also does. At the Southern site, spatial distribution is quite complicated, because of the complexity of terrain and asymmetry of dispersion matrix. A summary of the results obtained by the model is given in Table 6.11. Ambient air concentrations are clearly higher at the Southern site. This is related to the higher frequency of unstable situations and, more significatively, to the interaction between the plume and terrain.

Table 6.11: Summary of results.

	Primary lead smelting	Secondary lead smelting
South Europe (Martorell, SP)		
scale figure (μg/Nm^3)	0 - 0.5	0 - 0.5
max. concentration (μg/Nm^3)	0.3	0.065
North Europe (Kastrup, DK)		
scale figure (μg/Nm^3)	0 - 0.05 μg/Nm^3	0 - 0.05
max. concentration (μg/Nm^3)	0.004	0.004

The results obtained, can be quite differents when the emission values considered are others than the values used in this study.

It has been assessed only the lead emission from stacks and has not taken in consideration the fugitive emissions. They can increase clearly the ambient air concentrations obtained here.

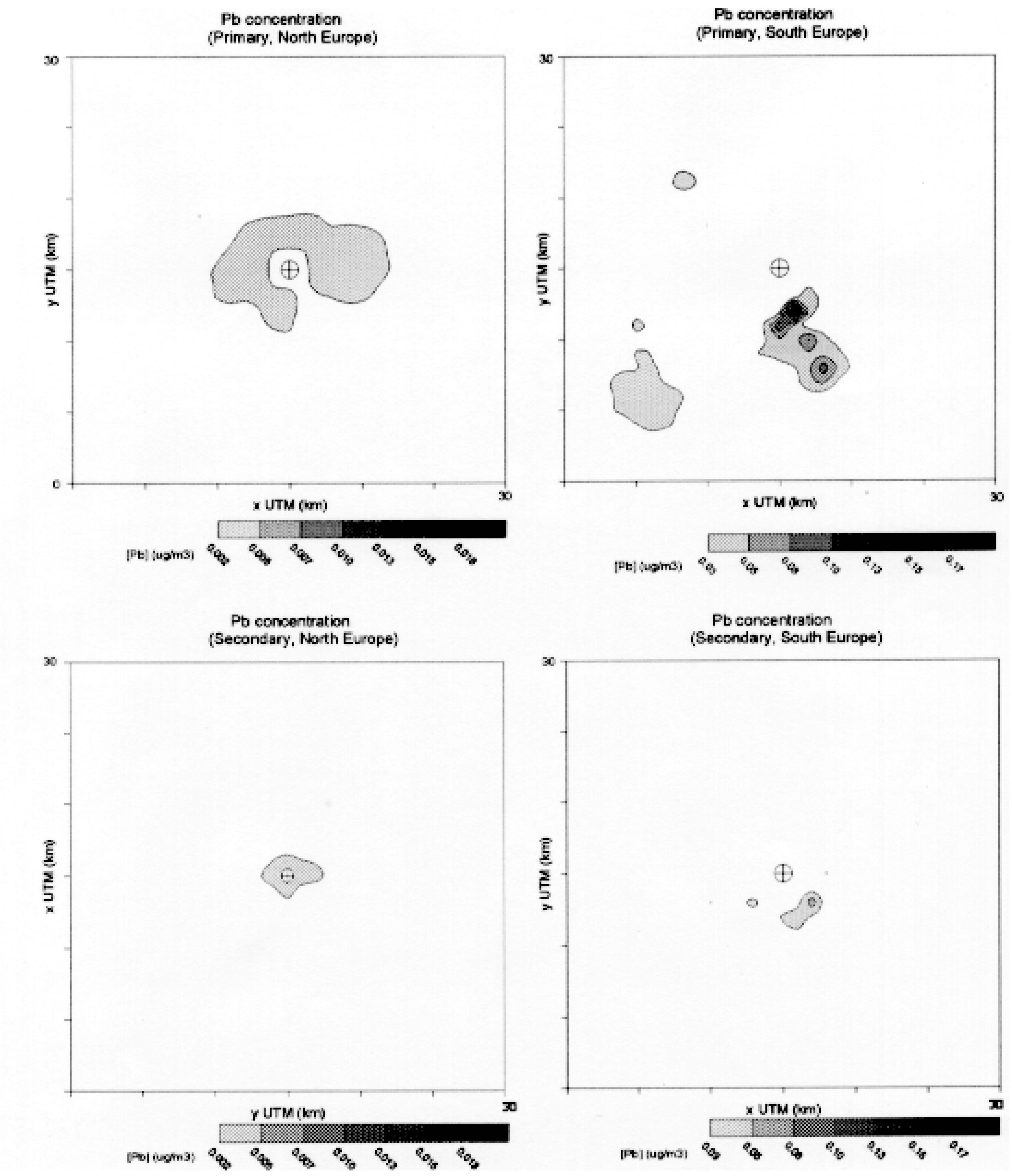

Figure 6.4: Lead air quality concentration at the Southern and Northern site after an emission from a primary and a secondary smelter.

. *Conclusions*

Some differences between atmospheric dispersion characteristics at an area in the South of Europe and other area in the North are highlighted in this work. In general, terrain is more complex in the South, while can be assumed essentially flat in the North. The winds are stronger in the North, while in the South long periods of calms are found. A predominance of neutral or stable atmosphere is found in the North, while in the South, unstable atmosphere is quite usual.

Ambient air concentrations found after simulating the dispersion of lead particles show the effect of both the orography and the meteorology. Thus, levels computed at the Southern site are much higher than levels at the Northern site. However, for the two defined sources (a primary and a secondary smelters), the proposed standard (an annual average of 0,5 µg/m^3) is never reached. The standard could be reached by an actual source in a particular site; specially in the South, this possibility seems quite plausible.

• *Acknowledgments*

We want to thank to Oriol Puig and Xavier Guinart from the Servei de Protecció del Medi Atmosfèric del Departament de Medi Ambient de la Generalitat de Catalunya; to D. Wilson for providing us with emission data corresponding to European smelters; to T. Mikkelsen from Risø National Laboratory for providing us with meteorological data taken at Kastrup (Copenhaguen, Denmark). We want to thank also to every one in the Air Quality Daughter Directive - Working Group on Lead for their friendship and support.

• *Literature cited*

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Annex 3: Campaign of suspended lead measurements at an urban station of Sabadell City and comparison with the traffic volume

An experimental campaign of one week in December 1995 in the city of Sabadell (Catalonia, Spain) was carried out in the frame of work developments for the elaboration of the Air Quality Daughter Directive on Lead.

A set of measurements of lead content in atmospheric particles is presented. The evolution of the daily cycle at a 4-hourly frequency has been studied and its correlation with the average hourly traffic was highly correlated. The concentrations are also compared, using two different sampling methods: a high volume sampler and a medium volume sampler. Results obtained manifest that the concentrations of lead in atmopheric suspended particles inside urban centres are due to traffic, because of the use of leaded gasoline.

. *Description*

Sabadell is a city located in the metropolitan area of Barcelona (Catalonia, Spain), with about 200,000 inhabitants. In December 1995 it was made a field experimental campaign measuring the content of lead in atmospheric suspended particles, following the evolution of the daily traffic cycle in a station of the aforementioned city, that was considered representative of the traffic conditions.

Figure 6.5 represents the average hourly intensities of the vehicles (in periods of 15 minutes). It can be observed that there are three peaks at day hours: 1) from 7 a.m. to 9 a.m.; 2) from 1 p.m. to 3 p.m. (Spanish lunch time); and 3) from 7 p.m. to 8.30 p.m. The night valley is really important, with almost no traffic between 3 a.m. and 4 a.m.

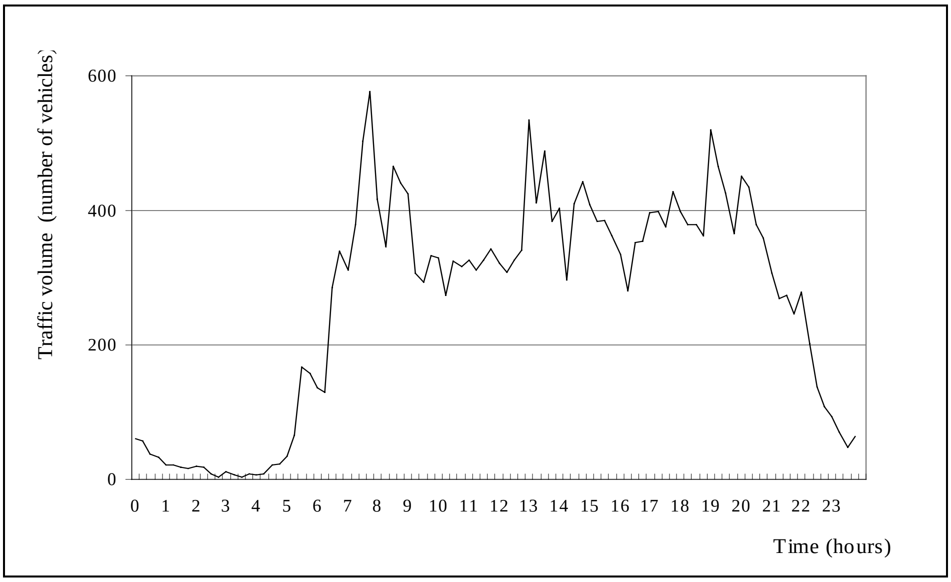

Figure 6.5: Hourly traffic intensities in the vicinity of the station.

The daily traffic average was 25,211 vehicles/day.

. *Equipment*

The content of lead in the atmospheric suspended particles was measured using two different sampling methods: a high volume sampler and a medium volume sampler, both of them equiped with a PM10 inlet. Afterwards, both series of samples were analysed in the laboratory by acid digestion (according to US EPA 40 CFR 50) and atomic absorption spectrometry (AAS).

. *Results*

The correlation between the two series of experimental results obtained with the different samplers can be considered good, showing a correlation coeficient of 0.66 (Figure 6.6). It should be considered that they are experimental measurements at a field, and not measurements in a laboratory.

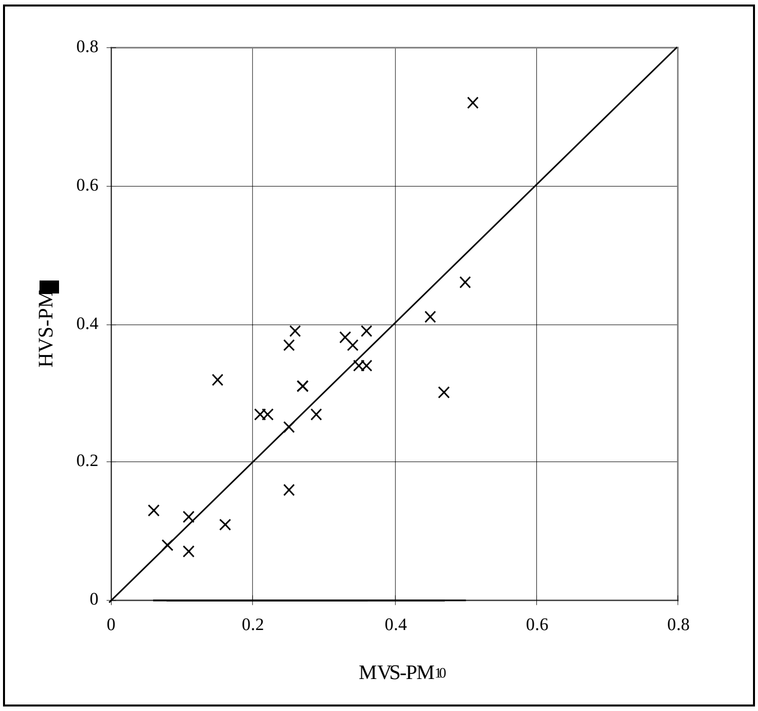

Figure 6.6: Comparison between PM10 lead concentrations from high volume and medium volume samplers .

The range of the measures is between 0.1 and 0.7 µg/m^3, being the maximum in the central hours of the day. Figure 6.7 represents five daily cycles corresponding to the working day of the week (Monday to Friday). It can be observed that the lead levels in the atmospheric suspended particles of the first four days is the same with a little tendency to decrease, but there are clearly higher levels on Friday. Also, it is evident the high correlation between the traffic cycle and the lead concentration in the atmospheric suspended particles.

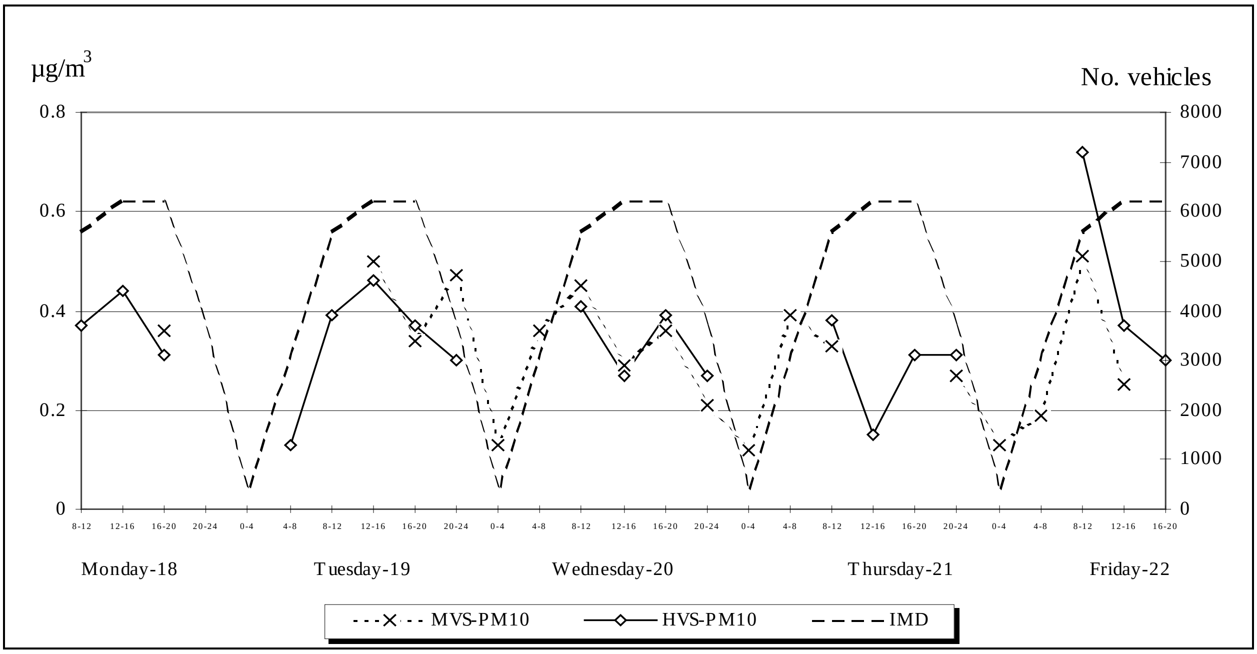

Figure 6.7: Comparison between the concentrations and the traffic.

Except for one measure, all the measurements are under 0.5 µg/m^3 (4-hourly periods).

Annex 4: Report on Standards for Measurement and Assessment of Lead Concentrations in Air

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The aim of this document is to draw up a report on the plan being prepared by the Working Group on Lead to establish a Daughter Directive on lead as an atmospheric pollutant. The report includes the results of the analysis based on the main document *position paper on lead* and other publications consulted

The following points are specifically developed: study of the methods used to determine the amount of lead in the atmosphere and the amount of lead in dustfall; the behaviour of such methods with respect to a possible decrease in the limit values of lead in air; the discussion of a recommendable working methodology; accuracy and precision; and the observations on Quality Assurance and Quality Control.

. *Atmospheric lead (aerosol)*

(a) Sample Collection

The normal method is based on the use of a high volume sampler (≈1000 m^3 air in 24 hours) with a fibre glass filter. If methods are required to detect smaller concentrations, fibre glass filters are inconvenient as they contain metal impurities, however, the problem may be overcome by using cellulose nitrate membranes which are far more expensive but are free from metal ions.

The current trend is to go for a reduction in the size of the membrane and thus collect a smaller volume of air and work with medium volume samplers (≈200 m^3 a day).

We would not recommend working with a small volume sampler (≈40 m^3) as it would mean either working too close to the detection limit or necessitate looking at more sensitive analytical methods.

We therefore believe that future recommendations should be to collect samples in a medium volume sampler using a cellulose nitrate membrane with a pore diameter of 0.45 µm, and employ the whole of the membrane for the analysis.

One of the reference methods recommended by the American Environmental Protection Agency (1), prescribes the use of one Teflon filter and a second quartz fibre filter working together in a medium volume sampler. However, this procedure would seem excessively complicated if determining amounts of lead is the only interest.

(b) Membrane attack

One of the problems referred to previously with the use of fibre glass filters is that after the acid digestion, the results indicate excessively high lead levels in blank values. This attack is carried out with hot nitric acid, in accordance with the recommendations of the EPA (2). Mixtures of nitric and hydrochloric acids can also be used although the use of hydrochloric acid would not seem to be absolutely essential.

In most countries the EPA method, or a variation on the EPA method, is used whether filters or membranes are used, however the method is referred most explicitly for fibre glass filters. For this reason it seems safer to recommend the use of the method referred to in German standards (3), which is specifically described for the attack on cellulose nitrate membranes. These are digested with a mixture of nitric and hydrofluoric acids and hydrogen peroxide, despite the problems associated with working with HF in routine analyses.

Since the authors believe that future recommendations should move towards the use of cellulose nitrate membranes, it is first essential that we guarantee that the EPA method gives good results with the membranes. If this remains unclear, the method of the German standard must be recommended.

(c) Preparation of the solution for measurement

If the air under study contains 0.1 µg of Pb per m^3, the amount of Pb collected in the filter will be as follows:

- with a high volume sampler (1000 m^3 a day): 100 µg.
- with a medium volume sampler (170 m^3 a day): 17 µg.
- with a small volume sampler (40 m^3 a day): 4 µg.

Only a quarter of the filter of the high volume sampler is taken for lead analysis, that is 25 µg of Pb, while in the other cases, the whole of the filter is taken.

After the filter (or a quarter of it) is cleaned with HNO_3, HNO_3 + HCl, or HNO_3 + HF + H_2O_2, the solution is levelled off to 100 ml. It should be borne in mind that the final solution must have an approximate acidity of 0.4M in nitric acid, therefore the problem solution under measurement will have the following lead concentration:

- from the high volume sampler: 250 µg Pb/l
- from the medium volume sampler: 170 µg Pb/l
- from the small volume sampler: 40 µg Pb/l

These are the concentrations which would be obtained with the specifications indicated with air containing 0.1 µg of Pb per m^3.

The limit of lead quantification of some of the main analytical methods are:

- Flame Atomic Absorption (AAS): 15 µg Pb/l (4).
- Graphite Furnace Atomic Absorption (GFAAS): 5 µg Pb/l (5) (Although GFAAS has a detection limit of 0.15 µg Pb/l (4), the recommended working interval for quantification lies between 5 µg Pb/l and 50 µg Pb/l (5)).
- Anodic Solution Voltamperometry in a Hanging Mercury Drip Electrode (DPASV-HMDE): 0.05 µg Pb/l (6-9).
- Anodic Solution Voltamperometry in Mercury Film Electrode (DPASV-MFE): 0.001 µg Pb/l (6-9).

- Inductively Coupled Excitation Plasma Emission Spectrometry (ICP-AES): 11 µg Pb/l (4).
- Inductively Coupled Plasma Pre-Excitation Mass Spectrometry (ICP-MS): 0.01 µg Pb/l (4).

As a result, any of the samplers would provide solutions which could be measured although the solutions given by the small volume sampler come dangerously close to the indicated limits.

(d) Methods available. Advantages and disadvantages. The effect of a possible reduction in the limit value.

Flame Atomic Absorption (AAS):

Atomic Absorption Spectroscopy (AAS) is the technique used most commonly in routine analysis to determine the amount of lead in environmental samples, and particularly AAS with a burner as source of vaporisation and excitation.

With the working methodology used in different countries, coinciding in general terms with the standards of the EPA and with standards ISO 9855 and VDI 2267, and considering the limit values established by the various legislations (which European Directive sets at 2 µg/m^3), AAS fulfills all the requirements which may be demanded of the chosen technique. In reality, under normal working conditions AAS has a detection limit of Pb of 15 µg/l (4) in the final solution subject to measurement, which is defined as 3 times the standard deviation from the blank value.

One of the advantages of this technique is that it is widely known by analytical chemists who have learned to work with it at University. Another advantage arises from the number of manufacturers of the necessary instrumentation which guarantee easy maintenance services. As the technique has been used for many years in many different fields of activity, the instrumentation on the market has become compact, robust and very reliable.

The cost of the instrument is not a disadvantage if it is to be used in the laboratory not only for determining the levels of lead but also of other metals.

With a possible reduction in the limit value of atmospheric lead, this (Flame AAS) would be the technique with the greatest limitations, even though it could be used with atmospheric contents of 0.01 µg Pb/m^3 of air (using the medium volume sampler) within a margin of concentrations already very close to the quantification limit of the instrument.

Since it is not recommendable for a routine method to work close to the detection limit, a wise recommendation would be to keep the AAS, under the conditions already mentioned, above limit of 0.03 µg Pb/m^3 air.

One way to lower the limit of atmospheric lead which might be measured using this technique would be to:

a) increase the volume of air collected.

b) take a larger fraction of the filter, or the whole filter.

c) after the attack, dissolve and level off to 50 or 25 ml, instead of 100 ml.

Point *c*) is the result of an additional advantage of AAS, where the volume of the problem solution consumed in each determination is small.

This would all give a far more concentrated final lead solution (variable depending on *a*), *b*) and *c*)), but would also contain a greater concentration of impurities from the atmospheric aerosol which, under certain circumstances, could make analysis more difficult. Part of this interference could be removed by making the filter mineralising procedure more drastic, for instance by working with HNO_3 and oxidisers (for example H_2O_2) in an attempt to eliminate the organic material, or by working with HNO_3 + HF to eliminate the silica.

It should be borne in mind that the smaller the volume used, the more care has to be taken in handling the final solution while measuring the lead concentration by means of AAS.

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS):

GFAAS is a spectroscopic technique of atomic absorption in which the excitation of the sample (excitation being understood to mean the whole complex process of evaporation of the solvent, sublimation and atomisation of the solution and electronic excitation of the atoms or ions of the elements under analysis) is carried out inside a high temperature graphite chamber (optimum temperature for lead, 2000°C). This excitation technique greatly reduces the background signal caused by the aleatory variations of the flame, and enables very low detection limit to be reached (for lead, as low as 0.15 µg/l (4)), although the recommended working interval for quantification is between 5 and 50 µg/l (5).

One significant advantage of this technique is therefore its sensitivity, as it allows precise determination of lead to concentrations as little as a third or a quarter of the concentrations used in AAS. Another advantage is the little amount of solution consumed, which the texts (5) place at only a few microlitres for each determination. This enables us to work extensively even with a total volume of 25 ml of filter material solution. This heightened sensitivity together with a reduction in the total volume of the problem solution would allow lead measurement to lower concentrations, even to a twelfth or a sixteenth of the concentrations needed for AAS.

With respect to the disadvantages of the technique, it is not as robust as AAS, and requires working with extreme care; maintenance is also more expensive. The technique is, however, directed at a single element just as AAS.

Anodic Solution Voltamperometry (DPASV):

Anodic Solution Voltamperometry (DPASV) is an electroanalytical technique in which the lead is preconcentrated electronically as a Pb(Hg) amalgam in a mercury electrode, a process which allows a significant preconcentration factor to be gained. Following this, electrochemical reoxidisation of the lead will enable us, at a characteristic potential of lead, to measure a current intensity which is proportional to the concentration of the amalgam in the electrode and to the lead concentration in the solution being measured.

For routine work it is recommendable to use a Hanging Mercury Drip Electrode (HMDE), and not a Mercury Film Electrode (MFE). The detection limits accepted for DPASV in HMDE are around 0.05 µg/l (6-9). With DPASV in MFE the detection limits are lower, around 0.001 µg/l (6-8) but with much smaller reproducibility. All detection limits mentioned here refer to the final solution under measurement.

An important advantage of this technique is that it allows analysis of more than one element. Therefore, by applying a preconcentration potential in the order of -1.2 V (vs. Ag/AgCl) on the same sample, we can simultaneously determine the Zn, Cd, Pb and Cu (6-8) from the solution peaks given at -1.2 V, -0.6 V, -0.4 V and 0 V respectively.

As with flame AAS, the kind of instrumentation necessary for voltamperometry is relatively inexpensive, especially in comparison with that used in the techniques described in the following sections.

Inductively Coupled Plasma Excitation Emission Spectroscopy (ICP-AES):

Apart from AAS, ICP-AES is the technique which is most commonly used in routine analysis of the amounts of lead in environmental samples. In some countries one method is used indistinctly from the other.

Its detection limit for lead is 11 µg/l (4) and it has the advantage of being a technique for multiple elements. The versatility of the technique, which can be used to determine many other elements than just lead, may compensate its high cost. Therefore, it would be recommendable if other metal elements in the air are to be detected, for example Cd. On the other hand, the high cost of the instrument, its expensive maintenance (mainly due to the use of an argon lamp) and the fact that it requires specialised operators, make its recommendation as an instrument used exclusively for lead determination unjustified.

The difficulty of calibration traditionally associated with AES techniques (which measured the intensity of the spectrum lines against wavelength) has disappeared with the introduction of instruments which measure spectral signals by discriminating the energy of the photons emitted. As a result, today the calibration is no more difficult with this technique than with the others.

Inductively Coupled Plasma Pre-Excitation Mass Spectrometry (ICP-MS):

ICP-MS is the most recent technique of those mentioned here. It is a very sophisticated technique and requires very complex, expensive instrumentation developing rapidly, which is becoming more and more compact and easier to handle. Although it can not currently be considered as competitive with AAS and ICP-AES, the technique has a great future as its detection limit for lead is extremely low, in the order of 0.01 µg/l (4).

For the moment, given existing lead levels, the very low detection limits of ICP-MS are of no particular value, however, the technique would be the best one if isotopic analysis of the lead were necessary.

Energy-dispersive X-Ray Fluorescence (XRF):

XRF is a classical technique of instrumental analysis which, unlike the other techniques mentioned, has the main advantage of carrying out the analytical measurement on the filter itself. The detection limit for lead is 0.05 µg/m^3.

The instrumentation necessary is not overly expensive and given the movements of prices in recent years, this could become a recommendable technique for routine analysis. The most important shortcoming is that it is difficult to calibrate.

. *Lead in dustfall*

The sample is collected in one of the sedimentable dust collectors of the type described in Table 3.11 of the Position Paper.

After acid digestion of the collected residue, the amount of lead is determined with one of the techniques described above. Although the Position Paper describes the use of a variety of techniques used in different countries (even ICP-MS), it would appear that AAS is the most widely used and the most recommendable.

The sample, which is an aqueous solution of the sedimented material, is concentrated to a relatively small volume (< 200 ml), is acidified with HNO_3 to an approximate concentration of 3M and is boiled for a long time (or is sound treated for a shorter time). The final solution is filtered, if necessary, and levelled off to an exact volume (200 or 250 ml), the lead content being determined by means of one of the techniques described above.

This treatment is recommended in the belief that there might be a fraction of lead dissolved in the aqueous part and the lead in the solid residue would be soluble in the 3M HNO_3 medium. In the event that we should wish to avoid making these hypotheses, it would be necessary to:

- evaporate to dryness.
- attack the residue with HNO_3, with HNO_3 + HCl or better with HNO_3 + HF (the HF being used to totally eliminate the residue of SiO_2 possibly contained in a fraction of the lead retained by adsorption or occlusion).
- the residue is dissolved with 3M HNO_3, is levelled off to a suitable volume and is analyzed in a standard way.

• *Recommendation of a Reference Method*

The recommended method for determining the amount of lead in aerosol is essentially based on sample collection for 24 hours in a medium volume sampler (≈200 m^3 a day) fitted with a cellulose nitrate membrane with a pore diameter of 0.45 µm. The whole of the membrane is taken and cleaned with HNO_3, HNO_3 + HCl (following the stages laid out in the EPA standards (2)), or with HNO_3 + HF + H_2O_2 (in accordance with the instructions of the VDI standard (3)). As previously mentioned, the EPA standard concentrates on the use of fibre glass filters, while the VDI centres on cellulose nitrate membranes. We believe that this could be the key issue to the choice of a method and it would be necessary to make comparative studies to determine whether the EPA standards give good results with the membranes. If this can not be confirmed, we recommend the VDI procedure.

The next step is to dilute the cleaned solution to a precise volume, between 25 and 100 ml. The final solution should have an approximate acidity of 0.4M in nitric acid.

Lead is determined by AAS or ICP-AES.

In order to determine the amount of lead in dustfall, the sample is collected in a dust collector and the sample (an aqueous suspension of the sedimented material) is concentrated to a relatively small volume (< 200 ml), is acidified with HNO_3 to an approximate concentration of 3M and is boiled for a long time (or is sound treated for a shorter time). The final solution is filtered, if necessary, and levelled off to an exact volume (200 or 250 ml), the lead content being determined by AAS or ICP-AES.

• *Accuracy and precision*

The accuracy depends on the calibration quality. If the final measurement is taken with AAS, the method used in calibration is usually the calibration curve (straight).

A base standard solution of 1000 mg Pb/l prepared by dissolving 1598 mg of $Pb(NO_3)_2$ in 1 l of water is taken for use. HNO_3 is added to achieve a final solution of 0.45M HNO_3 and this is used to prepare a working standard solution of 20 mg Pb/l with the same acidity.

On a daily basis, this standard solution is used in dilution to prepare calibrating solutions of 0.45M in HNO_3. These calibrating solutions are prepared at such concentrations that will preferably cover the range of concentrations where we believe the problem solution will fall.

The absorbency of the blank value (0.45M in HNO_3) and the standards must be measured until good repetitivity is achieved.

If HNO_3 + HCl has been used to clean the membrane, the solutions intended for calibrating as well as the blank values must contain a similar concentration of HCl.

If analysis gives indications that there might be significant matrix effects, it is recommendable to carry out calibration with the standard method of additions, which consists of measuring a series of solutions prepared from the problem solution, adding increasing volumes of the standard solution and extrapolating the measurements with a signal intensity of zero. This might be the case when the solution obtained from the attack on the membrane is reduced to a small volume in order to carry out measurement by AAS.

Precision is the variation between the repeated results obtained from a single object under analysis.

Variations brought about by different causes always behave in an accumulative manner, that is, the total variation is the variation which occurs in the sample collection plus the variation in the treatment of the filters or membranes, plus the variations occurring in handling in AAS, plus the variations in the AAS determinations. If we work correctly, the most significant of all these possible variations is the one caused by the treatment of the filters or membranes. Therefore, if the chemist pays special attention to this stage, the precision of the analytical results will be acceptable.

. *Quality Assurance and Quality Control*

The generic term Quality Assurance and Quality Control is taken to mean all the standards, measurements and organisation carried out to guarantee that the results obtained are representative, accurate, precise and can be traceable, and that optimum use is made of the available media. The characteristics of the procedures drawn together by standards EN 45001 (mentioned in the Position Paper) would seem to be the most suitable for use in laboratories working with atmospheric pollution.

. *References*

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