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TOXIC TRACE ELEMENTS
AND CHLORINATED HYDROCARBONS:
SOURCES, ATMOSPHERIC TRANSPORT
AND DEPOSITION

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SUMMARY

Toxic trace elements and chlorinated hydrocarbons represent a special class of environmental contaminants, because of their strong bioaccumulation and persistence. Atmospheric transport and deposition by precipitation scavenging and dry deposition is an important source of these substances in terrestrial and aquatic ecosystems.

The processing of mineral resources at high temperatures, such as coal and oil combustion in electric power stations and industrial plants, roasting and smelting of ores in non-ferrous metal smelters and ferrous foundries, refuse incineration, and kiln operations in cement plants, results in releases of volatile elements to the atmosphere. Some of these elements, e.g. As, Cd, and Pb, have been widely studied due to the serious health concern associated with them, and quantitative emission data are becoming available for many European countries.

Once emitted to the atmosphere, trace elements can be transported within air masses and deposited in remote areas, and source-receptor models have been formulated which can be used to relate measured concentrations in air to estimated emissions. The deposition pattern is also relatively well documented, both from precipitation analyses and from moss surveys.

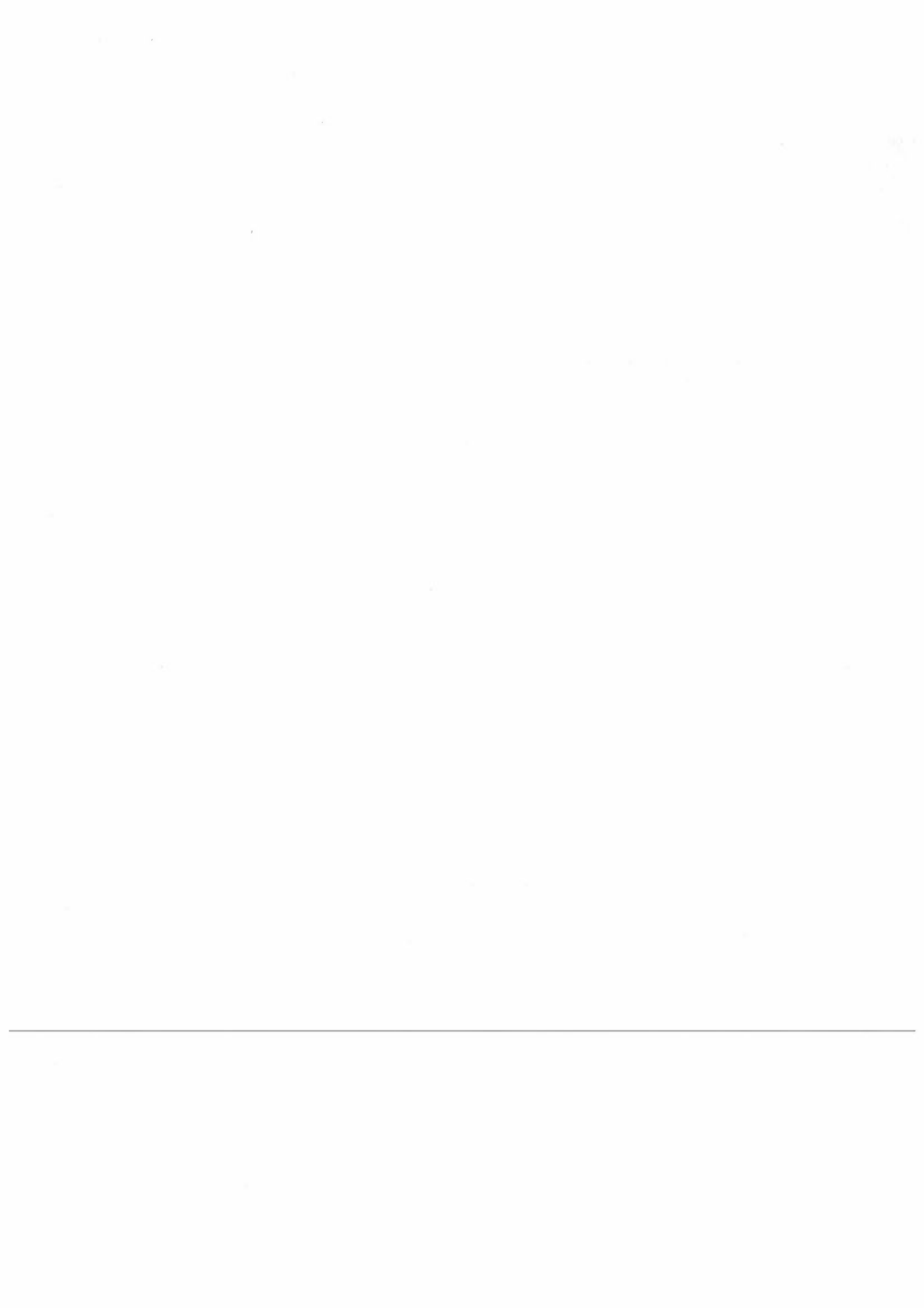
Mercury is present in the atmosphere mainly as gaseous, elemental mercury, which is not readily deposited by precipitation or taken up by plants or water surfaces. Ozone promotes precipitation scavenging. Large quantities of elemental mercury and gaseous mercury compounds are released by combustion processes, and the deposition of mercury by precipitation is clearly correlated with the deposition of other air pollutants. The relationship between the sources and the physico-chemical processes involved are not fully understood, however.

The chlorinated hydrocarbons of concern are pesticides, industrial chemicals or additives, and compounds formed as undesirable byproducts in industrial and combustion processes. The location and magnitude of the emissions are not well known, but may in some cases be inferred from production volumes.

Representative measurements of concentrations in air and precipitation are scarce, but indicate that the chlorinated hydrocarbons are dispersed and deposited on a regional scale where they have been used, and on the global scale. Deposition from the atmosphere is the most important source for the occurrence of chlorinated hydrocarbons in terrestrial and aquatic food-chains. Restrictions on the use of PCB's in the 1970's have not been effective in reducing concentrations in ambient air and precipitation.

CONTENTS

	Page
SUMMARY	1
INTRODUCTION	5
 PART I: TRACE ELEMENTS	
1 ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS	7
2 CHEMICAL SPECIATION OF As, Cd, Pb AND Hg IN EMISSIONS FROM HIGH-TEMPERATURE PROCESSES	13
3 BEHAVIOUR OF TRACE ELEMENTS IN THE ATMOSPHERE	15
4 DEPOSITION OF ATMOSPHERIC TRACE ELEMENTS	17
5 SOURCE-RECEPTOR MODELS FOR ATMOSPHERIC TRACE ELEMENTS	24
6 BUDGETS FOR THE EUROPEAN ATMOSPHERE	29
7 EFFECTS OF ATMOSPHERIC TRACE ELEMENTS ON THE ENVIRONMENT ..	29
 PART II: CHLORINATED HYDROCARBONS	
8 PRODUCTION AND APPLICATION OF CHLORINATED HYDROCARBONS	33
9 SOURCES OF CHLORINATED HYDROCARBONS	34
9.1 Insecticides	34
9.2 Industrial chemicals	36
10 CHLORINATED HYDROCARBONS IN AIR, PRECIPITATION, AND DRY DEPOSITION	38
11 ATMOSPHERIC DISPERSION	44
12 EFFECTS OF CHLORINATED HYDROCARBONS	46
13 CONCLUSIONS	48
14 REFERENCES	50



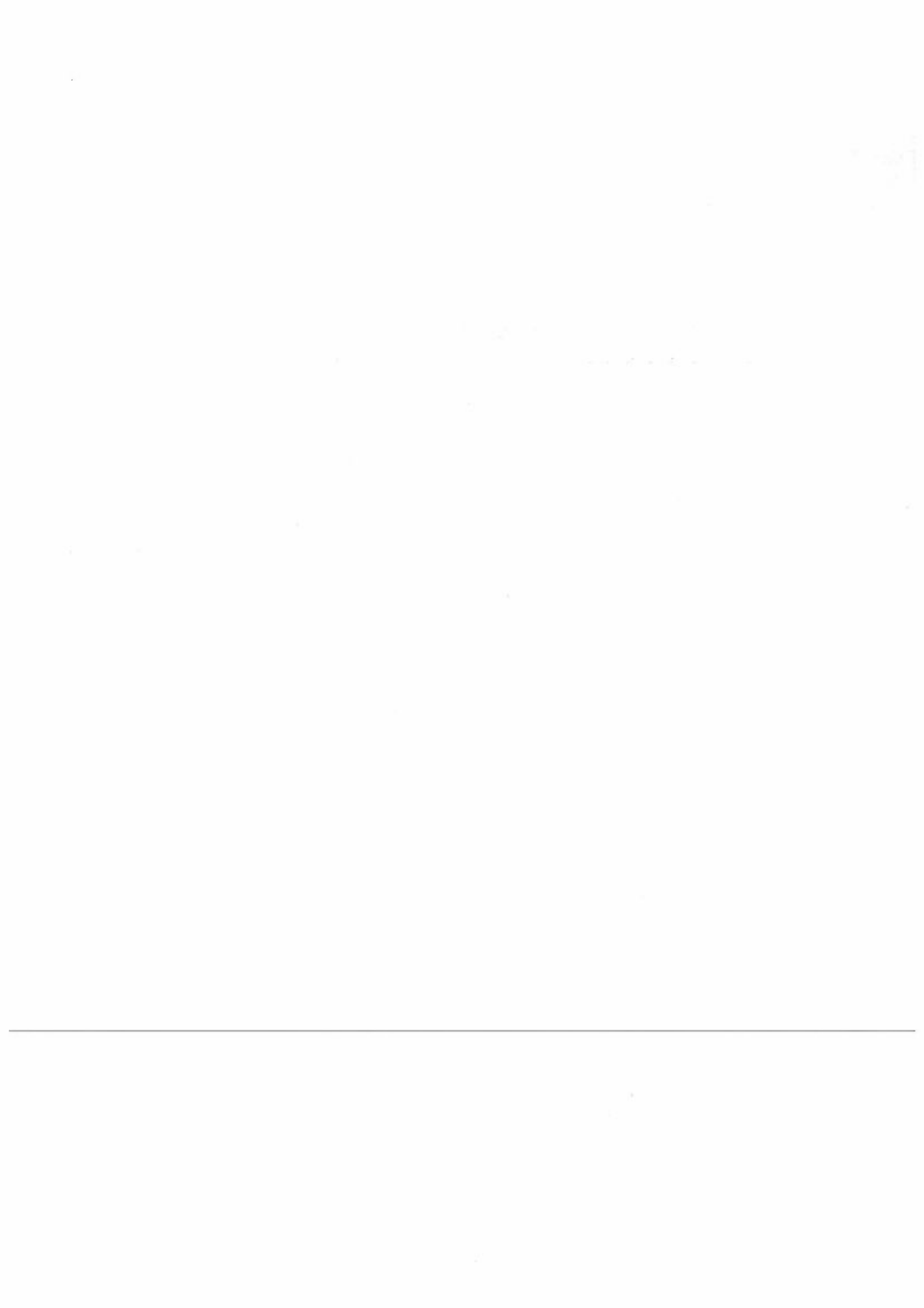
TOXIC TRACE ELEMENTS AND CHLORINATED HYDROCARBONS:
SOURCES, ATMOSPHERIC TRANSPORT AND DEPOSITION

INTRODUCTION

Atmospheric transport and deposition of pollutants over long distances have received attention, particularly in connection with the acid rain problem, and more recently, the photochemical oxidants and ozone formation.

However, atmospheric transport is also an important pathway for the dispersion of other environmental contaminants. This may be of concern when accumulation in soil and biota can result in the buildup of potentially toxic concentration levels, which are a function of the character of the recipient as much as of the actual input.

While the level of contamination of heavy metals and halogenated hydrocarbons in various biota has been extensively studied, quantitative data on the emissions, concentration levels in air, and ecosystem accumulation and transfer, have not yet been systematically related. It is the purpose of this report to examine available data, in order to see if there is a basis for such a systematic approach to describe the environmental cycle of two classes of environmental contaminants, the heavy metals and the chlorinated hydrocarbons.



PART I: TRACE ELEMENTS

1 ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS

The concentrations of so-called "anomalously enriched elements" in the atmosphere are mainly due to the volatility of these elements at the high temperatures of fossil fuel combustion, and many high-temperature industrial processes, particularly the extraction of non-ferrous metals from sulphides.

A first preliminary review of the atmospheric emissions of various trace elements from anthropogenic sources in Europe was prepared for 1979/1980 (Pacyna, 1983). The earlier surveys were concerned with either a single metal (van Enk, 1980; Hutton, 1982) or certain types of emission sources, e.g. fossil fuel combustion (Pacyna, 1982). As such, they were very valuable for control strategies, but less applicable for modelling of the long-range transport of air pollutants and their migration through the environment. The 1979/1980 survey (Pacyna, 1983) covered the atmospheric emissions of 16 elements from all major sources in Europe. The survey has recently been updated and improved. The elements are those which have high enrichment factors in ambient aerosols relative to the earth's crust, which implies that human activity has altered the geochemical cycles of these elements, as indicated in Table 1.

In addition, some information on the behaviour of the trace elements and their health effects is presented in Table 1. The improved emission estimates are shown in Table 2 for various source categories and in Table 3 for different countries in Europe. These estimates were based on the emission factors in Table 4, which were calculated separately for each of the European countries, statistics on the consumption of raw materials, and the production of various industrial goods in 1982. A comparison of the emission estimates for As, Cd, Pb and Zn with national data from some countries is given in Table 5.

Fossil fuel combustion, particularly solid fuels burned in thermo-electric power plants, is an important emission source for many elements. The elements Be, Co, Mo, Sb and Se are emitted chiefly from the combustion of coal, while Ni and V are released mainly from oil combustion. However, metallurgical industries, particularly extraction of zinc, lead, copper, and nickel, and recycling of scrapmetal, are the largest emitters of Cd, As, and Zn. Lead additives in petrol account for 60-70% of the Pb emissions to the atmosphere, but the use of lead additives is gradually being phased out in many European countries.

There are four factors that affect the amounts of the trace elements discharged: (1) mineral composition in fuels, ores, and other raw materials, (2) physical-chemical properties of the trace elements, (3) production technology employed, and (4) effectiveness of emission control devices.

The concentration range of some trace elements in coals, gasoline and fuel oils, used in Europe and the Soviet Union, are shown in Fig. 1. In some single fields of coal or crude oil, the trace element concentrations can be even higher. As an example, the content of arsenic in some Polish and Czechoslovakian brown coals can be as high as 500 to 1200 ppm.

Bituminous coal is more contaminated than the other types, while lignite has the lowest amounts of trace elements (Pacyna, 1980). However, to obtain an equal amount of electrical energy from the different types of coal, one needs to burn much more lignite than bituminous coal due to the low heat value of lignite. On this basis, the effective trace element emission factors for bituminous coal are actually lower than those for lignite. The limited information available indicates that approximately 30% of the trace metals in crude oils are retained in the residual fuel oil and the asphalt (Smith et al., 1975). Generally, the most contaminated crude oils are those from the Middle East, the North Sea, and Venezuela (Pacyna, 1982) while crudes from the Far East (Singapore, Indonesia), Africa (Algeria, Gabon, Nigeria), and North America are the lowest in trace elements. The trace element concentrations in selected industrial materials are shown in Fig. 2.

The physical-chemical properties of the trace elements play a very significant role in their mobilization. Several processes, such as coal and oil combustion in electrical power stations and industrial plants, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration and kiln operations in cement plants, all employ high ($>1000^{\circ}\text{C}$) temperatures. The higher the temperature, the larger the emissions of volatile elements. The combustion temperature directly affects the volatilization of trace elements in a furnace, their condensation on fine particles in the flue gas stream, and their atmospheric transport.

The type of production technology and the type and efficiency of the emission control equipment, are the key factors affecting the Cd and As emissions, particularly from non-ferrous metal smelters. Generally two types of technology are used in the European zinc plants: pyrometallurgical and electrometallurgical processes. The first type of plants employs thermal smelting in an imperial smelting furnace (ISF process) or a retort furnace (mainly vertical retort, VR). The major source of Cd in the Zn smelter operations is sintering of ore concentrates from roasters at high temperatures. Some European ISF smelters include equipment for the scavenging of Cd volatilized in the sintering stage. The consumption of fuel, both inside and outside retorts, or inside blast furnaces, results in a major volume of process gas containing Cd and other heavy metals. The emission factors for the Cd from pyrometallurgical zinc plants reported in the literature vary from 5.8 (UBA, 1982) to 500 g per tonne Zn produced (Pacyna, 1983). This large difference is probably due to differences in the effectiveness of the emission control equipment.

The emission of airborne pollutants from the electrolytic production of zinc is negligible. At present, four of the 18 primary zinc plants within the European Economic Community use ISF (ca 20% of the Zn production), and one VR (ca 6% of the Zn production). More than 70% of the Zn production in Eastern Europe comes from smelters with thermal smelting.

Smelting and converting processes in copper-nickel smelters are important sources of As emission. Thermal smelting technologies, including reverberatory smelting, flash smelting (the INCO and OUTOKUMPU processes), and other continuous smelting processes, emit much more pollutants than hydrometallurgical techniques. About 90% of all copper is presently produced by the thermal processes (Barbour et al., 1978).

More than 70% of the total electricity production in the European conventional power plants comes from single-fired installations (e.g. hard coal power plants), ca. 25% from dual-fired installations (mainly hard coal/petroleum products and petroleum products/natural gas) and the rest from triple-fired installations (mainly hard coal/petroleum products/natural gas). The use of multi-fired installations makes the emission calculations more difficult and results in some minor over-estimation because very often hard coal emission factors are used to assess emissions from hard coal/natural gas-fired power plants.

It should also be noted that the trace element emissions from non-conventional combustion, such as fluidized bed combustion or pulverized combustion of coal, are comparable to or lower than the emissions from conventional power plants (e.g. Abel et al., 1981; Carpenter, 1979).

The amounts of trace elements passing through control devices depend on the tendency of the element to concentrate on the fine particles, and the retention of these particles by the Control equipment. As an example, the penetration of several metals through a venturi wet scrubber and an electrostatic precipitator, installed on a coal-fired unit, is presented in Table 6 (Ondov, et al., 1979). Fig. 3 summarizes some average collection efficiencies (and penetrations) of control equipment installed in various European countries.

~~It is very difficult to generalize on the use of control techniques in various source categories in Europe. High efficiency electrostatic precipitators are installed in a majority of the European coal-fired power plants and non-ferrous metal smelters. The range of applicability of conventional electrostatic precipitators, however, is limited because they are most effective for particles in a fairly narrow range of electric resistivity. For example, low-sulphur coals~~

produce high-resistivity fly ash, and therefore the control efficiency is less. Application of so-called "hot-side" precipitators seems to overcome this problem.

Cement mills and clinker coolers are also equipped with electrostatic precipitators. Sometimes fabric filters are installed in the cement production, but this type of control devices is suitable only for dry and free flowing dust, and for flue gas temperatures suitable to the bag material.

In wet scrubbers the removal of particulate matter is practically independent of the temperature, although high operating temperatures increase the water consumption, resulting in the formation of steam plumes. This type of equipment is common in incineration plants, often together with electrostatic precipitators.

Many applications require the emissions to be spatially distributed. The spatial distributions of all the trace elements considered in Tables 2 and 3 are available in the 150 x 150 km grid used for EMEP. As examples, the emissions of As, Cd, Pb, V and Sb are shown in Figs. 4 to 8 respectively. The spatial distribution of these estimated emissions was based on the geographical location of the main point sources. The spatial distribution of the Pb emission was based on information on the total length of roads in a given grid, population density, and the geographical location of point sources.

Among the metals and metalloids of concern for their potentially harmful effects in the environment, mercury is unique for a number of reasons. The worldwide production of mercury is around 9000 t y^{-1} . Major usage includes caustic soda and chlorine manufacturing, electrical equipment, instruments, paints, and a variety of other uses. It has been estimated for the US that about 20% of this amount escapes to the air, while 49% is deposited in landfills, etc. Only 8% is recycled (Harris and Hohenemser, 1978). In addition to this amount come emissions from cement production, ferrous and non-ferrous metallurgy, and combustion of fossil fuels. The last source dominates in Europe. Recent emission estimates for Hg from anthropogenic sources in Europe are presented in Table 7 (Pacyna, 1987a). For some countries, however,

the Hg emissions from waste-related sources (incineration of municipal and sewage sludge wastes) and chlor-alkali production exceeds the Hg emissions from the combustion of coal. Recently, the Hg emission sources were reviewed by Lindqvist et al. (1984), and Lindqvist and Rodhe (1985). They conclude that present anthropogenic emissions of Hg represent at least 10%, and probably about 30%, of the present global deposition. Compared to the pre-industrial fluxes, the present anthropogenic emissions represent an addition of at least 20%. The major question, however, to what degree man has altered the biogeochemical cycle of Hg, remains to be answered.

Any expectations with respect to changes in future emissions from non-ferrous metal smelter in Europe are primarily related to changes in production technology and modernisation of environmental protection installations. The authors have reviewed the expansion plans of all major smelters in Europe (Serjeantson, 1986) and found no indication of a major change in production technology during the next few years. As there is no significant change in the production of Pb, Cu, Zn and Ni in Europe, and the modernisation of environmental protection installations mainly concerns the new acid plants, it is suggested that the emissions of As, Cd, Pb, and Zn from European smelters estimated in this work, will continue to be valid for the next 5 years at least.

Changes of the emission trends for coal and oil combustion in electric power plants and industry are more difficult to predict, because they are related to the export-import movements of fossil fuels. The present increase of the coal use in European electric-power plants (ca. 2% per year) is related mainly to the increasing demand for electricity in Europe (ca. 1% per year) and partly to the decrease of the heat values of some European coals (e.g. 1% decrease per year for Polish coals (Kopecki, 1981)). The expected increase of air pollution from coal combustion in the future due to the above factors, may be compensated for by the tendency to extend the use of dual-fired installations with natural gas in Europe. Thus, also the As, Cd, Pb and Zn emissions from the European electric power plants are not likely to change in the near future.

Among other industrial sources, waste incineration is becoming increasingly more important, particularly in Western Europe, due to emissions of Cd, Pb and other trace elements (e.g. Hg, Sb and Sn), and a need to incinerate increasing amounts of wastes.

Emissions of Pb from gasoline combustion are decreasing in Western Europe due to the lower use of Pb additives and introduction of unleaded gasoline. In some Eastern European countries, however, there are quite opposite tendencies. There is a discussion in Poland for example, to increase the octane number of so-called "blue gasoline" from 78 to 86 by adding more Pb additives (Matelski, 1987). The differences in the Pb policy in Eastern and Western Europe are already evident from recent measurements of long-range transport of heavy metals to Scandinavia (e.g. Amundsen, 1987).

2 CHEMICAL SPECIATION OF As, Cd, Pb AND Hg IN EMISSIONS FROM HIGH-TEMPERATURE PROCESSES

There is only limited information in the literature on the chemical speciation of metals emitted into the atmosphere. For arsenic, the inorganic forms dominate in the air over the emission areas. The major chemical species of arsenic and other elements evolved during high-temperature processes, are presented in Table 8. Trivalent arsenic is the most common form of the metal. Air samples from smelters or coal-fired power plants, contain mainly trivalent arsenic both in the vapor and particulate states. This is very important due to a general rule, that inorganic arsenic compounds are more toxic than organic arsenic compounds, and the trivalent state more so than the other states (e.g. NRCC, 1978). Methylated forms of arsenic are probably of minor significance.

Elemental cadmium and its oxide are the predominant chemical forms of this metal emitted from all the sources considered in this paper. These two forms seem to be the most toxic cadmium speciations, together with cadmium chloride (found in releases from refuse incineration). The chemical forms of lead have also been studied. Recently Harrison (1986) has reviewed the lead compounds present in ambient

air polluted by vehicle exhaust or by industrial emissions of the metal. Lead halides are emitted primarily as gases, condensing to form PbCl_2 , PbClBr and PbBr_2 particles. Among the lead compounds arising from smelting operations, PbO and elemental Pb are identified in smelter emissions, but not in the ambient air outside the smelter. Concerning gaseous phases of lead, the tetra-alkyl lead compounds that are observed in the atmosphere, reflect their usage in gasoline, and their relative abundance changes during the atmospheric transport.

The mercury from industries and power plants consists partly of elemental mercury and partly of oxidized forms. Rather limited information is available with respect to which volatile compounds dominate in the emission process, but it seems that reactive (or oxidized) forms are the more abundant in emissions from combustion processes.

Mercury species other than elemental Hg ($\text{Hg}(0)$) and dimethyl mercury, $(\text{CH}_3)_2\text{Hg}$ can also contribute. Slemr et al. (1981) suggest, that Hg emitted as dimethyl mercury is subject to relatively fast degradation to elemental mercury in the air. Brosset (1981) concludes, that $\text{Hg}(0)$ is mobilized to the atmosphere, where it is subjected to atmospheric oxidation processes to yield water soluble forms, and subsequently scavenged by wet or dry deposition.

Lindqvist and Rodhe (1985) proposed the following classification of Hg compounds in air and natural water systems:

- 1) Volatile: $\text{Hg}(0)$, $(\text{CH}_3)_2\text{Hg}$;
- 2) Reactive: Hg^{2+} , HgX_2 , HgX_3^- and HgX_4^{2-} with $\text{X} = \text{OH}^-$, Cl^- and Br^- ; HgO on aerosol particles; Hg^{2+} complexes with organic acids;
- 3) Non-reactive: CH_3Hg^+ , CH_3HgCl ; CH_3HgOH and other organomercuric compounds, $\text{Hg}(\text{CN})_2$; HgS and Hg^{2+} bound to sulphur in humic matter.

Considering the volatility of the As, Cd, Pb and Hg compounds in Table 8, As(o), As₂O₃, AsCl₃, Cd(o), and CdCl₂ are volatile, Pb(Cl,Br) is intermediately volatile, and CdO, Pb(o) and PbO are nonvolatile (Gerstle and Albrinck, 1982) at flue gas temperatures. The volatile species would be in the vapor state during high-temperature processes, whereas the nonvolatile compounds would continue to be emitted largely as fly ash, even at higher temperatures.

3 BEHAVIOUR OF TRACE ELEMENTS IN THE ATMOSPHERE

Because so little is known about the chemical speciation of trace elements in emissions, it is extremely difficult to infer chemical changes taking place in the atmosphere.

The relationship between the concentration of a volatile metal and the particle size in high-temperature processes has already been mentioned, when discussing the emissions from coal combustion. In the volatilization-condensation model the bulk concentration of the particles is related to their diameter, matrix composition, surface layer thickness, and flue gas concentrations. Investigations of the surface layer composition suggest that the outermost layer on the surface of emitted ashes often contains H₂SO₄, which permits surface adsorption of several elements. This primarily takes place on the fine particles in the 0.1 to 1.0 μm diameter range. The growth of particles and the size distribution of this incremental growth is described by the Fuchs-Sutugin relationship. Additionally, the presence of sulphuric acid on some particle surfaces may result in post-combustion formation of metal and/or ammonium sulphates, but how this affects the physico-chemical form of the trace elements has not been studied.

Small particles from high-temperature processes, are readily transported by the air over long distances. Several studies in the surroundings of copper and lead smelters in Poland (Glowiak et al., 1977; Kubacka et al., 1977; Pacyna et al., 1981) have been carried out to assess the "local deposition" of trace elements. "Local deposition" can be defined as the part of the trace element emission which is deposited in the same region as it is emitted. It was found that ca

11% of the trace elements released were deposited in the emission area. Based on studies of the long range transport of several trace elements in Western Europe, and on literature data (OECD, 1979), Pacyna et al. (1984a) inferred the local deposition within a 150 km grid to be 5% of the metal emissions from all sources. Locally, a substantially higher deposition may take place, depending upon distance, topography and meteorological conditions.

A major portion of the As, Cd, and other trace element emissions from high-temperature sources with tall stacks is therefore transported over long distances. The metal behaviour during the transport depends on the particle size-distribution, sink processes and meteorological conditions, such as the turbulent vertical rate of air exchange.

A review of the literature by Davidson and Osborn (1986) has shown that some information on the particle size-distribution is available for trace elements. Those elements having the greatest amount of data on size distributions include Pb, Cd, Cu, Fe, Mn and Zn. Their mass fraction below 0.5 μm aerodynamic diameter and mass-median diameters are shown in Table 9. According to the review by Davidson and Osborn (1986), Pb is primarily found in the smallest size range. Significant amounts of submicron Cd, Cu and Zn are also measured. Mn is predominantly submicron, but with appreciable amounts in the 1-10 μm range, while Fe is associated mostly with the largest size ranges. Davidson and Osborn (1986) mention the bimodal shape of the size distribution of trace elements with one peak occurring generally below 1 μm , and the other peak above 5 μm , thus similar to the bimodal spectra reported for total mass size distributions of atmospheric particles in urban areas. For some elements one mode often dominates. For Pb, the predominant mode is submicron; for Fe, the mode is supermicron.

Davidson and Osborn (1986) caution, however, that there are numerous problems with the size distribution data reported in their work. The problems are related mostly to the variety of measurement techniques used in reviewed papers, non-isokinetic sampling, and errors associated with the analytical data.

4 DEPOSITION OF ATMOSPHERIC TRACE ELEMENTS

Trace elements are removed from the atmosphere by dry deposition (sedimentation, interception and impaction) and by wet deposition (rainout, washout). The loss of particles to the surface by interception and impaction is frequently described in terms of a dry deposition velocity, which is the ratio between the deposition rate per unit area, and the ambient concentration at a fixed reference height above the surface. The dry deposition velocity of particles is strongly dependent on particle size, wind velocity, and surface characteristics. Both theoretical considerations and field experiments show that the deposition velocity is small for particles with aerodynamic diameter less than 1 μm , typically of the order of 10^{-3} m/s for grassland, snow, and water surfaces. Forests, however, represent a potentially larger sink, because of the larger surface area and roughness height. The actual deposition velocity for forested areas is not known. Some wind tunnel experiments can be interpreted to indicate deposition velocities up to 10^{-2} m/s, but extrapolations to forests are highly speculative. Moreover, consideration of the interactions between forest elements and the structure of the atmospheric boundary layer, indicates that there should be large spatial variations in the actual deposition (Wiman, 1984; Wiman and Ågren, 1985).

Precipitation scavenging of trace elements can be expected to occur by the same mechanism as the scavenging of sulphate aerosol. The fine particles are incorporated in cloud or fog droplets as cloud condensing nuclei, and picked up by the falling hydrometers. The scavenging ratio, which is the ratio of the concentration of the element in the precipitation, to the concentration of the same element in the precipitation forming air mass, is largely a measure of the liquid water content in the precipitating clouds (Scott, 1978).

The first major studies of the deposition of heavy metals from the atmosphere started in the United Kingdom at the beginning of the 1970's (e.g. Cawse, 1974). The concentrations of some 40 elements were determined in total (wet and dry) deposition at seven non-urban sites in the UK, as part of a survey commenced in 1970-1971 on behalf of

the Natural Environment Research Council (Cawse, 1980). The water soluble and insoluble fractions of the total deposition were analysed separately. At the same time analyses of the deposition of heavy metals were made in Norway (Brække, 1976), and in the USA (Andren et al., 1975; Feely et al., 1976) and in the FRG (Ruppert, 1975). Based on these and studies carried out in the 1980's, it can be concluded that the deposition velocities, needed for modelling of the heavy metal transport in the air, vary between 0.01 and 2.0 $\text{cm}\cdot\text{s}^{-1}$ (average annual deposition velocity). Ranges of deposition velocities for some major elements are given in Figure 9. The variations of the deposition velocities for a given heavy metal depend not only upon the meteorological parameters, and the aerodynamic size distribution of the aerosols, but also on the type of material on which the deposition takes place, e.g. crops, grass, soil, snow covered area, forest plants, etc. In some regions, atmospheric deposition may alleviate trace element deficiencies in plants (e.g. Hewitt and Smith, 1974). Concerning the contribution of wet and dry deposition to the total deposition of elements, Cawse (1980) concludes that wet deposition is an important contributor for Co, Zn, Cu, Pb (80 to 100%), Ni, As, Sb, Cr and Se (60 to 80%), but less important than dry deposition for Mn and V (ca. 35%). A recent study by Michaelis (1987) does not, however, confirm the wet and dry contributions for Cr and Pb suggested above. This latter study suggests only 40 to 50% for Pb and 10 to 30% for Cr as wet contributions, while up to 60% for V. The likely explanation of these differences is that the assessment by Cawse (1980) is on the basis of measurements in rural land areas, while Michaelis conducted his measurements on the shore of the North Sea.

Routine measurements of trace elements in precipitation started at a few stations in Norway in 1978. Strong seasonal variations of trace element concentrations in precipitation were explained by enhanced ~~long-range transport of pollutants under Arctic winter conditions~~ (Hanssen et al., 1980). Some relevant concentration measurements are given in Table 10.

The routine monitoring of trace elements in precipitation began in Sweden in the autumn of 1983 (Ross, 1986) with the aim to determine the atmospheric wet deposition of Cd, Cu, Fe, Mn, Pb and Zn. Trace

element concentrations in wet deposition were highest in southern Sweden and were decreasing northward. To explain the origin of trace elements measured in wet deposition in Sweden, Ross (1987) has calculated their enrichment factors, relative to crustal material. He concludes that Cd, Pb, and Zn were of predominantly anthropogenic origin. However, the Swedish Cd and Zn anthropogenic emissions are smaller than the wet deposition fluxes. Therefore, to explain the relatively high spatial and temporal correlation of Cd, Pb, and Zn concentrations, Ross (1987) concluded that their primary source is anthropogenic emissions which have been transported over long distances. Evidence for this hypothesis is that Cd, Pb, and Zn concentrations are well correlated to excess, non-marine SO_4^{2-} and poorly correlated to Na. Comparing his data with the literature, Ross (1986) believes that earlier estimates of trace element concentrations measured in wet deposition in rural areas of industrialized countries, likely were too high, due to the contamination problem. There is also a seasonal variation of the trace element concentrations in the wet deposition, particularly for Cu, Fe, and Mn.

Barrie et al. (1987) have reviewed literature data on the trace element concentrations in remote precipitation. This information is very important to assess the contribution of long-range transport of pollutants in comparison with their background concentrations. Barrie et al. (1987) concluded, however, that it is difficult to define a homogeneous region. Thus, the concept of "typical" remote concentrations may not be appropriate unless it is qualified by the distance from sources and the prevailing meteorological air masses.

Brosset (1987) has reported on the simultaneous presence of high soot particle concentration in the air and of high concentration of organic (e.g. CH_3HgCl) and inorganic Hg compounds in precipitation, as systematically observed in rural areas in Sweden. Brosset (1987) explains these observations by long-range transport of Hg from regions in Europe with extensive coal combustion. It would, however, be interesting to obtain more information on the possible presence of organic-Hg-inorganic compounds in the smoke from coal combustion. Earlier, the close correlation between airborne long-distance transported soot and the anthropogenic part of the total Hg has been demonstrated (Brosset,

1982). Recently, Brosset (1987) has shown that the main sources (coal combustion in Europe) of airborne soot particles observed in Sweden may also release organic-Hg-inorganic compounds amounting to 30 to 50% of the total Hg emission. However, this has not been confirmed by measurements.

Seasonal changes of the wet deposition of mercury were studied by Ahmed et al. (1987). They concluded, that the wet deposition of mercury increased in summer as this process is dependent on the amount of precipitation.

Recently the ECE has reviewed the trace element measurements at the EMEP stations, and the information is summarized in Table 11 (Pacyna, 1986). These data are based on questionnaires and represent primarily the EMEP stations in the central, western and northern parts of Europe. Of all the trace elements measured at these stations, Cd and Pb are most frequently reported.

Determination of the concentration of trace elements in samples of various moss species, particularly Hylocomium splendens, Pleurozium schreberii, or Hypnum cupressiforme, is an elegant way to measure to obtain a relative measure of the deposition from the atmosphere. Basically, the moss content gives an integrated value of the deposition during the last 2-4 years. Already in 1968 Rühling and Tyler (1968) measured the Pb content of mosses. Their main conclusion was that at least in southwestern Sweden, a considerable part of the lead found in mosses had originated in areas outside Sweden.

Correlation with deposition values obtained from precipitation gauges may be used to transfer the moss concentrations to absolute deposition values (Fig. 10). Since the commonly sampled species grow in sheltered locations, ~~dry the deposition contribution by this method is~~ limited to the gravitational settling of relatively coarse particles ($d \geq 10\mu\text{m}$).

Extensive moss sampling survey data are available for Sweden, Denmark, Finland and Norway (e.g. Rühling and Tyler, 1984). In 1985, moss samples were collected simultaneously in all four Nordic countries

(Rühling et al., 1987). It was concluded that the regional background deposition pattern for all metals shows a decrease from relatively high values in the southern parts of Scandinavia to low values towards the north. This suggests long-range transport of pollutants from Central Europe as a major contributor to the measured moss pollution. Important local enhancements of the concentrations in mosses were also found in the industrial regions of Scandinavia (e.g. Steinnes, 1987).

Moss samples were also collected to study the long-range transport of pollutants to the Norwegian Arctic (Ottar et al., 1986). The samples included the moss Hylocomium splendens and Drepanocladus uncinatus, and the lichen Cetraria delisei. In order to obtain concentration profiles, samples were collected along a transect from the Federal Republic of Germany, across Denmark and Norway. The mean concentrations of Cd, Pb, Cu and Ni in moss samples collected at various locations are shown in Fig. 11. Generally the concentrations decrease when approaching the Norwegian Arctic, and the low variances observed for the concentrations at different locations in the Arctic, suggest that long-range transport of air pollutants is the major contributor to these concentrations.

The above studies illustrate the use of moss species to measure the deposition of air pollutants. However, there are also some limitations when employing moss analysis (e.g. Steinnes, 1984). They are the following: 1) growth rate of moss may vary, 2) relative uptake may depend on quality of precipitation (pH, seasalt), 3) uptake may depend on temperature, 4) moss species may not occur in all regions, and 5) some elements may be leached from higher vegetation in addition to the atmospheric contribution. The moss analysis method is considered to be less reliable as indicator of the atmospheric deposition of Zn and V, and is not applicable for Mn.

Samples of peat from ombrotrophic bogs (Hvatum et al., 1983), have been used to show that the deposition of trace elements is a relatively recent phenomenon. The concentration, e.g. of lead and cadmium, is 10-50 times higher in the surface layer than in the underlying peat, indicating a very substantial increase in the atmospheric supply of these elements in recent times. In Central and Northern Norway where

surface levels are 5-10 times lower, there is a less distinct but still significant enrichment in the surface, indicating an impact of air pollution even in these areas (Steinnes, 1987). The data for Se at the surface and at a depth at 50 cm confirm the hypothesis of a natural source of atmospheric Se which also contributed in pre-industrial times; in the coastal districts of Central and Northern Norway, relatively high and constant Se values are apparent at different depths.

Deposition from the atmosphere is a significant contributor to the input of trace elements to the sea. This research started in the beginning of the 1970's and was mainly concentrated on the pollution of the North Sea (e.g. Goldberg, 1973; Cambray et al., 1975). A first international attempt to estimate the input of various elements to the sea by atmospheric deposition and via other pathways was made by a European group of experts on behalf of the International Council for the Exploration of the Sea (ICES, 1978).

In the 1980's van Aalst et al. (1982) employed a simple model to compare the long-term (ca. 1 year) average concentrations of various elements in the sea, and the wet and dry deposition for an area of 1000 km x 1000 km of the North Sea. The total air concentrations at the receptor were calculated as the sum of the contributions from the different emission areas (the "cells" of the emission grid) weighted by the probability that the wind would blow from that emission cell. The results showed good agreement between measurements and calculations. The data from this and other works (PARCOM, 1985) were recently reviewed by van Aalst and Pacyna (PARCOM, 1986) in order to assess the atmospheric inputs of trace elements to the North Sea. The estimates were compared with measurements at various coastal stations (PARCOM, 1986). The results are shown in Table 12.

A more advanced 3-dimensional trajectory model based on the Monte-Carlo method was recently employed to estimate the long range transport and deposition of Pb to the North Sea (Krell et al., 1986). The emission data used were the numbers from the improved 1979/1980 survey (Pacyna, 1985). Results from the first model calculation show that the

calculated and measured monthly mean depositions and surface concentrations of Pb over the sea differ by about a factor of 2. The total annual input of Pb to the North Sea has recently been determined for all the months of 1980 to be ca. 1440 t (Petersen, 1987). A relatively large contribution on the order of 50% was estimated for the U.K. The Netherlands, France, and FRG contributed about 12% each, Belgium 5%, Sweden 1.5%, Denmark 1% and Norway even less. However, conclusions from this work should be taken with caution. The results are based only on a one year period, which shows a significant month-to-month variability of the deposition.

The deposition in the Baltic Sea has also been the subject of study, starting with a work by Söderlund (1975) on the atmospheric transport of various compounds to the Baltic Sea. Rodhe et al. (1980) have estimated the deposition of heavy metals onto the Baltic as follows: 600 to 5000 t Pb, 200 to 2100 t Ni, 300 to 4000 t Cu and 2000 to 20000 t Zn. The river discharge of Zn and Cu was estimated to be of the same order of magnitude as the deposition from the atmosphere. For Pb the deposition seems to be significantly higher than the river discharge.

Recently a more complete study has been launched by the Baltic Marine Environment Protection Commission, also called the "Helsinki Commission" (HELCOM). A joint monitoring programme was introduced in 1985 on airborne pollution in the Baltic Sea area (EGAP). This programme measures various pollutants including trace elements. No data have been published yet. However, Brüggemann (1986) has reported a yearly deposition of 260 t Cd, 800 t Ni, 1000 t Cu, 2200 t Pb and 12000 t Zn to the Baltic Sea. These values are within the range of measured atmospheric inputs of metals to the North Sea (Table 12). In an independent study, Andreae and Froelich (1984) studying the As, Sb and Ge biogeochemistry in the Baltic Sea, used the 1979/1980 emission survey (Paeyna, 1983) to conclude that ca. 12% of the As emission from Europe is deposited from air to the Baltic sea, which can be compared to ca. 6% for Pb and V.

The atmospheric transport of various elements to the Mediterranean Sea has been studied by French scientists (e.g. Buat-Menard and Arnold, 1978; Arnold et al., 1982). They concluded that for most of the anomalously enriched elements in the Mediterranean aerosol (e.g. As, Cd, Cr, Hg, Sb, Pb and Zn), the atmospheric contribution can be explained by the transport of aerosols from the industrial regions of Western Europe. Arnold et al. (1982) indicated that the atmospheric flux of Pb, Zn, Cr and Hg to the entire Western Mediterranean basin is of the same magnitude as the rate of riverine and coastal inputs in the dissolved form.

Among the trace elements in precipitation, Hg deserves special attention, as precipitation is a major removal process for this element, which exists in two physical forms in the atmosphere. Lindqvist et al. (1984) have presented various ways of estimating the Hg scavenging ratios. This ratio is considerably lower for Hg than for other elements in the accumulation mode. Considering only the watersoluble part of Hg, the scavenging ratio is close to the ratio for other elements. However, many other forms of Hg may exist in the atmosphere, with different solubilities. Lindqvist et al. (1984) suggest that both particulate and gaseous water-soluble forms of Hg contribute significantly to the content of Hg in precipitation.

5 SOURCE-RECEPTOR MODELS FOR ATMOSPHERIC TRACE ELEMENTS

There is a large body of information in the literature on the trace element concentrations measured in the air throughout the world. The airborne trace element studies conducted before the mid-1970's have been summarized by Rahn (1976), while Wiersma and Davidson (1986) have reviewed data obtained or published during 1976-1983. The trace element concentrations presented in these reviews were measured in the atmosphere over remote areas. Similar information is presented in Table 13 to illustrate the case.

There are various reasons why remote area trace element data may be of interest. One of the major reasons is to obtain baseline values with

which urban and industrial air pollutant concentrations can be compared. However, even more interesting is to use the trace element concentrations at remote locations to study the origin of air pollutants measured far from emission sources. In other words, these remote area data can be used to study source-receptor relationships for air pollutants.

The development of emission surveys in Europe has made it possible to relate concentrations and deposition of trace elements in remote aerosols to their sources. The origin of the increased concentrations observed during short episodes of long range transport, has been discussed using air mass trajectories.

At the beginning of the 1980's extensive programmes were launched to study the long-range transport of trace elements to remote regions in Scandinavia (e.g. Lannefors et al., 1980; 1983). In these first projects on trace element transport across Sweden, Lannefors et al. (1980) used various techniques, such as enrichment factors and sector analysis, to assess the contribution of emissions from foreign sources to the concentrations measured in Sweden. The contribution from the Swedish emission sources was obtained with the help of a simple atmospheric dispersion model calculating concentrations at a given point from the local emissions. Lannefors et al. (1980) concluded that Swedish sources might contribute of the order of 1/4 to 1/2 of Ni and Pb to the yearly average concentration at the site of the measurements and 2/3 for V.

The first model calculation of the trace element transport from Central Europe to Scandinavia (Pacyna et al., 1984a) was made soon after the European emission survey had been completed, using a model developed in the OECD programme on long-range transport of sulphur pollutants in Europe (OECD, 1979; Eliassen and Saltbones, 1983). The following mass-balance equation was used in the model:

$$\frac{dq}{dt} = (1-\alpha) \cdot \frac{Q}{h} - k \cdot q \quad (1)$$

where

q = trace element concentration in air, $\text{ng}\cdot\text{m}^{-3}$

t = time, s

Q = trace element emission per unit area and time, $\text{ng}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

h = height of mixing layer, m

k = decay rate for the trace element considered (wet and dry deposition), s^{-1}

α = fraction of trace element emission deposited in the same grid element as it is emitted.

The concentrations of As, Cd, Cu, Cr, Mn, Pb, Sb, V and Zn were calculated for stations in the southern parts of Norway, Sweden and Finland and compared with measurements. An agreement within a factor of 2 was obtained for most of the time and particularly during the periods of enhanced measured concentrations.

The same trajectory model based on the mass-balance equation (1), was also used to study the winter transport of heavy metals to the Norwegian Arctic (Pacyna et al., 1985). An emission inventory for 16 elements from 12 major source regions in the USSR was prepared (NILU, 1984) and used together with the 1979/1980 emission survey for Europe. The model was used to calculate concentrations during the March 1983 episode of air pollution transport to the Norwegian Arctic. The best agreement between measured and estimated concentrations was obtained for Sb (relative difference only 14%). An agreement within a factor of 2-3 was reached for Pb, Se, V, As and Cr.

Often there is, however, a striking parallelity between the measured and calculated values from day to day. The basic reason for this is that the geographical position of the major (dominating) sources is well known. Also the relative magnitude of the major sources is relatively correct, while the absolute values are more uncertain. The difference between measured and calculated values also depends on the deposition factors etc. used in the model.

Summarizing, the measured concentrations and depositions of trace elements at remote locations in Europe and the Arctic can be related to the emission estimates with the help of trajectory models.

The Hg concentrations cannot, however, be estimated in this simple way.

Source-receptor relationships are also studied for mercury (Iverfeldt and Rodhe, 1988). The existence of a long-range transport from the European continent to the Nordic countries is indicated by the correlation between mercury concentrations in air and receptor oriented trajectories. A preliminary study indicates that the sources on the European continent are responsible for a major fraction of the mercury deposited by precipitation in the Nordic countries. This conclusion is based on the analyses of trajectories and a correlation between mercury and sulfate concentrations in rainwater. Data on pH in rainwater and soot and SO₂ in air also support the statements above. The existing south-north gradient of atmospheric mercury is more pronounced in precipitation than in air. In precipitation, the gradient exists for both total mercury and the water soluble fraction.

Statistical methods, such as multiple regression analysis, cluster analysis, time series analysis, principal component or factor analysis, and discriminant analysis have found several applications in studies of the origin of aerosols. They were also used to assess the impact of metal emissions in Europe on the concentrations measured in Scandinavia and the Arctic (e.g. Pacyna, 1988).

A sector analysis of daily mean concentrations from a measurement campaign at Birkenes, Rörvik and Virolahti in 1980 (Pacyna et al., 1984b), shows that the two southern sectors, which can be called the "European sectors", dominated at Birkenes and Rörvik. The NE sector was, however, of equal importance as the southern sectors at Virolahti, and the emission sources from the USSR seem to affect the concentrations in this sector.

~~The use of the trace element comparison as an atmospheric in a tracer~~ system has been suggested by Rahn et al. (1982) already in 1981-82 when they used the noncrustal Mn/V ratio to search for midwestern aerosols in the northeastern part of the USA. Later, the Mn/V tracer became a matter of discussions in the literature (e.g. Hidy, 1984). A major limitation of this technique appears in its application in areas where large amounts of V are emitted. Recently Rahn and Lowenthal (1984) have developed a tracer technique which uses seven elements (As, Sb, Se, Zn, In, noncrustal Mn, noncrustal V) to characterize the

aerosol. Particularly interesting is the application of this new tracer technique to the Arctic aerosol (Lowenthal and Rahn, 1985). In the first step, a principal component analysis was used to isolate the major types of aerosol present in a given sample. Then a group of trace elements was assigned to the factor representing the anthropogenic component, and used to build a tracer system. In order to localize the potential emission sources, Lowenthal and Rahn (1985) have used a discriminant analysis to construct source groups for each of the signatures. As discriminant analysis cannot resolve mixtures of sources, they used chemical element balance apportionment. Using the above techniques, Lowenthal and Rahn (1985) suggested, that 70% of the anthropogenic pollutants at Barrow, Alaska stems from the USSR sources. This fits very well the results obtained for Ny-Ålesund, Spitzbergen (Ottar et al., 1986).

Source-receptor relationships for trace elements in the Arctic were also the subject of studies applying other statistical techniques. Some of them are based on principal component analysis. Heidam (1986) studied the elemental composition of the Greenland aerosol by means of factor analysis of the logarithmic concentrations. The analysis showed that the atmospheric aerosol can be described by 4-5 different source-related and statistically independent components.

An interesting combination of pattern recognition technique and principal component analysis has been presented by Martinsson et al. (1984). The method was used to study the contribution of aerosol long-range transport to Scandinavia on the basis of cascade impactor measurements. The results indicate that contributions from foreign sources to the trace element concentrations in Sweden vary from 50 to 90% depending on the element.

Summarizing, the above mentioned statistical methods are very useful to assess the origin of trace elements measured at various remote locations. However, it has proven much harder to localize their sources, even to the major continent(s) of origin. To do so, it is necessary to use these techniques together with information on the meteorological situation, particularly on air mass trajectories and/or synoptic configurations, and accurate emission inventories. One should be aware, however, of the uncertainties of the trajectory computations.

6 BUDGETS FOR THE EUROPEAN ATMOSPHERE

For some regions the magnitude of emissions can be compared with the deposition of trace elements. Very interesting studies were performed for Hg by Lindqvist and Rodhe (1985). They compared estimated fluxes of mercury in Europe and Sweden with wet and dry deposition. The comparison is shown in Table 14. Lindqvist and Rodhe (1985) suggest that Europe is likely a net exporter of Hg through the atmosphere. However, it is recognized that a very significant part of the anthropogenic emissions from sources in Europe is deposited within the same region, as indicated by the Danish peat bog records (Pheiffer Madsen, 1981) and by data from sediment cores in freshwater lakes in Sweden (Johansson, 1984; Lindqvist et al., 1984). These data suggest that the Hg load on forest lakes in southern and central Sweden increased by a factor of 5 during the 20th century. At the same time only double amounts of Hg were suggested for northern Sweden. Thus, Lindqvist and Rodhe (1985) suggest that the present deposition in Central Europe and southern parts of Scandinavia is about 5 times higher than the pre-industrial deposition. Concerning the Swedish mercury budget, Lindqvist and Rodhe (1985) could not specify whether the present anthropogenic emissions are larger or smaller than the present background emissions. They also conclude from the Swedish budget in Table 14 that a very good agreement between emissions and deposition for Hg may not be very significant, as due to the long residence time of the airborne Hg, a large fraction of the Hg emissions from the Swedish sources can be deposited outside the country. Also, a significant part of the Hg deposition in Sweden may come from sources far away from the country. Similar budgets for the European atmosphere can be approached for other trace elements.

7 EFFECTS OF ATMOSPHERIC TRACE ELEMENTS ON THE ENVIRONMENT

The significance of atmospheric trace elements can be discussed on the basis of the extent to which human activity has altered their biogeochemical cycles. Many atmospheric trace elements can be measured around non-ferrous metal smelters, electric power plants, incinerators, and near major roads and streets, in concentrations resulting in health effects.

The toxic and mutagenic effects of various trace elements are well established (e.g. Nriagu, 1984). Some information in this connection is available from Table 1. The major goal of this chapter is to report on the influence of atmospheric trace elements transported over long distances on soil, plants, and natural waters.

The average concentrations of trace elements in remote areas are far too low to cause any adverse effects for most of the time. However, these concentrations can increase by one or two orders of magnitude during episodes of long-range transport of pollution from source regions (e.g. Pacyna and Ottar, 1985). A significant part of the pollutants from such transport is deposited in remote locations (e.g. Ottar et al., 1986). Deposition of atmospheric trace elements during many decades at remote locations has been documented (e.g. Wolff and Peel, 1985; Boutron et al., 1987). This deposition decides the significance of atmospheric trace elements on regional and global scales.

Bølviken and Steinnes (1987) have reported on the concentrations of various trace elements in samples from three horizons of natural podzolic soils in Norway: A₀ horizon (3-5 cm depth), B horizon (20-25 cm) and C horizon (> 60 cm). A strong enrichment was found for Pb, Cd and to some extent Zn, in the A₀-samples from the south of Norway compared to those further north. The south-north trend was less pronounced in the B horizon, and absent in the C horizon. Thus, Bølviken and Steinnes (1987) suggest that the excess contents of Pb and Cd observed in natural surface soils in the southernmost part of Norway is derived from longrange atmospheric transport. This applies in particular to soils rich in organic matter. The results for the natural surface soils correspond very well to those obtained for peat profiles from ombrotrophic bogs (Steinnes, 1984). Some elements such as Se and Hg need special comments as far as their regional distribution is concerned. The Se content is considerably higher in soils from coastal areas than in corresponding soils inland. This trend is also shown by the Se content of mosses. Thus, Se seems to have an additional emission source, and Steinnes (1987) suggests the decomposition of Se-enriched marine organisms at the sea surface. No south-north trend in Scandinavian soils was reported for Hg.

The content of trace elements from anthropogenic sources in vascular plants in coniferous forest ecosystems also shows a south to north trend, similar to the atmospheric deposition. Steinnes (1987) reports that Pb and Cd are about 5 times higher in Southern Norway than in Central Norway. Soil solution chemistry and metal budgets of spruce forest ecosystems in Southern Sweden was studied by Bergkvist (1987). He discussed factors affecting the transport of trace elements between various soil horizons, among others the content of soluble organic matter in the soil and the soil acidity. Bergkvist (1987) concludes that the studied forests were accumulating Fe, Cu and Pb, while losing significant quantities of Na, K, Mg, Ca, Al, Zn, Cd, and Ni. This is very important information as far as migration of pollutants through the individual environmental media is concerned.

The finding of high mercury levels in freshwater lakes in Sweden which have not been exposed to discharges from industrial or agricultural applications of alkyl Hg, was thought to be due to atmospheric inputs largely from sources outside Sweden. A very thorough investigation of the Hg levels in freshwater fish by the SNV Mercury project revealed, however, that in addition high levels were found in a belt across Sweden from Gothenburg to the Gulf of Bothnia, where emissions of mercury from industry (paper and pulp, chloralkali, and nonferrous metallurgy) have resulted in locally enhanced atmospheric deposition to the soil. The mercury is very strongly fixed to soil organic matter, both in the O (mor) and the B horizon. The mechanism responsible for enhanced mercury levels in fish is run off of colloidal humic material which later decomposes in the lakes, releasing MeHg⁺. The resulting level of Hg in freshwater fish is higher in acid lakes pH \leq 5.5, than in lakes which are in the bicarbonate buffering range pH $>$ 6.0 (Iverfeldt and Johansson, 1987).

~~The enhanced concentrations of some trace elements in soil and vegetation in Southern Norway do influence the uptake of these elements in animals feeding on natural vegetation. The liver Pb content of lambs from different areas of Norway was shown to be closely connected with the Pb deposition (Frøslie et al., 1985), as indicated by a correlation coefficient of 0.95 between lamb liver Pb and moss Pb. Significant positive correlations were also found for Cd, Se, and As.~~

However, this was not the case for Cu. The Cu load of sheep is highly dependent on levels of interfering elements like S, Zn and particularly Mo, a metabolic antagonist to Cu. Thus, the chronic copper poisoning in some districts of Norway is more the result of low levels of Mo in the forages, than due to the Cu atmospheric deposition (Frøslie et al., 1985).

Recently, a very extensive review of literature on the levels of trace elements in animals has been presented by Nyholm (1986). The review also contains information on the accumulation of trace elements in various animal organs and the toxic effects on wild and domestic animals.

Summarizing, the content of trace elements in animals is enhanced in some regions. Animals should be regarded here as "transmitters" of trace elements from air, soil, plants, water to man and as "indicators" of pollution. These enhanced levels of trace elements due to the atmospheric deposition are very often too low to cause any effect. Thus, the second role of "trace elements levels in animals", namely indication of pollution, seems to be the more significant.

In the past decade several compartment models have been developed to determine the human exposure to trace elements. The models were reviewed by Bennett (1984). Pacyna (1980) has described the transport of Cd, As, and Pb from air through water, soil, plants and diet to the human body in the surroundings of a 2000 MWe lignite-fired power plant in Turow, Southern Poland. Mass balances and transfer factors of the elements in different environmental media were estimated from measured concentrations. The estimated annual human exposure to As, Cd, and Pb through ingestion in the area of the Turow power plant is shown in Table 15. The data in Table 15 confirm, that trace elements can cause adverse effects in some regions. The total dietary intakes of Cd, Pb and other elements observed in the surroundings of large electric power plants, non-ferrous metal smelters, and incinerators can appear in levels higher than the WHO/FAO limits. However, this is not the case for receptors located far from emission source regions.

PART II: CHLORINATED HYDROCARBONS

8 PRODUCTION AND APPLICATIONS OF CHLORINATED HYDROCARBONS

Chlorination is one of the basic processes in synthetic organic chemistry. It is used in the production of intermediates, and for final products. Chlorinated products are often chemically more stable, have lower volatility, higher dielectric constants, and may possess other advantages in specialized drugs and pesticides. However, only few of the many thousand registered chlorinated organic compounds merit consideration on the basis of production volumes and potential bioaccumulation and other possible harmful effects. These are mainly pesticides, industrial chemicals and undesirable byproducts from the manufacturing or decomposition of chlorinated compounds. Table 16 lists some of the compounds and their field of application.

The uncritical, large-scale use of the insecticide DDT, preceded the general environmental movement in the 1960's and 1970's. As the many disadvantages became obvious, DDT was gradually replaced with less persistent and more efficient pesticides. Legal restrictions against the use of DDT as an insecticide were adopted in many European countries and USA in the 1970's. Polychlorinated biphenyls (PCB), an industrial chemical used mainly in technical applications, was first detected in environmental samples in 1966 (Jensen, 1966). Other organochlorine environmental contaminants are used as pesticides (e.g. lindane, toxaphene, chlordane), industrial chemicals (chlorinated paraffins), or compounds formed as undesirable byproducts of industrial chemical processes (hexachlorobenzene, octachlorostyrene) or by incomplete combustion or pyrolysis of organochlorine materials. The latter group includes chlorobenzenes, chlorinated dibenzodioxins and dibenzofurans.

9 SOURCES OF CHLORINATED HYDROCARBONS

9.1 INSECTICIDES

Statistical information on the production and application of chlorinated insecticides is available in FAO yearbooks (FAO, 1986). The FAO statistics are incomplete, because numbers are reported only by some countries. The total world consumption is therefore not generally known. Following the large-scale introduction of DDT in the 1950's, production and consumption of chlorinated insecticides increased until about 1970. Various other chlorinated hydrocarbons were introduced to replace DDT and particularly hexachlorocyclohexane (lindane), toxaphene, aldrin, dieldrin, and chlordane have been applied in extensive amounts.

Hexachlorocyclohexane (HCH) can exist in several isomers, and it is the γ -isomer (lindane) which is the active ingredient. Sometimes the technical mixture containing only 10-15% of the active ingredient is used, but preparations with 99% γ -HCH are also available. This is widely used to control soil pests, fumigation of storage rooms etc.

FAO statistics (1979) shows that huge amount of HCH have been used by different countries during the last decade. India used ca 7.7×10^4 t technical HCH during 1975-1977 (Tanabe et al., 1982). Technical HCH consists roughly of 70% α -HCH, 7% β -HCH, 13% γ -HCH, 5% σ -HCH and 5% of other impurities (Tatsukawa et al., 1972; Baumann et al., 1980). According to Jalees and Vemuri (1980), pesticides, including HCH, are likely to be used on an increasing scale in India in the future to improve the agricultural crop yield and for the eradication of diseases. Wang (1981) informs about the production and use of HCH in China over a long period. An amount of 2×10^4 t of technical HCH is produced annually in the Shenyang Chemical Plant alone (Anonymous, 1981). Japan used 5×10^5 t of technical HCH from 1948 to 1970. Although, accurate data on the world production and use of HCH are not yet available, it is safe to assume that the major consumption areas of HCH are concentrated in the northern hemisphere, especially on the Asian Continent. The above presented numbers for India, China and Japan should be considered together with the consumption of HCH in the

Soviet Union. Komarov (1980) indicated that it is huge, but no statistics are available.

Olafson (1978) reported a large consumption of lindane in eastern Australia where it has been applied in the sugar cane growing regions adjacent to the Great Barrier Reef.

Lindane is also used in Europe. In Poland, lindane is used as a fungicide (the mixture includes among others 20% pure γ -HCH and 2.5% of Hg) and to control many soil pesticides, as reported by Janicki (1976). He also suggested that γ -HCH is used in Poland to keep parking lots, airports, roads and railways clean of insects. Janicki (1976) indicates that 2.9×10^3 t of γ -HCH are used for these purposes in the United Kingdom. This amount seems to be overestimated when comparing with the agriculture application of γ -HCH. In Norway, 6.6 t of lindane were used in 1982 and the γ -HCH content was not less than 99% according to Paulsen (1984, personal information). About 9 t of lindane were used in Denmark in 1981 (Kemikaliekontrollen, 1982) and 6 t in Sweden in the same year (Bekämpningsmedel, 1982). In Finland, lindane is used as an agriculture insecticide and a forest pesticide (Tiittanen and Blomquist, 1982). The first application consumed 7.3 t lindane, with only 49 kg of the active ingredients, in 1981. Of tree forest pesticides in use, one is applied for the protection of unbarked timber against insect infestations and the two others are used to protect planted pine seedlings against the large pine weevil, *Hylobius abietis*. All three contain lindane as the active ingredient. The amount used in 1981 was 24.6 t pesticides containing 4.9 t lindane and these values have not changed significantly from year to year. No information exists on this lindane application in other countries.

In the EPP0 (European and Mediterranean Plant Protection Organization) area lindane is widely used for disinfection of empty storage rooms (Mathys, 1984), however, no numbers are available.

The application of toxaphene and chlordane is far less than the use of lindane.

Toxaphene is manufactured by chlorination of di-terpenes, and is a mixture of many different chemical compounds. Its main application was the control of insects in cotton in the USA. Nearly 22,000 tonnes were used in 1976 (FAO, 1978). In 1982, the use of toxaphene in USA was limited to existing stock (USA, 1982). Its use in Europe has been very limited, but yearly consumption rates of 400-600 tonnes have been reported by Poland and Hungary (FAO, 1980). Chlordane, another complex mixture of chlorinated cyclodiene-like compounds, is mainly used for termite control. Aldrin and dieldrin likewise, and for control of soil insects in general.

Agricultural pesticides are usually applied by spraying aqueous solutions or emulsions. Losses to the atmosphere occur by evaporation of spray droplets, or from plant leaves subsequent to the application, and can vary greatly depending on conditions and equipment used. Evaporative losses will be particularly serious when spraying from aircraft or helicopters, and in warm climates (Cunningham, 1962).

Evaporation from plant and soil surfaces will mainly occur during the first few weeks after application.

The importance of vapor pressure, soil composition, and humidity for the evaporation of pesticides from soil has been discussed by Spencer (1975) and Spencer et al. (1974). Hydrophobic chlorinated compounds, such as DDT, are strongly fixed to the soil, particularly to soil with a high content of organic material. It is not unusual to find that concentration levels of DDT in soils are virtually unchanged for several years after application (e.g. Kveseth et al., 1979).

9.2 INDUSTRIAL CHEMICALS

Polychlorinated biphenyls were introduced in 1929 by the Monsanto Chemical Corporation. Production increased worldwide in the 1950's and 1960's reaching a peak of 70,000 t/y in 1970. Because of excellent chemical stability, high dielectric constant, heat conductivity and non-flammability, it has been widely used in electrical transformers and capacitors, and in hydraulic and heat exchange systems. It has

also been used as plasticizer in polymers, marine antifouling paints, as additives in sealants and adhesives, and in certain types of copying paper.

Restrictions on the production and use of PCB's were introduced in the early seventies. The OECD Council recommended in 1971 that PCB should not be used as dielectric fluid in "small" condensers. EEC regulations limit the use to closed systems. Production in USA was stopped in 1979, while production in Europe continued at a rate of 10-15 000 t/y. Of the accumulated world production of $0.7-1 \cdot 10^6$ t, nearly 60% was used in closed electrical equipment, 15% to nominally closed systems, and 25% to dispersive uses (Pearson, 1982). A large fraction resides in landfills in the USA (NAS, 1979).

Destruction by incineration requires combustion temperatures in excess of 1200-1400 °C and relatively long residence time in the combustion zone. An alternative method involves treatment with sodium metal dispersions (EPRI, 1979).

Polychlorinated terphenyls (PCT's) are used mainly in adhesives, sealants etc., and an annual production rate of 5000 t has been suggested (Pearson, 1982). It was still manufactured in Japan in 1977 (Doguchi, 1977). Polychlorinated naphthalenes (PCN's) have been used as dielectric medium in small capacitors, and as an oil additive. The production rate was estimated at 5000 t/y (Kover, 1975).

Much larger production volumes occur for polychlorinated paraffins, which are extensively used as oil additives and as softener in vinyl chloride polymer together with phthalates. In 1977 the world consumption (excluding Eastern Europe) was 230 000 t, almost half of which was used as PVC plasticizer (Campbell and McConnell, 1980).

Certain organochlorine compounds are also produced as undesired side products of industrial processes. One example of this is hexachlorobenzene, which is a side product in the production of many chlorinated compounds (Quinlivan and Ghassemi, 1977). It may also be formed in electrolysis of chloride melts and solutions, when carbon or graphite

anodes are used. Production of anhydrous magnesium chloride from magnesium oxide with carbon and chlorine also leads to formation of hexachlorobenzene and octachlorostyrene (Norsk Hydro, 1978).

However, chlorinated aromatic hydrocarbons are also readily synthesized from chlorinated alkyl radicals in combustion processes, much in the same way as benzene and polycyclic aromatic compounds are synthesized from "normal" alkyl radicals in hydrocarbon flames (Buser and Bosshardt, 1978; Oehme et al., 1987). Pyrolysis and incomplete combustion of other chlorinated compounds resulting in synthesis from chlorinated alkyl radicals, is also the major source of another important class of compounds, the polychlorinated dibenzodioxins and dibenzofurans, although the allegedly most toxic of these, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) was first recognized as a dangerous contaminant in the herbicide 2,4,5-trichlorophenoxyacetic acid.

The formation occurred when 1,2,4,5-tetrachlorobenzene was treated with sodium hydroxide to form 2,4,5-trichlorophenate. Under the influence of excess heat, condensation of 2 phenate molecules leads directly to TCDD and sodium chloride. Naturally, chlorophenols are suspect precursors for PCDD and PCDF's. Penta- and tetrachlorophenols are used extensively as fungicidal wood and leather preservatives.

Polychlorinated biphenyls may be formed, in small amounts, along with chlorobenzenes and chlorophenols in combustion processes (Ballschmiter et al., 1987).

10 CHLORINATED HYDROCARBONS IN AIR, PRECIPITATION, AND DRY DEPOSITION

The determination of chlorinated hydrocarbons in air by gas chromatography and electron capture detection - or mass spectrometry, requires that the air samples are preconcentrated on glass fibre filters for aerosols, and on a suitable solid absorbent for the gaseous component. Polyurethane foam (PUF) plugs (Bidleman and Olney, 1974) are widely used for preconcentration of the gaseous fraction, but the collection efficiency may not be 100% for the more volatile compounds such as

hexachlorobenzene. Usually 2 or more plugs placed in series are analyzed to give an indication of the degree of breakthrough. Other adsorbent media include XAD-2 resin (Doskey and Andren, 1979) and Tenax. A comparison of PUF with Tenax for collection of chlorinated hydrocarbons was made by Billings and Bidleman (1980). The quantification of complex mixtures such as PCB's and toxaphene is a difficult analytical problem. PCB's were first detected and quantified in environmental samples on the basis of a characteristic elution pattern on packed chromatographic columns. With the advent of glass capillary columns, individual PCB and toxaphene compounds may be quantified separately, but results are still usually reported relative to standards prepared from commercial mixtures.

It is also advisable to include several steps of sample cleanup and prepreparation before the gas chromatography analysis, in order to avoid position interferences from the collection medium and the solvents (Oehme and Stray, 1982). Some recent measurements of ambient airborne concentrations are given in Table 17.

A general finding from the measurements was that typically more than 90% of the chlorinated hydrocarbons occurred in the gas phase. The data demonstrate the widespread occurrence of chlorinated hydrocarbons in the troposphere even at remote locations, and substantial agreement between results obtained by different research groups. It is also seen that the concentration levels of compounds with long atmospheric residence times, such as α -HCH and HCB are remarkably similar all over the world.

High concentrations of airborne DDT, toxaphene, and PCB's are found in regions where these compounds are emitted, viz. in South-Eastern Asia, North America, and Europe.

There are few measurements of chlorinated dibenzodioxins and dibenzofurans in ambient air. Buck and Kirschmer (1987) report data for 11 sites in Nordrhein-Westfalen in Germany (Table 18). Generally, the concentrations were in the pg/m^3 range, and the distribution of isomers in outdoor air and samples from combustion processes (incinerators and mobile sources) were very similar.

Various methods have been used to quantify the deposition of chlorinated hydrocarbons by analysis of rain and snow samples, or to obtain measures of the dry deposition or the combined dry and wet deposition, in order to estimate the total deposition to a given area.

The wash-out or precipitation scavenging ratio (W) may conveniently be defined as the concentration in precipitation (ng/l) divided by the concentration in air (ng/l). For particles, and gases which are efficiently incorporated in cloud droplets, this ratio comes close to the inverse of the liquid water concentration, i.e. in clouds, $W \leq 10^6$ (Scott, 1978). The observed scavenging ratio for PCB's and DDT are generally 1-2 orders of magnitude lower, which agrees well with the observed association of these compounds with aerosol particles. Observed washout coefficients for more volatile and water-soluble chlorinated hydrocarbons are in close agreement with solubility data.

Bidleman and Christensen (1979) used glass collectors to collect precipitation samples on an event basis at a coastal site in South Carolina. The results were compared with measured air concentrations to obtain precipitation scavenging factors and dry deposition velocities for PCB's, chlordane, toxaphene and DDT. The observed washout factor for DDT and heavy PCB's (Arochlor 1254) were more than 2 orders of magnitude higher than estimated from vapour solubility data, but 1-2 orders of magnitude less than for trace elements in aerosol. The concentration of toxaphene in precipitation was of the same order of magnitude as expected from solubility data.

Similar washout factors for PCB's can be obtained from Murphy and Rzeszutko's (1979) data for Lake Michigan. It is concluded that, although PCB and DDT exist primarily in the vapour phase in the atmosphere, the partitioning between the vapour phase and adsorption on particles is such that these compounds are removed mainly by rainout or washout of particles, not by vapour dissolution in raindrops. Atkins and Eggleton (1971) also ascribed high concentrations of DDT in precipitation in London to adsorption on particles.

For determination of deposition with rainfall over longer sampling periods, Wells and Johnstone (1978) used polyurethane foam coated with silicone in a funnel arrangement to collect and concentrate chlorinated hydrocarbons. Murphy et al. (1981) used a similar method, but with an automatic opening lid to prevent deposition in dry periods. Södergren (1972) used nylon nets impregnated with silicone oil to measure "total deposition". A network of 11 stations in Sweden was operated for 4 three-month periods in 1972-73 (Södergren, 1975). Larsson and Okla (1987) repeated Södergren's measurements, correcting for the different gas chromatographic quantification procedure. Their results show that, while the deposition of DDT has decreased strongly since 1972, there is no significant trend in the deposition of PCB.

Various authors have used aluminium pans, aluminium pans with water or water/glycerol, filter papers impregnated with propanediol and butanediol, glass plates coated with glycerol, or glass plates coated with mineral oil to measure dry deposition of chlorinated hydrocarbons, mainly DDT and PCB. The validity of using these artificial substitutes for estimating the actual deposition to natural surfaces, depends on the actual uptake rates or deposition velocities. For actual deposition velocities of ~ 0.5 cm/s, where the atmospheric turbulent transfer and molecular diffusion in the gas phase are rate-determining, the substitution may be justified. However, artifacts may occur because the sorption of organic compounds in solvents such as mineral oil is reversible. This is mainly the case for compounds more volatile than pp'DDE (Heesen et al., 1979).

Organochlorine residues in rainwater in the North Sea area were studied by Wells and Johnstone (1978), who operated 7 precipitation sampling stations on the east coast of Great Britain for one year from June 1975 to May 1976. Annual deposition ranged from 1.4-10 $\mu\text{g}/\text{m}^2$ for PCB's, and 0.15-6 $\mu\text{g}/\text{m}^2$ for DDT, and the deposition of both these components decreased from South England to the north. This was also the case for γ -HCH, but not for α -HCH.

Chlorinated hydrocarbons may also be detected in vegetation samples, e.g. in mosses and lichens (Thomas and Herrmann, 1980; Carlberg et al., 1983; Villeneuve and Holm, 1984). However, it was also shown by Larsen et al. (1985) that hexachlorobenzene, γ - and α -HCH accumulated in moss samples from artificial rainwater, could also easily be desorbed. Their conclusion was that the concentrations of chlorinated hydrocarbons in vegetation samples exist in dynamic equilibrium with the concentrations in ambient air and precipitation.

Since mosses lack cuticula, their ability to retain hydrophobic chlorinated hydrocarbons may be less than that of higher plants, which contain waxes, fats, and terpenes. More than tenfold concentration differences of PCB's in foliage have been found between different species of higher plants (Buckley, 1982). Interestingly, a conifer (*Pinus strobus*) had the lowest levels. Concentration levels in all species studied decreased with increasing distance from the source, a former PCB dumping site. The concept of a dynamic equilibrium between ambient air concentrations and concentrations in vegetation has also been advocated by Travis and Hattemer-Frey (1988). Drawing on data from Bacci and Gaggi (1985, 1986, and unpublished), they suggest that vegetation bio-concentration factors for chlorinated hydrocarbons can be related to water-air and water-octanol partitioning constants. Finally, it should be added that Atkins and Eggleton (1971) found rather low deposition velocities ($V_d \leq 0.1$ cm/s) for uptake of chlorinated hydrocarbons in grass, in wind tunnel experiments with radioactive tracers.

The dry deposition of gas-phase chlorinated hydrocarbons to water surfaces depends on the partition coefficient between the gaseous phase and the aqueous phase. Depending on the ratio of the dissolved concentration and the concentration in air, the water surface can act both as a source and a sink. The rate of transfer is limited, however, by the molecular and turbulent diffusion resistances both in the aqueous and gaseous phase (Liss and Slater, 1974). Mackay et al. (1986) have recently discussed the transfer processes for organic compounds, and conclude that a steady-state non-equilibrium situation may occur in which intermittent short periods of deposition are followed by longer periods of slow re-emission to the atmosphere. This particularly

applies to PCB's in Lake Michigan, where the concentration of dissolved species is ~ 4 ng/l, corresponding to an equilibrium atmospheric concentration of 5-20 ng/m³ (Murphy et al., 1987). Since this is higher than the observed atmospheric concentration, a net evaporation will occur. In less polluted waters, the situation may be reversed. Swackhamer and Armstrong (1986) also discussed the PCB budget for Lake Michigan, and concluded that evaporative emission from the surface was a major loss mechanism. Larsson and Södergren (1987) have studied PCB partitioning from contaminated sediments in artificial pools, also showed that evaporation from the surface occurred, particularly at higher temperatures, when the total PCB concentrations exceeded 4 ng/l. About 40% of the total is associated with algae and other particles, and the authors also argue that the "dissolved" fraction was largely associated with dispersed micelles. Clearly natural waters do not always behave like ideal liquids, and accurate determinations of the truly dissolved concentrations in relation to the airborne concentration is required for model predictions.

The observed concentrations of PCB's and DDT in precipitation are substantially higher than expected from the concentrations of these compounds in air samples and their aqueous solubilities (Table 19). The precipitation scavenging efficiency for atmospheric particles is high, however, so that the fraction adsorbed to particles may be important. Junge (1977) proposed a general adsorption isotherm for chlorinated hydrocarbons based on the saturation vapour pressure and the available aerosol surface area. Bidleman et al. (1986) were able to correlate the ratio of the amount collected on a filter (F) to the amount collected on the backup adsorbent (A) to ambient temperature and the concentration of suspended particles (TSP), for several individual chlorinated hydrocarbons, by the relationship

$$\log [A \times (TSP)/F] = m/T + b.$$

In typical urban air, with TSP = 60 $\mu\text{g}/\text{m}^3$, the average fraction of PCB (Arochlor 1254), pp'DDE and pp'DDT retained by the filter is typically 2.1, 2.0, and 8.9% at 20°C, increasing to 25, 24 and 74% at 0°C. α -HCH and HCB are not significantly adsorbed to particles even at 0°C, and chlordane is intermediate (0.7% at 20°C, 11% at 0°C).

In rural air, and particularly in remote locations, the concentration of airborne particles will be much less, and the fraction adsorbed to particles correspondingly lower.

11 ATMOSPHERIC DISPERSION

Long range atmospheric transport and deposition has for a long time been regarded as an important process in the global distribution and occurrence of chlorinated hydrocarbons in remote places such as Antarctica (Peterle, 1968), Barbados (Risebrough, et al., 1968; Seba and Prospero, 1971) and in the air over the North Atlantic (Harvey and Steinhauer, 1974).

Descriptive models of the global transport have been put forward, e.g. by Pooler (1971), and by Woodwell et al. (1971).

Depending on their atmospheric lifetimes and the distribution of emission sources, the chlorinated hydrocarbons are dispersed in the atmosphere on the local, regional, and global scale. Very limited information exists on specific source strengths and concentration and deposition on the local scale. Certainly, evaluated airborne concentrations and concentrations in soil and vegetation will occur within a distance of 10-100 km from the source. However, only a small fraction (<5%) of the amount released to the atmosphere will be deposited on this local scale.

The ^{continental} regional scale, up to 5000 km, is of particular interest in relation to the situation in Europe and on the North American Continent. These areas are highly industrialized, densely populated and include both agricultural areas and vulnerable aquatic ecosystems. The general situation with respect to source-receptor relationships for air pollutants on this scale is also fairly well known from international cooperative programmes (OECD, 1977; Eliassen and Saltbones, 1983). The typical residence time for an air parcel will be determined by the wind speed in the lowest 1-2 km of the troposphere, and will typically be 2-5 days, and sulphur oxides, which are efficiently removed by dry deposition and precipitation scavenging processes, are largely (~80%) retained within the region.

However, within ca. 1000 km from the main sources, ambient airborne concentrations are more influenced by advection and dispersion than by dry deposition and precipitation scavenging processes. Interestingly the observed concentrations of polychlorinated biphenyls in ambient air are between 100 and 1000 pg/m³ as annual averages both in Europe and North America. The source strength can be tentatively inferred by analogy with other air pollutants for which the annual emissions are known, for example sulphur oxides or trace elements. This simple reasoning results in an estimated emission source strength of the order of 10³ tonnes/year for total PCB's in Europe. Only a minor fraction is deposited within Europe. Precipitation accounts for an input to the North Sea (6x10⁵ km²) of ~2 tonnes, and 1-2 tonnes to the Baltic, and the total amount deposited with precipitation within Europe is probably not more than 10-20 tonnes.

Whether or not there is a net dry deposition of PCB's to water surfaces depends on the concentration of PCB's dissolved in the water. A concentration of 1 ng/m³ air corresponds to 0.1-1 ng/liter of water, and concentrations in contaminated water bodies such as the Great Lakes (Swackhamer and Armstrong, 1986) and the Baltic (Kihlström and Berglund, 1978) are in this range, so that the water surface may function both as a source and a sink, depending on ambient air concentrations, temperature, buildup and decline of algal biomass, etc.

For water bodies with shorter residence times, such as the North Sea, or the Baltic, dry deposition may be an important input, possibly accounting for as much as 10-50 tonnes/year (van Aalst, et al., 1982).

The terrestrial cycling of PCB's is also influenced by a dynamic equilibrium between the concentration of PCB in air, and the concentration in plant material. Multiplication of typical PCB concentrations in foliage with typical biomass production rates (~1000 g/m²·a) gives a rate corresponding to a deposition velocity of <0.1 cm/s. PCB's and other chlorinated hydrocarbons are rather efficiently retained in soils, however.

In combination, precipitation scavenging and dry deposition lead to an assumed residence time for PCB's in the atmosphere of the order of

5-10 days. This explains that PCB's and DDT also have a global background concentration.

Depending on the place and time of release, distribution within the troposphere of the northern hemisphere is relatively rapid, typically 30 days. Exchange between the Southern and Northern hemispheres across the tropical convergence zone is slower, about 1 year. The α -isomer of hexachlorocyclohexane is a good example of a compound which is rather evenly distributed in the global atmosphere at a concentration level of $\sim 300 \text{ pg/m}^3$. From the consumption data, we may assume that the total annual emission of this compound to the atmosphere is ~ 30000 tonnes, more than 30 times the amount contained in the atmosphere up to 10 km. The residence time, therefore, cannot be more than ~ 10 days. This is about the time, which is required for equilibrium between the atmosphere and the ocean surface, with an assumed "average" deposition velocity of 0.1 cm/s. The water/air partitioning coefficient for α -HCH is $2 \cdot 10^3$ at 20°C and increases with decreasing temperature. An airborne concentration of 300 pg/m^3 corresponds to an aqueous concentration of 0.6-6 ng/l, which implies that one year of α -HCH emissions is stored within 20 m of the oceans, mainly at low temperatures. Thus, the ocean-atmosphere equilibrium and the vertical mixing of the oceans determine the relationship between emissions and ambient air concentrations of α -hexachlorocyclohexane.

12 EFFECTS OF CHLORINATED HYDROCARBONS

The adverse effects of chlorinated hydrocarbons in the environment is due to their persistence and high lipid/water partition coefficients. Thus, the concentration of chlorinated hydrocarbons in fish fat is largely a measure of the aquatic concentration of these compounds, and not particularly related to the food intake. Further strong bio-accumulation occurs in fish-eating birds and mammals.

DDT was shown to cause eggshell thinning in predatory birds in the late 1960's, caused by the widespread use of DDT as a pesticide in agriculture. This thinning of eggshells also occurred in marine predatory birds, such as the whitetailed eagle, probably due to biomagnification in the aquatic environment of DDT from atmospheric fallout (Helander et al., 1982).

Following the discovery of PCB's in the Baltic, polychlorinated biphenyls have been shown to cause reproduction failure in seals and otter in this area (Helle et al., 1976 a,b; Sandegren et al., 1980). This, and the occurrence of open skin lesions and skeletal disorders have reduced the populations of the 3 indigenous seal species in the Baltic to only a few per cent of the original numbers. Porpoises and sea otters have also become almost extinct in the same area. Chlorinated hydrocarbons in fish also cause reproduction failure in wild and farm mink (Jensen et al., 1977).

There is an extensive literature on the concentrations of chlorinated hydrocarbons in biota, and on the toxicology and effects of these compounds. A comprehensive review of this literature is beyond the scope of this report. In addition to the examples given above, however, reference should be made to the OECD Wildlife Sampling and Analysis Programme (OECD, 1980).

For humans, enrichment in the terrestrial food chain, via herbivorous animals, meat, and dairy products, is more important for the general population than the fish consumption. The toxicology of organochlorine pesticides and 2,3,7,8-TCDD has been reviewed for the Commission of the European Communities (Mercier et al., 1981). More recently the toxicology and environmental exposure situation for PCB's, PCDD's and PCDF's have been reviewed by the World Health Organization (Rantanen et al., 1987). While reporting cases of occupational and accidental exposures, and recommending procedures for prevention and management of accidents, this report also shows that the exposure of the general population, mainly through ingestion of contaminated food (aquatic organisms, meat, and dairy products) results in levels of PCB's and PCDD/PCDF's in human fat tissue and mothers milk, which give reason for serious concern.

Chlorinated hydrocarbons in soil and vegetation may also be transferred to watercourses. Olson et al. (1978) found seasonal variations of PCB's in freshwater fish (roach) corresponding to surface runoff intensity. A likely explanation is runoff of PCB's in association with colloidal soil particles, and that PCB's are released to the water and fish when the humus is broken down in the aquatic environment. This would also lead to reemission of PCB's to the atmosphere.

13 CONCLUSIONS

There is enough quantitative information available to describe the airborne concentrations and deposition of trace elements on the basis of known emissions and atmospheric processes. The concentration levels of several trace elements, in particular Pb and Cd in air, have decreased markedly over the passed 10-20 years, due to control measures and to improvements in industrial technology. This situation may not apply to atmospheric mercury, which is not correlated with the trace elements associated with the submicron aerosols. This is due to the chemical properties of mercury which is present in the atmosphere both in oxidized forms and as elemental mercury vapour. Knowledge of the emission of mercury from fossil fuel combustion and other sources is still incomplete, however, and information on the chemical speciation lacking. Re-emission of already deposited mercury is a complicating factor.

The situation is even more complicated for chlorinated hydrocarbons, where emissions are difficult to quantify because of their fugitive character. There are few measurements of airborne concentrations, and the mechanisms and rates of deposition are not well defined. Atmospheric deposition has been shown to be highly significant in relation to the occurrence of DDT and PCB's in aquatic ecosystems, however. Restrictions in the use of DDT have reduced environmental contamination levels, but the regulations have not been effective for PCB's. Airborne concentrations and deposition of this contaminant is at the same level today as in 1973. As a consequence, the environmental damage is still significant.

It is an open question if this is due to re-emission and recycling of material already released to the environment, or to failure to contain and control these substances. The continued presence of these substances in air and precipitation, more than 15 years after control regulations were passed, calls for an explanation.

Trace elements, mercury, and organochlorine compounds are strongly fixed to soil organic matter and to sediments. Re-emission from sediments has been suggested both for mercury and for organochlorines, and surface runoff is an important mechanism for the transport of all these environmental pollutants to the aquatic environment.

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14 REFERENCES

- Abel, W.T., Rice, R.L., Shang, J.Y., Turek, D.G. and Ayers, W.J. (1981) Combustion of western coal in a fluidized bed. Morgantown WV, USA, Department of Energy, Morgantown Energy Technology Center, 32 pp.
- Ahmed, R., May, K., and Stoeppler, M. (1987) Wet deposition of mercury and methylmercury from the atmosphere. The Science of Total Environment, 60, 249-261.
- Amundsen, C.E. (1987) Langtransport av luftforurensninger studert ved analyse av filterprøver fra Birkenes. Trondheim, Universitetet i Trondheim (in Norwegian).
- Amundsen, C.E., Hanssen, J.E., Rambeck, J.P., Semb, A., and Steinnes, E. (1986) Long-range transport of trace elements to Southern Norway studied by I.N.A.A. of air filters. In: Proc. Modern Trends in Activation Analysis Conf., Copenhagen, Denmark.
- Andreae, M.O., Asami, T., Bertine, K.K., Buat-Menard, P., Duce, R.A., Filip, Z., Förstner, U., Goldberg, E.D., Heinrichs, H., Jernelov, A., Pacyna, J.M., Thornton, I., Tobschall, H.J. and Zoller, W. (1984) Changing biogeochemical cycles. In: Changing Metal Cycles and Human Health, Ed. by J.O. Nriagu. Berlin, Springer-Verlag. pp. 359-374.
- Andreae, M.O. and Froelich, P.N. (1984) Arsenic, antimony and germanium biogeochemistry in the Baltic Sea. Tellus, 36B, 101.
- Andren, A.W., Lindberg, S.E., and Bate, L.C. (1975) Atmospheric input and geochemical cycling of selected trace elements in Walker Branch Watershed. Oak Ridge, TN, Oak Ridge National Laboratory (ORNL Report NSF-EATC-13).
- Anonymus (1981) Pesticides in China. Kongetsu no Noyaku (Monthly Review of Pesticide), 114-116 (in Japanese).
- Arnold, M., Seghaier, A., Martin, D., Buat-Menard, P., and Chesselet, R. (1982) Geochimie de l'aerosol marin au-dessus de la Mediterranee Occidentale. Vies Journées Etud. Pollutions, Cannes, France.
- Atkins, D.H.F. and Eggelton, A.E.J. (1971) Studies of Atmospheric Washout and Deposition of BHC, Dieldrin and p, p' DDT using Radio-labelled Pesticides. Internat. Atomic Energy Agency, SM/142a/32, 521.

ATMOS (1986) Emission activities. The Netherlands. In: Proc. the 4th Meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters, Oslo.

van Aalst, R.M., van Ardenne, R.A.M., de Kreuk, J.F., and Lems, Th. (1982) Pollution of the North Sea from the atmosphere. Delft, The Netherlands. Netherlands Organization for Applied Scientific Research, (TNO Report CL 82/152).

van Aalst, R.M., van Ardenne, R.A.M., de Kreuk, J.F. and Lems, Th. (1983) Pollution of the North Sea from the Atmosphere. Delft, the Netherlands. TNO.

Bacci, E., and Gaggi, C. (1985) Polychlorinated biphenyls in plant foliage: Translocation or volatilization from contaminated soils? Bull. Environ. Contam. Toxicol., 35(5), 673-681.

Bacci, E., and Gaggi, C. (1986) Chlorinated pesticides and plant foliage: Translocation experiments. Bull. Environ. Contam. Toxicol., 37(6), 850-857.

Ballschmiter, K., Niemczyk, R., Schäfer, W., and Zoller, W. (1987) Isomer-specific identification of polychlorinated benzenes (PCBz) and -biphenyls (PCB) in effluents of municipal waste incineration. Fres. Z. Analyt. Chem., 328, 583-587.

Barbour, A.K., Castle, J.F., and Woods, S.E. (1978) Production of non-ferrous metals. In: Industrial Air Pollution Handbook. Ed. by A. Parker. London, McGraw-Hill. pp. 419-493.

Baumann, K., Angerer, J., Heinrich, R., and Lehnert, G. (1980) Occupational exposures of hexachlorocyclohexane. 1. Body burden of HCH isomers. Int. Arch. Occup. Environ. Health, 47, 119-127.

Barrie, L.A., Lindberg, S.E., Chan, W.H., Ross, H.B., Arimoto, R., and Church, T.M. (1987) On the concentration of trace metals in precipitation. Atmos. Environ., 21, 1133-1135.

~~Bekämpningsmedel (1982) The use of pesticides in Sweden, Stockholm.~~

Bennett, B.G. (1981) Exposure commitment assessments of environmental pollutants. Vol. 1. No. 1. London, Monitoring and Assessment Research Centre (MARC Rept. 23).

- Bennett, B.G. (1984) Modeling exposure routes of trace metals from sources to man. In: Changing Metal Cycles and Human Health, J.O. Nriagu, ed. Berlin, Springer-Verlag, 345-356.
- Bergkvist, B. (1987) Soil solution chemistry and metal budgets of spruce forest ecosystems in S. Sweden. Water, Air and Soil Poll., 33, 131-154.
- Bidleman, T.F., and Olney, C.E. (1974) High volume collection of atmospheric polychlorinated biphenyls. Bull. Environ. Contam. Toxicol., 11, 442-450.
- Bidleman, T.F., and Christensen, E.J. (1979) Atmospheric removal processes for organochlorines. J. Geophys. Res., 84, 7857-7862.
- Bidleman, T.F., Billings, W.N., and Foreman, W.T. (1986) Vapor-particle partitioning of Semivolatile Organic Compounds: Estimates from Field Collections. Environ. Sci. and Technol., 20, 1038-1043.
- Bidleman, T.F., Wideqvist, U., Jensson, B., and Söderlund, R. (1987) Organochlorine pesticides and polychlorinated biphenyls in the Atmosphere of Southern Sweden. Atmos. Environ., 21, 641-647.
- Billings, W.N., and Bidleman, T.F. (1980) Field comparison of polyurethane foam with Tenox-GC resin for high volume sampling of chlorinated hydrocarbons. Environ. Sci. Technol., 14, 679-683.
- Billings, W.N., and Bidleman, T.F. (1983) High volume collection chlorinated hydrocarbons in urban air using three solid adsorbents. Atmos. Environ., 17, 383-391.
- Boutron, C.f., Patterson, C.C., Petrov, V.N., and Barkev, N.I. (1987) Preliminary data on changes of lead concentrations in Antarctic ice from 155,000 to 26,000 years BP. Atmos. Environ., 21, 1197-1202.
- Braun, H., Vogg, H., Halbritter, G., Bräutigam, K.-R., and Katzer, H. (1984) Comparison of the Stack Emissions from Waste Incineration Facilities and Coal Fired Heating Power Stations. Recycling International, 1, 1-2.
-
- Brække, F.H. (1976) Impact of acid precipitation on forest and freshwater ecosystems in Norway. SNSF Project Research Report, Phase 1, 1972-75. Oslo, Norwegian Institute for Forest Research.

Brosset, C. (1981) The mercury cycle. Water, Air, and Soil Poll., 16, 253-255.

Brosset, C. (1982) Total airborne mercury and its possible origin. Water, Air and Soil Poll., 17, 37-50.

Brosset, C. (1987) The behaviour of mercury in the physical environment. Water, Air, and Soil Poll., 34, 145-166.

Brügmann, L., (1986) Contamination of the Baltic Sea atmosphere by metal concentration levels and inputs, ATMOS 47INFO. 5-E Paper presented at the Fourth Meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters, Oslo, 28-30 October.

Buat-Menard, P., and Arnold, M., (1978) The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna Volcano. Geophys. Res. Lett., 5, 245.

Buck, M., and Kirschmer, P. (1987) Measurements of polychlorinated dibenzo-p-dioxins and dibenzofurans in outdoor air in North-Rhine-Westphalia. Essen, FRG. Landesanstalt für Immissionsschutz, (LIS-Bericht Nr 62).

Buckley, Edward H. (1982) Accumulation of airborne polychlorinated biphenyls in foliage. Science, 216, 520-522.

Buser, H.R., and Bosshardt, H.-P. (1978) Polychlorierte Dibenzo-p-dioxine, Benzofurane und Benzole in der Asche kommunaler und industrieller Verbrennungsanlage. Mitt. Gebiete Lebensm. Hyg., 69, 191-199.

Bølviken, B., and Steinnes, E. (1987) Heavy metal contamination of natural surface soils in Norway from long-range atmospheric transport: further evidence from analysis of different soil horizons. In: Proc. Int. Conf. Heavy Metals in the Environment, New Orleans, September.

Cambray, R.S., Jefferies, D.F., and Topping, G. (1975) An estimate of the input of atmospheric trace elements into the North Sea at Clyde (1972-73). AERE Harwell, England (AERE Report R 7733).

Campbell, I., and McConnell, G. (1980) Chlorinated paraffines and the environment. 1. Environmental occurrence. Environ. Sci. Technol., 14, 1209-1214.

- Carlberg, E., Ofstad, E., Drangsholt, H., and Steinnes, E. (1983) Atmospheric deposition of organic micropollutants in Norway studied by means of moss and lichen analysis. Chemosphere, 12, 341-356.
- Carpenter, R.L. (1979) Fluidized bed combustion emissions toxicology program. Status report. Albuquerque, NM, USA Lovelace Biomedical and Environmental Research Institute, 49 pp.
- Cawse, P.A. (1974) A survey of atmospheric trace elements in the U.K. (1972-73). AERE Harwell, England (AERE Report R 7669).
- Cawse, P.A. (1980) Deposition of trace elements from the atmosphere in the U.K.. In: Inorganic Pollution and Agriculture, Ministry of Agriculture, Fisheries and Food, 326, London.
- Cawse, P.A. (1981) Trace elements in the atmosphere of the U.K. - Paper given at ESNA meeting, Aberdeen.
- Cunningham, R.T., Brann, J.L., Jr., and Fleming, G.A. (1962) Factors affecting the evaporation of water from droplets in airblast sprayings. J. Econ. Entomol., 55, 192.
- Davidson, C.I., and Osborn, J.F. (1986) The sizes of airborne trace metal containing particles. In: Toxic Metals in the Atmosphere. J.O. Nriagu and C.I. Davidson, eds., John Wiley & Sons.
- Dawson, R., and Riley, J.P. (1977) Chlorine-Containing Pesticides and PCB in British Coastal Waters. Estuar. Coast. Mar. Sci., 4, 55-65.
- Diederer, H.S.M.A., Hartog, J.C. den, Hollander, J.C.Th., Kaayk, J., and Schulting, F.L. (19..) Nivean's van luchveroutrouwing gemeten over de periode januari 1979-Maart 1981. TNO, Delft (Rapport CMP 81/02).
- Doguchi, M. (1977) Ecotoxicol. Environ. Saf., 1, 239.
- Doskey, P.V., and Andren, A.W. (1979) High-volume sampling of Airborne PCB's with Amberlite XAD-2. Anal. Chim. Acta, 110, 129.
- Eisenreich, S.J., Looney, B.B., and Thornton, J.D. (1981) Airborne organic contaminants in the Great lakes ecosystem. Environ. Sci. Technol., 15, 30-38.

- Eliassen, A. and Saltbones, J. (1983) Modelling of long-range transport of sulphur over Europe: a two year model run and some model experiments. Atmos. Environ., 17, 1457-1473.
- van Enk, R.H. (1980) The pathway of cadmium in the European Community. European Appl. Res. Rept. Environ. and Nat. Res. Sec., 1:1.
- EPRI (1979) Disposal of Polychlorinated Biphenyls (PCB's) and PCB-contaminated Materials. FP-1207. Palo Alto, California, Electric Power Research Institute.
- EUR (1981) Ecotoxicology of cadmium, 1981. Ecotoxicology Section of the Scientific Advisory Committee to examine the Toxicity and Ecotoxicity of Chemical Compounds. Brussels, Commission of the European Communities (EUR Rep. 7499 EN).
- FAO (1978, 1980, 1986) FAO Production yearbooks. Rome. Food and Agriculture Organisation.
- Feely, H.W., Volchok, H.L., and Toonkel, L. (1976) Trace metals in atmospheric deposition, New York, U.S. ERDA, Health and Safety Laboratory (Environmental Quarterly Report HASL-308).
- Frøslie, A., Norheim, G., Rambæk, J.P., and Steinnes, E. (1985). Heavy metals in lamb liver: contribution from atmospheric fallout. Bull. Environ. Contam. Toxicol., 34, 175-182.
- Gerstle, R.W. and Albrinck, D.N. (1982) Atmospheric emissions of metals from sewage sludge incineration. J. Air Poll. Contr. Ass., 32, 1113-1123.
- Glowiak, B.J., Palczynski, R.J., and Pacyna, J.M. (1977) Environmental lead and mercury in the area of a copper smelter. New York, U.S. ERDA, Health and Safety Laboratory (Environmental Quarterly Report HASL-321).
- Goldberg, E.D. (1973) North Sea Science. Cambridge, MS. MIT Press.
-
- Grahn, O. and Rosén, K. (1983) Deposition och transport av metaller i några stora avrinningsområden i sydvästra, mellersta och norra Sverige. Solna, Statens Naturvårdsverk.
- Granat, L. (1982) Opublicerade uppgifter om tungmetalldeposition.

- Hanssen, J.E., Ramback, J.P., Semb, A., and Steinnes, E. (1980) Atmospheric deposition of trace elements in Norway. In: Proc. Ecological Impact of Acid Precipitation Conf., Sandefjord, Norway. Ed. by D. Drabløs and A. Tollan.
- Hapke, H.-J., ed. (1983) Hexachlorocyclohexan als Schadstoff in Lebensmitteln. Weinheim, FRG. Verlag Chemie.
- Harrison, R.M. (1986) Chemical speciation and reaction pathways of metals in the atmosphere. In: Toxic Metals in the Atmosphere. J.O. Nriagu and C.I. Davidson, eds. New York, John Wiley & Sons, pp. 319-334.
- Harris, R.C. and Hohenemser, C. (1978) Mercury. Measuring and managing the risk. Environment, 20, 25-36.
- Harvey, G.R., and Steinhauer, W.G. (1974) Atmospheric Transport of Polychlorobiphenyls to the North Atlantic. Atmos. Environ., 8, 777-787.
- Heesen, Th.C., Young, D.R., McDermott-Ehrlich, D. (1979) Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB residues. Atmos. Environ., 13, 1677-1680.
- Heidam, N.Z. (1986) Trace metals in the Arctic aerosol. In: Toxic Metals in the Atmosphere. Nriagu, J.O. and Davidson, C.I., eds. New York, John Wiley & Sons.
- Heinrichs, H. and Mayer, R. (1977) Distribution and cycling of major and trace elements in two Central European forest ecosystems. J. Environ. Quality, 6, 402-407.
- Helander, B., Olsson, M., and Reutergårdh, L. (1982) Residue levels of organochlorine and mercury compounds in unhatched eggs and the relationship to breeding success in white-tailed sea eagles *Haliaeetus Albicilla* in Sweden. Holarctic Ecology, 5, 349- .
- Helle, E., Olsson, M., and Jensen, S. (1976a) DDT and PCB levels and reproduction in ringed seal from the Bothnian Bay. Ambio, 5, 188- .
- Helle, E., Olsson, M., and Jensen, S. (1976b) PCB levels correlated with pathological changes in seal uteri. Ambio, 5, 261-263.

- Hewitt, E.J., and Smith, I.A. (1974) Plant Mineral Nutrition. Cambridge, England. English University Press.
- Hidy, G.M. (1984) Source-receptor relationships for acid deposition: pure and single? A critical review. JAPCA, 39, 518-531.
- Hoff, R.M., and Chan, K-W. (1986) Atmospheric concentrations of chlordane at Mould Bay, N.W.T., Canada. Chemosphere, 15, 449-452.
- Hovmand, M.F. (1979) Atmospheric heavy-metal deposition on land and sea. In: International Council for Exploration of the Sea, 67th meeting, Warsaw.
- Hutton, M. (1982) Cadmium in the European Community, London. Monitoring and Assessment Research Centre (MARC Report 26).
- Hutton, M. and Symon, C. (1986) The quantities of cadmium, lead, mercury, and arsenic entering the U.K. environment from human activities. Sci. Total Environ., 57, 129-150.
- Hvatum, O.Ø., Bølviken, B. and Steinnes, E. (1983) Heavy Metals in Norwegian Ombrotrophic Bogs. In: Environmental Biogeochemistry. Ed. R. Hallberg. Stockholm (Ecol. Bull., 35) pp. 351-356.
- ICES (1978) Input of pollutants to the Oslo Commission area, Cooperative Research 77. Charlottenlund, Denmark. Int. Council for the Exploration of the Sea.
- Iverfeldt, Å., and Johansson, K. (1987) Mercury in run-off water from small watersheds. Verh. Internat. Verein. Limnol., Stuttgart.
- Iverfeldt, Å., and Rodhe, H. (1988) Atmospheric transport and deposition of mercury in the Nordic countries. Progress report to the Nordic Council of Ministers, Copenhagen.
- Jalees, K., and Vemuri, R. (1980) Pesticide in India. Int. J. Environ. Stud., 15, 49-554.
-
- Janicki, K. (1976) Pestycydy, gleba, człowiek. Warszawa, Wiedza Powszechna, pp. 1-152 (in Polish).
- Jensen, S. (1966) New Scientist, 32, 612.

- Jensen, S., Kihlström, J.E., Olsson, M., Lundberg, C., and Orberg, J. (1977) Effects of PCB and DDT on mink (*Mustela vison*) during the reproductive season. Ambio, 6, 239- .
- Johansson, K. (1984) Mercury in sediment in Swedish forest lakes. Verh. Internat. Verein, Limnol., 22, 2359-2363.
- Junge, C.E. (1977) Basic Considerations About Trace Constituents in the Atmosphere as Related to the Rate of Global Pollutants. Advancements in Environmental Sciences and Technology. New York, Wiley & Sons. pp 7-25.
- Kawano, M., Tanabe, S., Inoue, T., and Tatsukawa, R. (1985) Chlordane compounds found in the marine atmosphere from the southern hemisphere. Trans. Tokyo Univ. Fisheries, 1985(6), 59-66.
- Kemikaliekontrollen (1982) Statistiske oplysninger vedrørende forbrug og salg af bekæmpelsesmidler for 1981. Lyngby (in Danish).
- Kendall, P.M.H., Bevington, C.F.P. and Pearse, D.J. (1985) Atmospheric Cadmium Emission and Deposition in the Netherlands. Kockengen, Metra Consulting BV.
- KHM (1983) Project Coal, Health and Environment. Vällingby, Sweden. The Swedish State Power Board.
- Kihlström, J.E., and Berglund, E. (1978) An Estimation of the Amounts of Polychlorinated Biphenyls in the Biomass of the Baltic. Ambio, 7, 175-178.
- Komarov, B. (1980) The destruction of nature in the Soviet Union. New York, Sharpe Inc.
- Kopecki, K. (1981) Energy future in Poland, Omega, Wiedza Powszechna. pp. 247 (in Polish).
- Korolev, S.M. (1984) Input of organochlorine pesticides from the atmosphere onto the Baltic Sea water area. Baltic Marine Environment Protection Commission. Helsinki Commission. First meeting of the group of airborne pollution into the Baltic Sea Area. Stockholm, 18-21 Sept.
- Kover, F.D. (1975) Environmental Hazard Assessment - Chlorinated Naphthalenes. Washington. Environmental Protection Agency.

Krell, U., Lehmhaus, J., and Roeckner, E. (1986) Atmospheric input of heavy metals into the North Sea: First results of a 3-dimensional trajectory model. In: Proc. WMO Conf. on Air Pollution Modelling and Its Application, Leningrad, USSR, 18-24 May.

Kubacka, J., Pacyna, J.M., and Palczynski, R.J. (1977) Chemical composition of metalloferrous dust discharged from stacks of the copper smelters. Scientific Papers of Environmental Protection Engineering Institute, Technical University of Wroclaw, Wroclaw, Poland.

Kveseth, N.J., Bjerk, J.E., Fimreite, N., and Stenersen, J. (1979) Residues of DDT in a Norwegian fruit-growing district two and four years after the termination of DDT usage. Arch. Environ. Contam. Toxicol., 8, 201-212.

Lannefors, H.O., Hansson, H.-C., Winchester, J.W., Akselsson, K.R., Pallon, J.H., Johansson, S.A.E., Darzi, M. and Rheingrover, S.W. (1980) Interelement and multi-station concentration evidence for large scale aerosol sulfur transport accross Sweden. Tellus, 32, 548.

Lannefors, H.O., Hansson, H.-C., and Granat, L. (1982) Background aerosol composition in Southern Sweden - 14 micro and macro constituents measured in seven particle size intervals at one site during one year. In: Applications of Particle Induced X-ray Emission Analysis to Ambient Aerosol Studies. Ph. D. thesis, University of Lund, Sweden.

Lannefors, H.O., Hansson, H.-C., and Granat, L. (1983) Background aerosol composition in Southern Sweden - fourteen micro and macro constituents measured in seven particle size intervals at one site during one year. Atmos. Environ., 17, 87.

Larsen, B.R., Løkke, H., and Rasmussen, L. (1985) Accumulation of chlorinated hydrocarbons in moss from artifical rainwater. Oikos, 44, 423-429.

Larsson, P., and Södergren, A. (1987) Transport of Polychlorinated Biphenyls (PCB's) in Freshwater Microcosms from Sediment to Water and Air. Water, Air, Soil. Poll., 36, 33-46.

Larsson, P., and Okla, L. (1987) Preliminary final report of the project: Transport of persistent organic chemicals to and from the atmosphere. (In Swedish.) University of Lund, Ecology Department.

- Lindqvist, O., Jernelöv, A., Johansson, K., and Rodhe, H. (1984) Mercury in Swedish Environment. Global and Local Sources. Solna, National Swedish Environmental Protection Board (SNV PM 1816), pp. 121.
- Lindqvist, O., and Rodhe, H. (1985) Atmospheric mercury - a review. Tellus, 37B, 136-159.
- Liss, P.S., and Slater, P.G. (1974) Fluxes of gases across the air - sea interface. Nature, 247, 181-184.
- Lowenthal, D.H., and Rahn, K.A. (1985) Regional sources of pollution aerosol at Barrow, Alaska during winter 1979-1980 as deduced from elemental tracers. Atmos. Environ., 19, 2011-2024.
- Mackay, D., Paterson, S., and Schroeder, W.H. (1986) Model describing the rates of transfer of organic chemicals between atmosphere and water. Environ. Sci. Technol., 20, 810-816.
- Martinsson, B.G., Hansson, H.-C. and Lannefors, H.O. (1984) Atmos. Environ., 18, 2167-2182.
- Matelski (1987) Przegląd Techniczny (Technical Weekly), 10, 14. (in Polish).
- Mathys, G. (1984) The use of lindane in the countries of European and Mediterranean Plant Protection Organization. Private communication.
- Mercier, M. (Rapporteur) (1981) Criteria (Dose/Effect Relationships) for Organochlorine Pesticides. Report of a working group of experts prepared for the Commission of the European Communities, Directorate-General for Employment and Social Affairs, Health and Safety Directorate. Oxford, Pergamon Press.
- Michaelis, W. (1987) Experimental studies on dry deposition of heavy metals and gases. In: Proc. 16th Int. Techn. Meeting on Air Pollution Modelling and Its Applications, NATO, Lindau, FRG.
-
- Miljøverndepartementet (1984) Kommunal avfallshandtering - idag og fram mot år 2000. Oslo (Rapport T-580).
- Mukherjee, A.B. (1986) The discharge of lead, cadmium and mercury into the ecosystem in relation to Finish industry. Helsinki University of Technology (SF-02150).

Murphy, T.J., and Rzeszutko, C.P. (1977) Precipitation inputs of PCB's to Lake Michigan. J. Great Lakes Res., 3, 305-312.

Murphy, T.J., Mullin, M.D., and Meyer, J.A. (1987) Equilibration of polychlorinated Biphenyls and toxaphene with Air and Water. Environ. Sci. Technol., 21, 155-162.

National Academy of Sciences (1979) Polychlorinated Biphenyls. Washington D.C.

Naturvårdsverket (1982) Monitor 1982. Tungmetaller och organiska miljögifter i svensk natur.

Naturvårdsverket (1987) Monitor 1987. Tungmetaller - förekomst och omsättning i naturen.

NILU (1984) Emission sources in the Soviet Union. Lillestrøm, Norwegian Institute for Air Research (NILU TR 4/84).

Norsk Hydro (1978) Magnesiumfabrikkene får bukt med de mystiske klorerte hydrokarboner. (Magnesium plant gets rid of chlorinated hydrocarbons). Miljøvernaktuellet, Juni 1977, p 4-5 (In Norwegian).

NRCC (1978) Effects of arsenic in the Canadian Environment. Ottawa, National Research Council Canada (NRCC No. 15391).

Nriagu, J.O., ed. (1984) Changing Metal Cycles and Human Health, Dahlem-Konferenzen, Berlin. Springer-Verlag.

Nürnberg, H.W., Valenta, P., and Nguyen, V.D. (1983) The wet deposition of heavy metals from the atmosphere in the Federal Republic of Germany. In: Proc. Int. Conf. on Heavy Metals in the Environment, Heidelberg. Edinburgh, CEP Consultants.

Nyholm, E. (1986) Metaller i däggdjur och fåglar. Solna, Sweden. Naturvårdsverket (SNV PM Rept.).

OECD (1977) The OECD programme on Long Range Transport of Air Pollutants. Measurements and Findings. Paris, Organisation for Economic Co-operation and Development.

OECD (1979) The OECD Programme on Long Range Transport of Air Pollutants. Measurements and Findings, Second Edition. Paris, Organization for Economic Co-operation and Development.

OECD (1980) Chemical trends in wildlife. An International Co-operative Study. Paris, Organisation for Economic Co-operation and Development.

Oehme, M., and Stray, H. (1982) Quantitative determination of ultra-traces of chlorinated compounds in high volume air samples from the Arctic using polyurethane foam as a collection medium. Fres. Z. Anal. Chem., 311, 665-673.

Oehme, M., and Manø, S. (1984) The long-range transport of organic pollutants to the Arctic. Fres. Z. Anal. Chem., 319, 141-146.

Oehme, M., Manø, S., and Mikalsen, A. (1987) Formation and presence of polycyclic compounds in the emissions of small and large scale municipal waste-incinerators. Chemosphere, 16, 143-153.

Olafson, R.W. (1978) Effect of agricultural activity on levels of organochlorine pesticides in hard coals, fish and molluscs from the Great Barrier Reef. Mar. Environ. Res., 1, 87-107.

Olsson, M., Jensen, S., and Reutergårdh, L. (1978) Seasonal variation of PCB levels in fish - a factor of importance when planning aquatic monitoring programmes. Ambio, 7, 66-69.

Ondov, J.M., Ragaini, R.C., and Bierman, A.H. (1979) Elemental emissions from a coal-fired power plant. Comparison of a venturi wet scrubber system with a cold-side electrostatic precipitator. Environ. Sci. Technol., 13, 588-601.

Ottar, B., Hov, Ø., Iversen, T., Joranger, I., Oehme, M., Pacyna, J.M., Semb, A., Thomas, W., and Vitols, V. (1986) Air pollutants in the Arctic. Final report of a research programme conducted on behalf of British Petroleum Ltd. Lillestrøm, Norwegian Institute for Air Research (NILU OR 30/86).

Pacyna, J.M. (1980) Coal fired power plants as a source of environmental contamination by trace metals and radionuclides. Habilitation thesis. Technical University of Wroclaw, Poland.

Pacyna, J.M. (1982) Trace element emissions from coal- and oil-power plants in Europe. Methodology of calculations. Lillestrøm, Norwegian Institute for Air Research (NILU TR 5/82).

Pacyna, J.M. (1983) Trace element emission from anthropogenic sources in Europe. Lillestrøm, Norwegian Institute for Air Research (NILU TR 10/82).

- Pacyna, J.M. (1985) Spatial distribution of the As, Cd, Cu, Pb, V and Zn emissions in Europe within a 1.5 grid net. Lillestrøm, Norwegian Institute for Air Research (NILU OR 60/85).
- Pacyna, J.M. (1986) Atmospheric heavy metals measured at the EMEP stations. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Rept. 3/86).
- Pacyna, J.M. (1987a) Atmospheric emissions of arsenic, cadmium, mercury and zinc in Europe in 1982. Lillestrøm, Norwegian Institute for Air Research (NILU OR 17/88).
- Pacyna, J.M. (1987b) Atmospheric emissions of Cd and Hg from anthropogenic sources in FRG. Lillestrøm, Norwegian Institute for Air Research (NILU OR 65/87).
- Pacyna, J.M. (1987c) Atmospheric emissions of As, Cd, Pb and Hg from high-temperature processes in power generation and industry, and their atmospheric transport. In: Lead, Mercury, Cadmium and Arsenic in the Environment, Ed. by T.C. Hutchinson and K.M. Meema. Chichester, John Wiley.
- Pacyna, J.M. (1988) Source-receptor relationships for atmospheric trace elements in Europe. In: Acid Precipitation. Vol. 2. Sources, Emissions, and Mitigation, ed. D.C. Adriano. New York, Springer-Verlag.
- Pacyna, J.M., Zwozdziak, A., Zwozdziak, J., Matyniak, Z., Kuklinski, A., and Kmiec, G. (1981) Zagadnienia ochrony powietrza atmosferycznego dla stanu istniejacego i perspektywicznego na obszarze pilotowym wojewodztwa legnickiego. (Air pollution problems caused by the LGOM copper smelter complex - present situation and perspectives.) Wroclaw, Poland Technical University of Wroclaw (Report SPR 14-81) (in Polish).
- Pacyna, J.M., Semb, A., and Hanssen, J.E. (1984a) Emission and long-range transport of trace elements in Europe. Tellus, 36B, 163-178.
- Pacyna, J.M., Ottar, B., Hanssen, J.E., and Kemp, K. (1984b) ~~The chemical composition of aerosols measured in Southern Scandinavia.~~ Lillestrøm, Norwegian Institute for Air Research (NILU OR 66/84).
- Pacyna, J.M., and Ottar, B. (1985) Transport and chemical composition of the summer aerosol in the Norwegian Arctic. Atmos. Environ., 19, 2109-2120.

Pacyna, J.M., Ottar, B., Tomza, U., and Maenhaut, W. (1985) Long-range transport of trace elements to Ny Ålesund, Spitsbergen. Atmos. Environ., 19, 857-865.

PARCOM (1985) Sixth Annual Report of the Paris Commission, Anex 6. London.

PARCOM (1986) Report from the Fourth Meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters, Oslo 28-30 October.

Patton, G.W., Hinkley, D.A., Walla, M.D., Bidleman, T.F., and Hargrave, B.T. (1987) Airborne organochlorines in the Canadian high Arctic. Paper presented at: 6th International Symposium of the Commission on Atmospheric Chemistry and Global Pollution on: Global Atmospheric Chemistry. Peterborough, Canada, August 23-28, 1987.

Paulsen, J. (1984) The sales of lindane in Norway - private communication from Landbruksdepartementets Giftnemnd, Ås - NLH.

Pearson, C.R. (1982) Halogenated aromatics. In: Hutzinger, O. (ed.): Handbook of environmental Chemistry. Anthropogenic compounds. Vol 3, part B. Berlin, Springer Verlag, pp 89-116.

Peterle, T.J. (1968) DDT in antarctic snow. Nature, 224, 620.

Petersen, G. (1987) Methodology for model calculations of the atmospheric input of trace metals into the North Sea and the Baltic Sea. In: Proc. PARCOM Meeting, ATMOS-5, Berlin, 10-12 November.

Pheiffer Madsen, P. (1981) Peat bog records of atmospheric mercury deposition. Nature, 283, 127-129.

Pooler, F. J.r. (1971) Atmospheric transport and dispersion of pesticides. In: Proc. 162nd Natl. Meet. Am. Chem. Soc., Washington D.C.

Quinlivan, S.C., and Ghassemi, M. (1977) Sources, characteristics and treatment and elisposal of industrial wates ontaining hexachlorobenzene. J. Hazardous Materials, 1, 343-359.

Rahn, K.A. (1976) The chemical composition of the atmospheric aerosol. Technical Report. Kingston, R.I., Graduate School of Oceanography, University of Rhode Island.

Rahn, K.A., Lowenthal, D.H., and Lewis, F.N. (1982) Elemental tracers and source areas of pollution aerosol in Narrangansett, RI. Techn. Rept., Narrangansett, RI. University of Rhode Island.

Rahn, K.A., and Lowenthal, D.H. (1984) Elemental tracers of distant regional pollution aerosols. Science, 223, 132-139.

Rantanen, J.H., Silano, V., Taskowski, S., and Yrjheikki, E. (eds. 1987). PCB's, PCDD's and PCDF's: Prevention and control of accidental and environmental exposures. København, WHO (Environmental Health Series, 23), 227 p.

Risebrough, R.W., Huget, R.J., Griffin, J.J., and Goldberg, E.D. (1968) Pesticides: transatlantic movements in the northeast trades. Science, 159, 1233.

Rodhe, H., Söderlund, R., and Ekstedt, J. (1980) Deposition of airborne pollutants on the Baltic. Ambio, 9, 168-173.

Rosén, K. (1982) Supply, loss and distribution of nutrients in three coniferous forest watersheds in central Sweden. Uppsala, Sveriges lantbruksuniversitet. (Rapporter i skogsekologi och skoglig marklära, 41.)

Ross, H.B. (1986) Trace metals in the atmosphere. The wet deposition of trace metals in Sweden. The selenium cycle. Stockholm, University of Stockholm.

Ross, H.B. (1987) Trace metals in precipitation in Sweden. Water, Air and Soil Poll., 36, 349-363.

Rühling, Å., and Tyler, G. (1968) An ecological approach to the lead problem. Botaniska Notiser, 121, 321-342.

Rühling, Å., and Tyler, G. (1984) Recent changes in the deposition of heavy metals in Northern Europe. Water, Air and Soil Poll., 22, 173-180.

Rühling, Å., Rasmussen, L., Pilegaard, K., Mäkinen, A., and Steinnes, E. (1987) Survey of atmospheric heavy metal deposition in the Nordic countries in 1985-monitored by moss analyses. København, Nordisk Ministerråd (NORD 1987:21).

- Ruppert, J. (1975) Geochemical investigations on atmospheric precipitation in a medium-sized city (Göttingen, FRG), Water, Air and Soil Poll., 4, 447.
- Sandegren, F., Olsson, M., Reutergårdh, L. (1980) Der Rückgang des Fishotter - population in Schweden. In: Der Fishotter in Europa - Verbreiten, Bedrohung, Erhalten. Reuther, C. und Festetics, A. (Red.), Selbstverlag, Oderhaus u. Göttingen, p. 107.
- Sartorius, Seifert, B., and Vahrenholt, F. (1977) Emissionsquellen und Immissionssituation für Cadmium in der Bundesrepublik Deutschland. Luft, 37, 11.
- Schladot, J.D., and Nürnberg, H.W. (1982) Report Jül 1976. Jülich, Nuclear Research Center.
- Scott, B.C. (1978) Parameterization of sulphate removal by precipitation. J. Appl. Meteorol., 17, 1375.
- Seba, D.B., and Prospero, J.M. (1971) Pesticides in the lower atmosphere of the northern equatorial Atlantic ocean. Atmos. Environ., 5, 1043.
- Semb, A. (1978) Deposition of trace elements from the atmosphere in Norway. Ås, Norway, SNSF Project (SNSF FR 13/78).
- Serjeantson, R., ed. (1986) Non-ferrous Metal Works of the World, 4th ed. Park House, England, Metal Bulletin Books Ltd.
- Slemr, F., Seiler, W., and Schuster, G. (1981) Latitudinal distribution of mercury over the Atlantic Ocean. J. Geophys. Res., 86, 1159-1166.
- Smith, J.C., Ferguson, T.L., and Carson, B.L. (1975) Metals in new and used petroleum products and by-products. Quantities and consequences. In: The Role of Trace Metals in Petroleum. Ed. by T.F. Yen. Ann Arbor, Ann Arbor Press, pp. 123-148.
-
- Spencer, W.F., Cliath, M.M., Farmer, W.J., and Shepherd, R.A. (1974) Volatility of DDT residues in sorts affected by flooding and organic matter applications. J. Environ. Quality, 3, 126-129.
- Spencer, W.F. (1975) Movement of DDT and its derivatives into the Atmosphere. Residue reviews, 59, pp 91-117.

- Steinnes, E. (1984) Use of mosses in heavy metal deposition studies. In: Proc. EMEP Workshop on Heavy Metals, Lillestrøm, 27-29 August.
- Steinnes, E. (1987) Impact of long-range atmospheric transport of heavy metals to the terrestrial environment in Norway. In: Lead, Mercury, Cadmium and Arsenic in the Environment. Ed. by T.C. Hutchinson and K.M. Meema. Chichester, John Wiley.
- Swackhamer, D.L., and Armstrong, D.E. (1986) Estimation of the atmospheric and nonatmospheric Contribution and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes. Environ. Sci. Technol., 20, 879-883.
- Södergren, A. (1972) Chlorinated hydrocarbons residues in airborne fallout. Nature, 236, 395-397.
- Södergren, A. (1975) Monitoring DDT and PCB in airborne fallout. In: Environmental Quality and Safety. Eds. F. Coulson and F. Korte. Stuttgart, G. Thime Publ., pp 803-810.
- Södergren, A., and Larsson, P. (1982) Transport of PCB's in laboratory model ecosystems from sediment to the atmosphere via the surface microlayer. Ambio, 11, 41-45.
- Söderlund, R., (1975) Some preliminary views on the atmospheric transport of matter to the Baltic Sea. Solna, Sweden (NTIS Report N 76-13641).
- Tanabe, S., Tasukawa, R., Kawano, M., and Hidaka, H. (1982) Global distribution and atmospheric transport of chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern Indian, and Antarctic Oceans. J. Oceanogr. Soc. Japan, 38, 137-148.
- Tatsukawa, R., Wakimoto, T., and Ogawa, T. (1972) BHC residues in the environment. In: Environmental Toxicology of Pesticides. Ed. by F. Matsumara, C.M. Boush and T. Misato. New York, Academic Press. pp. 229-238.
-
- ~~Thomas, W. and Hermann, R. (1980) Nachweis von Chlorpestiziden, PCB, PCA und Schwermetallen mittels epiphytischer Moose als Biofilter entlang eines Profils Durch Mittel-europa. Staub, 40, 440-444.~~
- Tiittanen, K., and Blomquist, H. (1982) Sales of pesticides in Finland in 1981. Kemia - Kemi, 7-8, 528-530.

Travis, C.C., and Hattemer-Frey, H.A. (1988) Uptake of organics by aerial plant parts: A call for research. Chemosphere, 17, 277-283.

UBA (1977) Luftqualitätskriterion für cadmium. Berlin, Umweltbundesamt (Berichte 4/77).

UBA (1981) Cadmium-Bericht. Ein Beitrag zum Problem der Umweltbelastung durch nicht - oder schwer abbaubare Stoffe - dargestellt am Beispiel Cadmium. A. Thormann, red. Berlin, Umweltbundesamt.

UBA (1982) Anhörung zu Cadmium; Protokoll der Sackverständigenanhörung. Berlin, Umweltbundesamt.

USA (1982) Federal Register, 47 (229) 53784-53793.

Valli, R. (1988) Rough estimations of emissions of heavy metals in Finland. Helsinki.

Villeneuve, J.-P., and Holm, E. (1984) Atmospheric background of chlorinated hydrocarbons studied in Swedish lichens. Chemosphere, 13, 1133-1138.

Wang (1981) The status of pesticides in China and their future. J. Pest. Sci., 6, 397-399.

Watson, W.D. (1979) Economic considerations in controlling mercury pollution. In: The Biogeochemistry of Mercury in the Environment, ed. J.O. Nriagu. Amsterdam, Elsevier.

Wells, D.E., and Johnstone, S.J. (1978) The occurrence of organochlorine residues in rainwater. Water, Air, Soil. Poll., 9, 271-280.

Wiersma, G.B. and Davidson, C.I. (1986) Trace metals in the atmosphere of rural and remote areas. In: Toxic Metals in the Atmosphere. J.O. Nriagu and C.I. Davidson, eds. New York, John Wiley & Sons, pp. 201-266.

Wiman, B.L.B. (1984) Aerosol dynamics in coniferous forests, Ph.D. thesis, University of Lund, Sweden.

Wiman, B.L.B., and Ågren, G.I. (1985) Aerosol depletion and deposition in forests - a model analysis. Atmos. Environ., 19, 335-347.

Wolff, E.W., and Peel, D.A. (1985) The record of global pollution in polar snow and ice. Nature, 313, 535-540.

Woodwell, G.M., Craig, P.P., and Johnson, H.A. (1971) DDT in the biosphere: Where does it go? Science, 174, 1101-1107.

Table 1: Perturbations of the geochemical cycles of metals by society (after Andreae et al., 1984).

Element	1) Scale of perturbation			2) Most diagnostic environments	3) Mobility	4) Health concern	5) Critical pathway
	global	regional	local				
As	+	+	+	A, Sd, So, W, P	v,s,a	+	A,W
Be	?	?	+	A	-	(+)	A
Cd	+	+	+	A, Sd, So, W, P	v,s	+	A,F
Co	-	c	+	Sd	r ⁶	E	F
Cr	-	+	+	A, Sd, W, Gw, P	v,s	E	W,F
Cu	+	+	+	A, Sd, W, So, P	v,s	E ⁷	F
Hg	(-)	+	+	A, Sd, Fish, So, (P)	v,a	+	F,A
Mn	-	c,+	+	A, Sd	r,	E	A
Mo	(+)	+	+	A, W, So, Sd	s,	E	F,W
Ni	(+)	+	+	A, Sd, P	v,	E	F,W,A
Pb	+	+	+	A, Sd, I, W, So, P	v,a	+	F,A ⁸
Sb	+	+	+	A, Sd, So, P	v,s	(+)	F,W,A
Se	+	+	+	A, So, P	v,s,a	E	F
V	+	+	+	A, P	v,	(+)	A
Zn	+	+	+	A, Sd, W, So, P	v,s	E	F

- 1) + = significant perturbation; (+) = possible perturbation; (-) = enriched relative to crustal abundances, but the enrichment may not be anthropogenic; - = no perturbation; ? = not enough information; c= enhanced due to mobilization of crustal materials (soil, dust).
- 2) A = air; Sd = sediments (coastal, lake); So = soils; I = ice cores; W = surface waters; Gw = groundwaters; P = peat.
- 3) v = volatile; s = soluble; r= soluble only under reducing conditions; a = mobile as alkylated organometallic species.
- 4) + = toxic in excess; (+) = toxic, but little data available; E = essential, but toxic in excess.
- 5) F = food; W = water, A = air.
- 6) hexavalent form volatile and toxic, trivalent form essential.
- 7) organometallic forms only.
- 8) exposure through hand-to-mouth activity is critical for lead in children.

Table 2: Emission of trace elements in Europe in 1982 (in t/year).

EUROPE	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	V	Zn.
1. Conv.therm.p.pl.*1	330	21	130	790	1200	1380	1010	350	4580	1300	120	160	12600	1510
2. Indust.comm.comb.*2	380	29	150	1210	1580	2040	1380	490	7470	1610	150	220	21800	1780
3. Wood combustion	30		15			1500			385	420				600
4. Gasoline combustion							90		1330	68340				
5. Mining	30					190	280		1640	820		0.2		300
6. Primary n-f metal*3														
6.1 Copper-nickel	3040		260			7850				3990				2060
6.2 Zinc-cadm.	220		450			440				4030		10		18400
6.3 Lead	360		10			120			140	3640				130
7. Second n-f metal*4														
7.1 Copper			5			60				410	1			1780
7.2 Zinc														3760
7.3 Lead			2							150				270
8. Iron, steel metal	330		50		15400	1710	14770		340	3900				9410
9. Refuse incineration	8		40	4	50	260	110		10	540	100	30	19	650
10. Phosphate fertilizer						88			80					190
11. Cement production	210		10		660					610				3740
12. Industr. applic.*5	130		5											
13. TOTAL	5000	50	1100	2000	18900	15500	17700	850	16000	90000	380	420	34500	44600

*1 Conventional thermal power plants.

*2 Combustion of fuel for industrial, commercial and residual purposes.

*3 Primary non-ferrous metal production.

*4 Secondary non-ferrous metal production (scrap).

*5 Industrial application of metals.

Table 3: Emission of trace elements from all sources in Europe in 1982 (t/year).

Element	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn	Zr
<u>Country</u>																
Albania	17	0.1	1	3	5	70	1	1	1	92	140	-	1	40	40	2
Austria	26	0.2	5	22	200	130	1	180	6	180	1120	1	5	550	230	7
Belgium	85	0.5	12	55	640	610	13	610	25	380	2100	11	11	910	700	52
Bulgaria	147	1.4	66	47	180	290	9	220	22	290	1580	7	10	700	1760	45
Czechoslovakia	94	3.1	21	86	790	320	15	710	44	470	1130	17	18	940	760	99
Denmark	7	0.1	6	23	50	40	2	40	6	180	650	12	4	600	130	5
Finland	106	0.2	8	23	120	250	3	110	7	240	1120	1	4	560	220	8
France	171	1.4	32	103	1100	450	17	1190	34	900	8680	30	18	2340	3640	51
German Fed.Rep.	95	3.9	37	136	2150	1550	24	2050	60	1010	1750	50	46	2220	820	130
German Dem.Rep.	351	4.7	80	108	530	380	64	430	61	550	5560	25	24	970	6660	150
Greece	15	0.2	3	17	80	60	2	50	6	270	1390	2	3	370	200	10
Hugary	16	0.6	5	24	200	510	3	160	10	160	600	3	5	390	200	20
Iceland	-	-	-	-	-	1	-	-	-	4	40	-	-	10	1	-
Ireland	4	0.1	1	8	10	10	-	10	2	65	440	-	1	200	40	3
Italy	96	0.8	36	150	1060	390	11	930	38	1300	8600	16	24	3950	2020	25
Luxemburg	3	v.s.	1	1	200	20	-	190	-	15	170	1	-	30	90	-
Netherlands	34	0.3	6	38	260	110	9	250	10	320	2200	9	8	980	290	8
Norway	41	v.s.	2	6	40	60	1	50	2	66	730	-	1	160	120	1
Poland	597	8.2	180	151	1160	1310	40	1010	97	650	3000	43	37	670	4040	250
Portugal	11	v.s.	2	10	30	30	3	20	2	97	380	-	1	270	100	1
Romania	116	2.4	43	61	620	230	16	550	33	340	1160	13	13	660	720	76
Spain	263	0.9	133	61	570	570	9	470	20	510	4200	5	11	1370	3920	30
Sweden	183	0.1	16	36	200	240	7	170	9	320	1050	-	5	1000	430	3
Switzerland	4	v.s.	1	5	40	20	-	30	1	50	450	-	1	130	60	-
United Kingd.	117	4	31	130	1130	580	38	1030	60	900	8610	40	36	2070	2230	150
USSR	2098	15.0	309	631	7150	6530	99	6880	260	6010	30930	80	120	11260	13190	470
Yugoslavia	272	0.8	86	40	200	290	7	180	16	280	1960	5	8	720	1930	29
Total	5000	50	1100	2000	18900	15500	390	17700	850	16000	90000	380	420	34500	44600	1700

v.s. - very small

Table 4: Emission factors for the release of trace metals to the atmosphere.

Source Category	Unit	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Coal Combustion - electric utilities - industry & domestic	lb/MJ ⁻¹	15-100	5-25	80-500	60-200	10-35	70-450	15-150	90-600	50-300	10-50	7-50	20-300	70-500
	g/t ⁻¹	0.2-2.1	0.1-0.5	1.7-12	1.4-5	0.5-3.0	1.5-12	0.4-2.5	2.0-15.0	1.0-10.0	0.2-1.5	0.8-2.0	1.0-10.0	1.5-12.0
Oil combustion - electric utilities - industry & domestic	lb/MJ ⁻¹	1.0-5.0	4-30	15-100	60-400		10-100	10-70	60-250	40-300		6-50	120-900	30-220
	g/t ⁻¹	0.02-0.2	0.05-0.2	1.0-5.0	0.5-3.0		1.0-5.0	0.3-1.5	5-20	2.0-6.0		0.3-1.5	6.0-20	1.0-7.0
Pyrometallurgical Non-ferrous Metal Production - mining	g/t ⁻¹	5.0-10.0	0.1-0.5		20-100		50-100		ca. 100	500-1000	1.0-10.0	1.0-2.5		50-100
	g/t ⁻¹	200-400	10-50		60-80		100-500		85	3000-8000	50-100	10-50		50-120
- Pb production - Cu-Ni production - Zn-Cd production	g/t ⁻¹	1000-1500	200-400		1700-3600				900	1300-2600	50-200	50-150		500-1000
	g/t ⁻¹	50-150	200-1000		50-150					1200-2500	10-20	20-50		10000-18000
Secondary Non-ferrous Metal Production	g/t ⁻¹													
Steel & Iron Manufacturing	g/t ⁻¹	0.5-3.5	1.04-0.4	4.0-40.0	0.2-4.0		1.5-40.0		0.05-10.0	1.5-20.0	0.005-0.01	0.001-0.003	0.1-2.0	10-45
Refuse Incineration - municipal - sewage sludge	g/t ⁻¹	1.1-2.8	0.4-10	0.7-7.0	7.0-14	1.0-15	1.8-9.0		0.7-3.0	10-20	3.0-6.0	0.2-0.5		20-60
	g/t ⁻¹	5.0-10	1.0-12	50-150	10-60	5-20	50-100		10-50	80-100	5-20	1.0-10	3.0-20	50-150
Phosphate Fertilizers	g/t ⁻¹		0.5-2.0		1.0-5.0				1.0-5.0	0.4-2.0		0.003-0.009		10-50
Cement Production	g/t ⁻¹	0.2-1.0	0.01-0.60	1.0-2.0					0.1-1.0	0.02-16.0				2.0-20.0
Wood Combustion	g/t ⁻¹	0.1-0.5	0.1-0.3		1.0-2.0	0.1-0.5			1.0-3.0	2.0-5.0				2.0-10.0

Table 5: Comparison of the 1982 European survey of trace element emissions by Pacyna (1987a) referred as "this work" with national emissions.

Element	Emission (t/y)	Reference
<u>As</u>		
UK	117.4	This work
	315.0	Hutton and Symon, 1986
Sweden	183.4	This work
	130.0	Naturvårdsverket, 1982 for 1977/78
FRG	351.2	This work
	500	Braun et al., 1984
<u>Cd</u>		
UK	30.6	This work
	14.0	Hutton and Symon, 1986
FRG	79.9	This work
	83.6	UBA, 1977 for 1973
	83.5	Sartorius et al., 1977 for 1977
	78.6-89.6	EUR, 1981 for 1980
	79.0	Schladot and Nürnberg, 1982
	90.0	UBA, 1981 for 1981
Sweden	16.4	This work
	12.0	Naturvårdsverket, 1982 for 1977/78
Finland	8.0	This work
	7.0	Murkherjee, 1986
	4.0	Valli, 1988
Denmark	6.3	This work
	5.0	Murkherjee, 1986; after National Swedish Environmental Protection Board
Norway	2.1	This work
	1.7-2.7	Murkherjee, 1986; after National Swedish Environmental Protection Board
The Netherlands	5.5	This work
	3.8	Kendall et al., 1985
<u>Pb</u>		
UK	8614	This work
	7590	Hutton and Symon, 1986
FRG	5562	This work
	6500	Nürnberg et al., 1983
Sweden	1053	This work
	950	Naturvårdsverket 1987 - data for 1985
Finland	1122	This work
	1055	Murkherjee, 1986
	400	Valli, 1988
<u>Zn</u>		
Sweden	425.6	This work
	1200.0	Naturvårdsverket, 1982 for 1977/78
FRG	6663.3	This work
	10000.0	Braun et al., 1984
	7000.0	Nürnberg et al., 1983
Finland	220.0	This work
	2500.0	Valli, 1988

Table 6: Penetration, in %, of elements contained in particles emitted from a venturi wet scrubber and an ESP-equipped coal-fired generating unit (Ondov et al., 1979).

Element	Penetration range		Element	Penetration range	
	ESP	Venturi		ESP	Venturi
As	4.3-11.5	2.5-7.5	Sb	3.1-7.7	3.0-6.6
Be	0.5-0.9		Se	3.8-8.1	10 - 21
Cd	3.3-8.8		V	1.6-3.7	0.5-1.1
Co	1.2-3.2	0.06-2.1	W	3.1-7.2	1.7-3.5
Cr	1.2-12.1	0.6-36	Zn	2.3-6.3	0.3-8.5
Mo	1.8-6.8	0.9-2.2	Zr	0.5-1.6	0.05-0.14
Mn	0.3-1.6	0.07-4.6			
Pb	2.2-5.5				

Table 7: Emission factors and emissions of mercury from anthropogenic sources in Europe in 1982. (Pacyna, 1987a).

COUNTRY	Hard coal combustion in el.p.plants		Lignite combustion in el.p.plants		Combustion of coal in industrial, residential and commercial furnaces, t/y	Roasting and smelting, t/y		Waste-related ⁶ sources, t/y	Combustion ⁴ of fuel-wood, t/y	Chlor-alkali ⁵ production, t/y	TOTAL t/y
	E.factor, µg/TJ ¹	Emission, t/y	E.factor, µg/TJ ¹	Emission, t/y		Pb production	Zn production				
Albania											0.6
Austria	9.5	v.l.	19.0	v.l.	0.4	v.l.	0.2		0.2		1.1
Belgium	24.7	1.4	9.5	0.2	0.4	0.3	0.2	0.2	0.3		12.6
Bulgaria			24.7	1.5	5.7	0.4	0.7	0.2	0.1	3.0	8.6
Czechoslovakia	22.8	1.0	26.6	4.1	8.0	0.1	v.l.	1.0	0.2	1.5	14.9
Denmark	9.5	0.7			0.2				v.l.	0.1	2.0
Finland	9.5	0.2	13.3	0.1	0.2	0.4	1.2	1.0	0.4	1.0	3.0
FRG	7.6	1.5	28.5	11.0	3.2	0.4	2.0	1.9	1.1	6.5	16.7
GDR		10.7	15.2	9.3	9.3	0.8	3.0	12.8	1.1	15.6	64.3
Greece			24.7	0.7	11.4	0.2	0.1		0.1	2.6	23.7
Hungary	17.1	0.1		1.1	0.6	v.l.			0.2		1.5
Iceland					1.3				0.3	0.1	2.9
Ireland					v.l.				v.l.		v.l.
Italy	9.5	0.6	20.9	0.2	v.l.	0.1	1.3	1.0	0.5	4.0	10.8
Luxemburg	9.5	v.l.	20.9	0.1	3.2				v.l.		v.l.
Netherlands	9.5	0.4			v.l.	v.l.	1.5	4.0	v.l.	1.9	8.8
Norway	9.5	v.l.			v.l.	0.6	0.1	0.1	0.1	0.5	1.3
Poland	22.8	7.6	41.8	3.5	25.7	0.2	1.3	0.1	0.3	1.4	40.0
Portugal	11.4	v.l.			0.2				0.1	2.3	2.6
Romania			30.4	1.9	11.0	0.1	1.5		0.5	2.6	16.1
Spain	11.4	1.0	20.9	1.6	2.1	0.3			0.2	2.6	9.3
Sweden	9.5	v.l.			0.4	0.1			1.9	1.4	7.3
Switzerland	11.4	v.l.			v.l.				0.1		0.1
UK	22.8	14.7			5.7	0.4	0.6	6.5	v.l.	9.7	37.6
USSR (Europe)	22.8	26.2	34.2	16.4	36.7	0.4	2.0		4.6	13.0	99.3
Yugoslavia			30.4	3.8	0.8	0.2	0.7		0.4	0.6	6.5
TOTAL		66.1		55.5	132.8	4.0	18.6	31.0	12.9	70.9	391.8

Notes

- v.l. = very low (below 0.05 t/y)
- Emission factors were calculated by Pacyna (1982). It was assumed that 95% of Hg enters the atmosphere as a vapour. Two third of the total energy production in the USSR is produced in European part of the country.
 - These data were obtained from Pacyna (1983). It was assumed that similar amounts of Hg were emitted into the atmosphere from combustion of coal in industrial, residential and commercial furnaces in 1978/1979 and in 1982.
 - The following emission factors were used:
 - for primary lead production: 3 g/t Pb produced
 - for primary zinc production: 8 g/t Zn produced
 It was assumed that 30% of the total lead and zinc production in the USSR is produced in the European part of the country.
 - An emission factor of 5.2 g/t was used and wood density was assumed to 346 kg/m³. It was also assumed that a half on total wood combustion in the USSR takes place in the European part of the country.
 - An emission factor of 5.2 g/t Cl₂ produced was used for most of the countries except for:
 - UK (Hutton and Symon, 1986)
 - the Netherlands (ATMOS, 1986)
 The data were obtained from Pacyna (1983) and are representative for 1979, assuming only small changes between emissions in 1979 and 1982. However, for some countries national data were accepted:
 - the Netherlands (ATMOS, 1986)
 - Norway (Miljøverndepartementet, 1984)
 - Sweden (Naturvårdsverket, 1987)
 - UK (Hutton and Symon, 1986)
 - Emission data from Pacyna (1987b).

Table 8: Major chemical species evolved during fossil fuel combustion and industrial processes (Pacyna, 1987c).

Process	As	Cd	Pb	Hg
Coal combustion	As(o), As_2O_3 As_2S_3	Cd(o), CdO CdS	$PbCl_2$, PbO, PbS, Pb	gaseous Hg
Oil combustion	As(o), As_2O_3 Organic arsines	Cd(o), CdO	PbO	gaseous Hg
Non-ferrous metal production	As_2O_3	CdO, CdS	PbO, $PbSO_4$	
Iron and steel manufacturing		CdO	PbO	
Refuse incineration	As(o), As_2O_3 , $AsCl_3$	Cd(o), CdO $CdCl_2$	Pb(o), PbO, $PbCl_2$	gaseous Hg

Table 9: Mass fraction below 0.5 μm aerodynamic diameter and MMD for some trace elements (after Davidson and Osborn, 1986)*¹.

Metal	n	Mass Fraction < 0.5 μm	MMD (μm)
Pb	35	0.51 \pm 0.11	0.53 \pm 0.23
Cd	17	0.25 \pm 0.20	1.5 \pm 1.3
Cu	19	0.28 \pm 0.16	1.5 \pm 1.2
Fe	29	0.087 \pm 0.078	3.8 \pm 2.0
Mn	18	0.12 \pm 0.11	2.4 \pm 1.3
Zn	26	0.27 \pm 0.14	1.3 \pm 0.82

*1 Based on the information from backup filters. The number of size distributions considered is denoted by "n". Values shown are arithmetic averages and standard deviations.

Table 10: Concentrations of trace elements in precipitation, $\mu\text{g}/\text{l}$.

	West Germany Heinrichs & Mayer (1977)	Chilton England Cawse (1981)	Denmark Hovmand (1979)	Gårdsjön Sweden Grahn and Rosén (1983)	Velen Sweden Granat (1982)	Birkenes Norway Hanssen et al. (1980)	Hälsingland Sweden Rosén (1982)	Jergul Hanssen et al. (1980)
Na	1000	3700	2500	850	350	-	250	-
Ca	1200	1900	-	170	250	-	550	-
Al	190	600	-	17	80	-	43	-
V	-	7	-	0.3	3	1.8	0.3	0.3
Cr	2.1	3	-	0.2	1	-	0.2	-
Mn	19	14	15	2	8	7	3.3	4
Fe	150	350	150	17	100	-	30.2	-
Ni	1.4	11	-	0.4	2	-	0.3	-
Cu	21	24	2.5	0.7	5	-	5.8	-
Zn	360(?)	75	25	28	25	18	29.0	8
As	-	2	-	-	1	0.8	0.3	0.5
Cd	1.2	-	0.3	0.2	0.3	0.3	0.2	0.2
Sb	0.3	0.6	-	-	0.8	0.6	-	0.2
Pb	38	40	15	6	20	11	10	3.5
Amount of precipitation	1066	672	608	-	-	~1400	681	~500

Table 11: General information on heavy metals measurements in Europe based on questionnaires (Pacyna, 1986).

Country	No. of EMEP stations measuring heavy metals	Heavy metals measured	Type of sample		Sampling period	Precipitation sampler		Analytical method ³
			Aero-sol	Precipitation		Wet only	Bulk	
Belgium	3 ¹	As, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	x		24 h			XRF
Czechoslovakia	2	23 various elements	x		1 month			AAS & INAA
Denmark	3	25 various elements	x		24 h			PIXE
Fed. Rep. of Germany	5	Cd, Cu, Fe, Mn and Pb	x	x	24 h and 1 month		x	AAS
Finland	3 ²	Cd and Pb		x	1 month	x		AAS
Netherlands	2	Br, Cd, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn	x	x	24 h (aerosol) 1 month (precip.)		x	(AAS, ICP-AES, XRF)
Norway	4	Cd, Pb, Zn, Ni		x	1 week		x	AAS
Sweden	9	Cd, Cu, Fe, Mn, Pb, Zn, Cr, Ni, V, As		x	1 month		x	GF AAS
Switzerland	3 ¹	Cd, Cu, Pb, Zn		x			x	
Turkey	4 ²	Cd, Co, Cr, Fe, Mn, Ni, Pb		x	8 h per 15 days			AAS
United Kingdom	1	Br, Pb	x		1 week			AAS & INAA

1 only one is EMEP station

2 not EMEP station

3 XRF - X-ray fluorescence

AAS - atomic absorption spectroscopy

INAA - instrumental neutron activation analysis

GF AAS - graphite furnace AAS

ICP - inductively coupled plasma

Table 12: Atmospheric inputs of trace metals into the North Sea in $t \cdot y^{-1}$ (PARCOM, 1986).

Element	Measurements (PARCOM, 1986)	Model estimates (PARCOM, 1986)	Earlier estimates (review in PARCOM, 1985)
As	40-120	42	220-720
Cd	45-240	14	110-430
Cr	300-900	70	70-1400
Cu	400-1600	130	1400-10000
Hg	10-30	-	<36
Ni	300-950	150	360-3600
Pb	2600-7400	2600	3600-13000
Zn	4900-11000	1200	7200-58000

Table 13: Trace element concentrations in air, ng/m^3 .

	Chilton S.England (1) 1972-1973	Tange Denmark (2) Spring 1973	Birkenes S.Norway (2) Spring 1973	Birkenes (2) Autumn 1973	Birkenes (3) 1978-1979	Birkenes 1985	Velen (5) Sweden 1978	Jergul (3) N. Norway 1978-79
Al	330	461	114	85	71	96	-	
Na	930	945	403	478	523	287	-	
Mn	25	21	9	10	5.4	5.9	6.7	4
Cu	20	14	5	7	7		2.4	
Cr	5.3	1.3	0.9	1.2	1.0	0.9	2.8	
Fe	370	420	96	95	-	-	88	
Zn	175	45	29	36	-	17	24	6
V	17	7.7	2.2	2.6	3.1	2.4	2.5	0.31
Ti	-	46	8.6	6.8	-		5	-
As	5.9	-	-	0.7	1.0	0.7	-	0.8
Se	1.6	0.5	0.5	-	0.6	0.3	-	0.3
Sb	2.7	1.0	0.9	24	0.46	0.47	-	0.1
Pb	180	-	-	0.33	19	11	21	6.4
Cd	-	-	-		0.28	0.11	-	0.13

Data from: Cawse, 1974 -(1)
 Semb, 1978 -(2)
 Hansssen et al., 1980 -(3)
 Amundsen et al., 1986 -(4)
 Lannfors et al., 1982 -(5).

Table 14: Mercury budgets for atmospheres of Europe (outside USSR) and Sweden in the late 1970's in 10^6 g/y (after Lindqvist and Rodhe, 1985).

Process	Flux		Method of estimate
	Europe	Sweden	
Present anthropogenic emissions	500 (400-1000)	5 (5-7.5)	For Europe: Pacyna (1987a) and Watson (1979) For Sweden: KHM (1983) and Pacyna (1987a)
Present background emissions	50 (<150)	5 (<15)	Lindqvist and Rodhe (1985)
Total present emissions	550 (300-1200)	10 (5-22.5)	
Wet deposition	100 (50-200)	5 (2-10)	Rainwater concentrations listed by Lindqvist and Rodhe (1985)
Dry deposition	100 (<150)	5 (2-10)	Average concentration of soluble mercury $<0.2 \text{ ng/m}^3$, deposition velocity $<0.5 \text{ cm/s}$
Total present deposition	200 (50-350)	10 (4-20)	
Pre-industrial deposition	50-100	<5	For Europe: $10-20 \text{ } \mu\text{g/m}^2 \cdot \text{y}$, from Pheiffer Madsen (1981).

Table 15: Annual human exposure of As, Cd and Pb through ingestion, in the area of the Turow power plant.

Element	Unit	Estimated exposure		Literature values (Bennett, 1981)	Effects level (Bennett, 1981)
		Adults	Children		
As	$\frac{\mu\text{g}}{\text{kg}}$ of body	14.0	11.4	~ 10.0	15 - 340
Cd	$\frac{\mu\text{g}}{\text{kg}}$ of kidneys	60.0	52.8	14.0-16.0	200
Pb	$\frac{\mu\text{g}}{\text{kg}}$ of blood	16.7	14.5	10.0-13.0	10.0-60.0

Table 16: Trivial names, acronyms, trade names, chemical composition, structural formula and main uses of some chlorinated hydrocarbons.

Trivial name and/or acronym	Trade name(s)	Chemical composition	Structural formula	Usage, source of occurrence
DDT		Dichlorodiphenyl-trichloroethane		Insecticide
DDE		Dichlorodiphenyl-ethylenedichloride		DDT degradation product
Aldrin		Hexachlorocyclodlene		Insecticide
Dieldrin		Hexachlorocyclodlene epoxide		Insecticide
Toxaphene (PCC)	Campechlor, Phenacide, Phenatox, polychlor-camphene	Chlorinated camphene (more than 670 identified compounds)		Insecticide (cotton)
Chlordane	Octachlor	Chlorinated cyclodienes (-45 compounds)		Insecticide (termites)
Hexachlorocyclohexane (BHC, HCH, HCCH)	Hexachloran, hexachlor, hexycian	Technical mixture of alpha-, beta-, delta-, and gamma-HCH		Insecticide
Lindane, -BHC	gamma-hexachlorohexane			Insecticide
HCB		Hexachlorobenzene		Fungicide, unwanted by product in industrial chlorination processes, formed in combustion of chlorinated hydrocarbons.
Pentachlorophenol PCP	Dowicide, santophen	pentachlorophenol		Fungicide, wood and leather preservative

Table 16 cont.

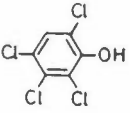
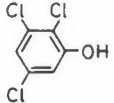
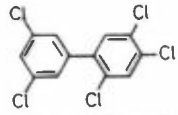
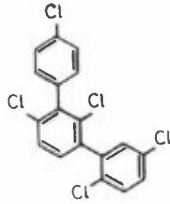
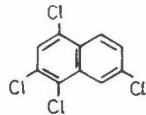
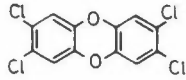
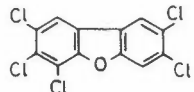
Trivial name and/or acronym	Trade name(s)	Chemical composition	Structural formula	Usage, source of occurrence
Tetrachlorophenol (Impurity in PCP)				Fungicide, wood, and leather preservative
Trichlorophenol		Trichlorophenol	 (2,4,5-trichlorophenol)	Intermediate in the production of 2,4,5 trichlorophenoxyacetic acid (herbicide) and other chemicals.
PCB	Arochlor, Chlophen, Phenochlor, Kanechlor, Fenchlor, Sovol	Polychlorinated biphenyls with up to 60% chlorine. 210 possible compounds and isomers	 (3,5,3',4',6'-pentachlorobiphenyl)	Dielectric, coolant, hydraulic fluid, softening agent etc.
PCT	Arochlor (e.g. 5460), Chlophen-Harz, Kanechlor C	Polychlorinated terphenyls		Additive to sealants, and adhesives
PCN	Halowax	Polychlorinated naphthalenes		Dielectric in small condensers, oil additive.
CP	Chlorowax, cerechlor	Chlorinated linear aliphatic hydrocarbons C ₁₀ -C ₁₃ , 50-70% Cl C ₁₄ -C ₁₇ , 45-60% Cl C ₂₀ -C ₃₀ , 40-70% Cl		<ul style="list-style-type: none"> - High pressure lubricants, flame retardants, cutting oils etc. - Softener in PVC. - Pigments, high pressure lubricants, flame retardants.
PCDD		Polychlorinated dibenzodioxin	 (3,4,7,8-tetrachlorodibenzodioxin)	Condensation of chlorophenols, impurity in other chlorinated hydrocarbons, formed in combustion processes
PCDF		Polychlorinated dibenzofurans	 (2,3,4,7,8-pentachlorodibenzofuran)	Condensation of chlorophenols, impurity in other chlorinated hydrocarbons, formed in combustion processes

Table 17: Measured concentration levels of chlorinated hydrocarbons in ambient air, pg/m^3 .

			α - and γ -HCH		HCB	DDT	DDE	Chlor- dane	Toxa- phene	PCB's light heavy		Ref.
USA												
Columbia, S.C.	1978-79	-	-	294	38		577	2990	2090	950	Billings and Bidleman (1983)	
North Inlet, S.C.	" "	-	-	-	13		101	630	215	160	Bidleman and Christensen (1979)	
Great Lakes area	1979?	300	2000	200	30		-	-	1000		Eisenreich et al. (1981)	
EUROPE												
Netherlands (Delft)	1979-81	250	360	100	57	17	-	-	960		Diederens et al. (1981)	
England, Channel coast	1974				~20				400	800	Dawson & Riley (1977)	
Baltic Sea	1983	138	111	-	255	(70)	-	-	-	-	Korolev (1984)	
Sweden, Stockholm and Aspvreten	1983-85		490	64	7.2		8.4	25	109	56	Bidleman et al. (1987)	
Norway, Lillestrøm	1981		1200	162	-		-	-	-	-	Oehme and Manø (1984)	
Kårvatn	1981		26	-	-		-	-	-	-	Oehme and Manø (1984)	
ARCTIC												
Spitsbergen	1981-83	540	40	150	n.d.		-	-	-	28*	Oehme and Manø (1984)	
Ellesmere Is.	1986-87	450	37	170	2		40	40	10	6	Patton et al. (1987)	
Ellesmere Is.	1986-87	-			-		30	-	-	-	Hoff and Chan (1986)	
SOUTHERN HEMISPHERE												
Eastern Indian ocean	1980	500	64		260		-	-	-	-	Tanabe et al. (1982)	
Indian ocean	1983	-	-	-	93		-	-	-	-	Kawano et al. (1985)	
Antarctic ocean	1980		390	150	-	-	-	-	-	-	Tanabe et al. (1982)	

* 5-chlorobiphenyl

Table 18: Average values and ranges of PCDD-/PCDF-concentrations in outdoor air in the Rhine-Ruhr-district (pg/m^3) (after Buck and Kirschmer, 1987).

PCDD	Average values	Concentration ranges	PCDF	Average values	Concentration ranges
2,3,7,8-	*	*	2,3,7,8-	0.09	* - 0.20
1,2,3,7,8-	0.02	* - 0.13	1,2,3,7,8-/		
			1,2,3,4,8-	0.14	0.04 - 0.35
1,2,3,4,7,8-	0.03	* - 0.08	2,3,4,7,8-	0.10	0.02 - 0.31
1,2,3,6,7,8-	0.06	* - 0.28	1,2,3,4,7,8-	0.13	0.02 - 0.48
1,2,3,7,8,9-	0.03	* - 0.08	1,2,3,6,7,8-	0.08	0.01 - 0.25
			2,3,4,6,7,8-	0.14	0.02 - 0.50
Σ TCDD	*	*	Σ TCDF	1.63	* - 4.42
Σ PeCDD	0.51	* - 1.66	Σ PeCDF	1.55	0.43 \rightarrow 5.13
Σ HxCDD	0.61	0.15 - 2.16	Σ HxCDF	0.79	0.14 - 2.24
Σ HpCDD	1.14	* - 4.61	Σ HpCDF	1.02	0.16 - 2.66
OCDD	0.98	* - 4.53	OCDF	0.49	* - 6.13
PCDD	3.23	0.15 - 10.09	PCDF	5.48	1.50 - 14.15

* = \leq detection limit

Table 19: Vapour pressures and aqueous solubilities of chlorinated hydrocarbons.

Compound	Temperature	Vapour pressure		Solubility $\mu\text{g}/\text{l}$	Water/air* partitioning coefficient
		ppb	$\mu\text{g}/\text{m}^3$		
α -HCH	20 ⁰ C	73	880	1500	$1.7 \cdot 10^3$ 1)
γ -HCH	20 ⁰ C	19	230	6000	$2.6 \cdot 10^4$ 1)
HCB	25 ⁰ C	25	320	6	~ 2
PCB					
Arochlor 1242	4 ⁰ C	30	310	190	$0.6 \cdot 10^{-3}$ 2)
	20 ⁰ C	329	3250	277	$0.85 \cdot 10^{-2}$ 2)
Arochlor 1254	4 ⁰ C	4	49	39	$0.8 \cdot 10^3$ 2)
	20 ⁰ C	29	337	43	$0.13 \cdot 10^3$ 2)
Arochlor 1260	4 ⁰ C	1.3	15	14.0	$0.9 \cdot 10^3$ 2)
	20 ⁰ C	8.3	92	14.4	$0.15 \cdot 10^3$ 2)
DDT	20 ⁰ C	0.32	4.7	9	$2 \cdot 10^3$ 3)
Toxaphene	20 ⁰ C	8.8	140	550	$4 \cdot 10^3$ 2)
Dieldrin	20 ⁰ C	3.8	60	33	$5.4 \cdot 10^2$ 3)

- References (1): Hapke, H.-J. (1983)
 (2): Murphy et al. (1987).
 (3) Atkins & Eggleton (1971).

* The ratio of the equilibrium concentration in aqueous solution to the gaseous concentration in air, expressed on a weight/volume basis.

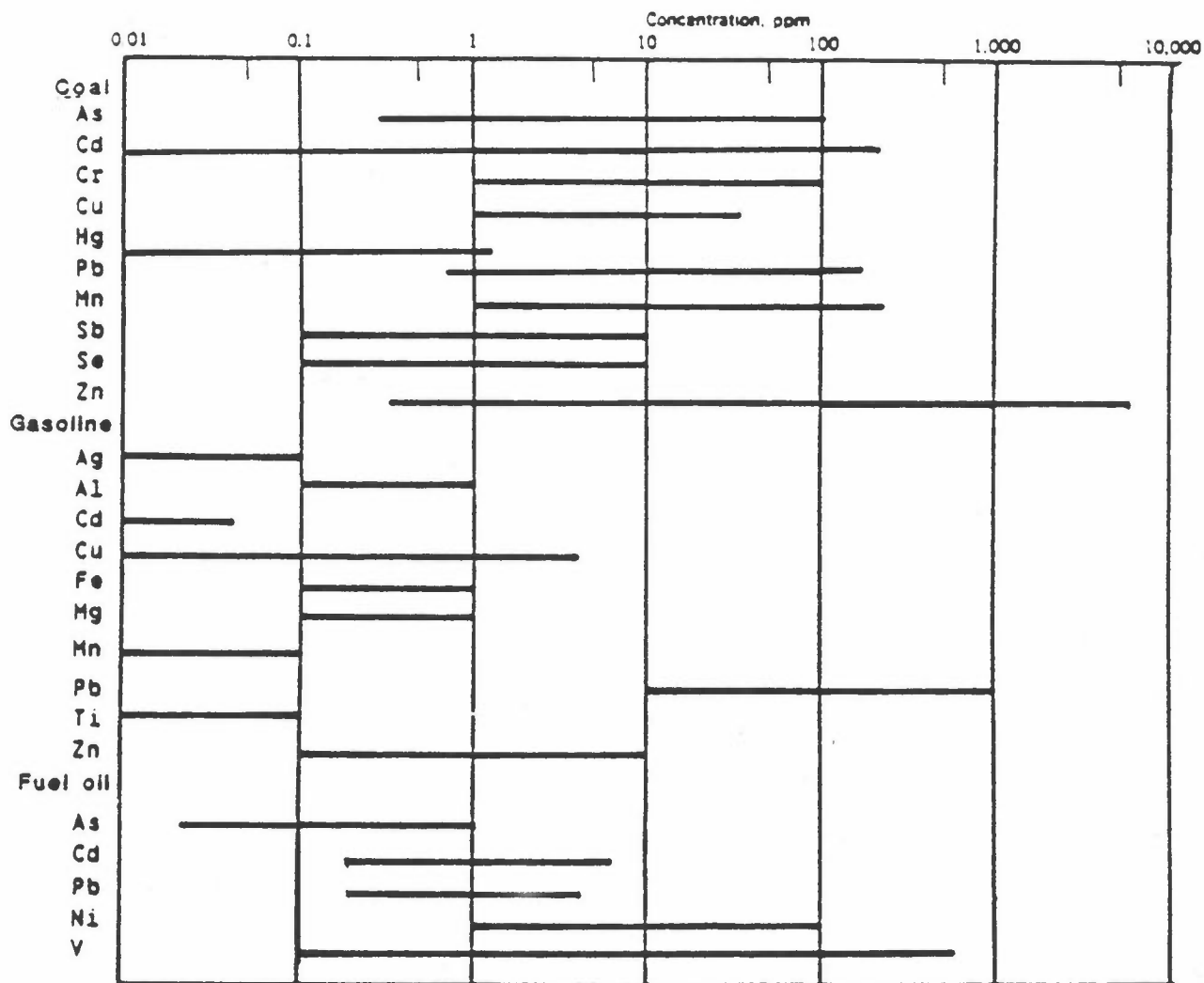


Figure 1: Range of trace elements in fuels.

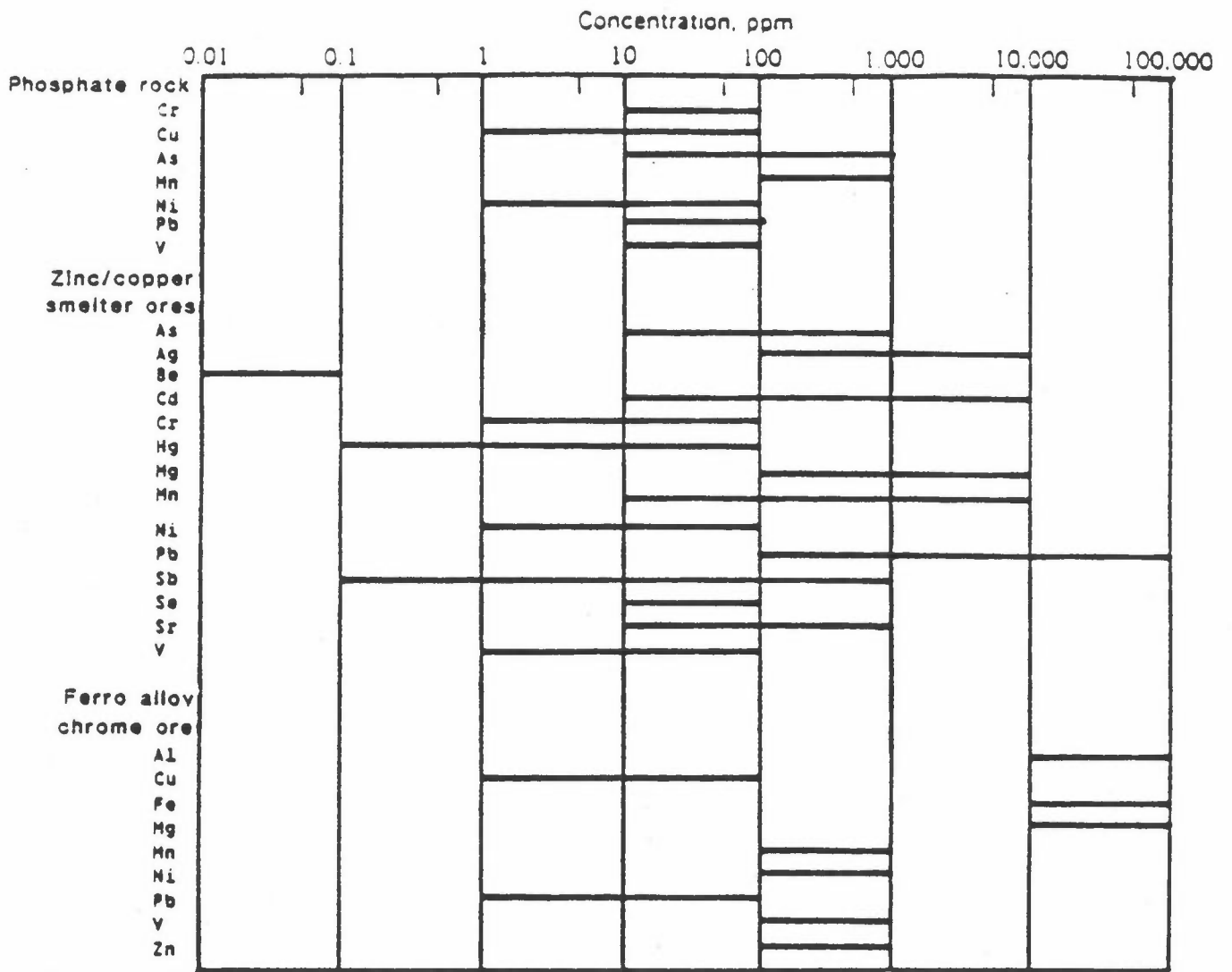


Figure 2: Range of trace elements in industrial materials.

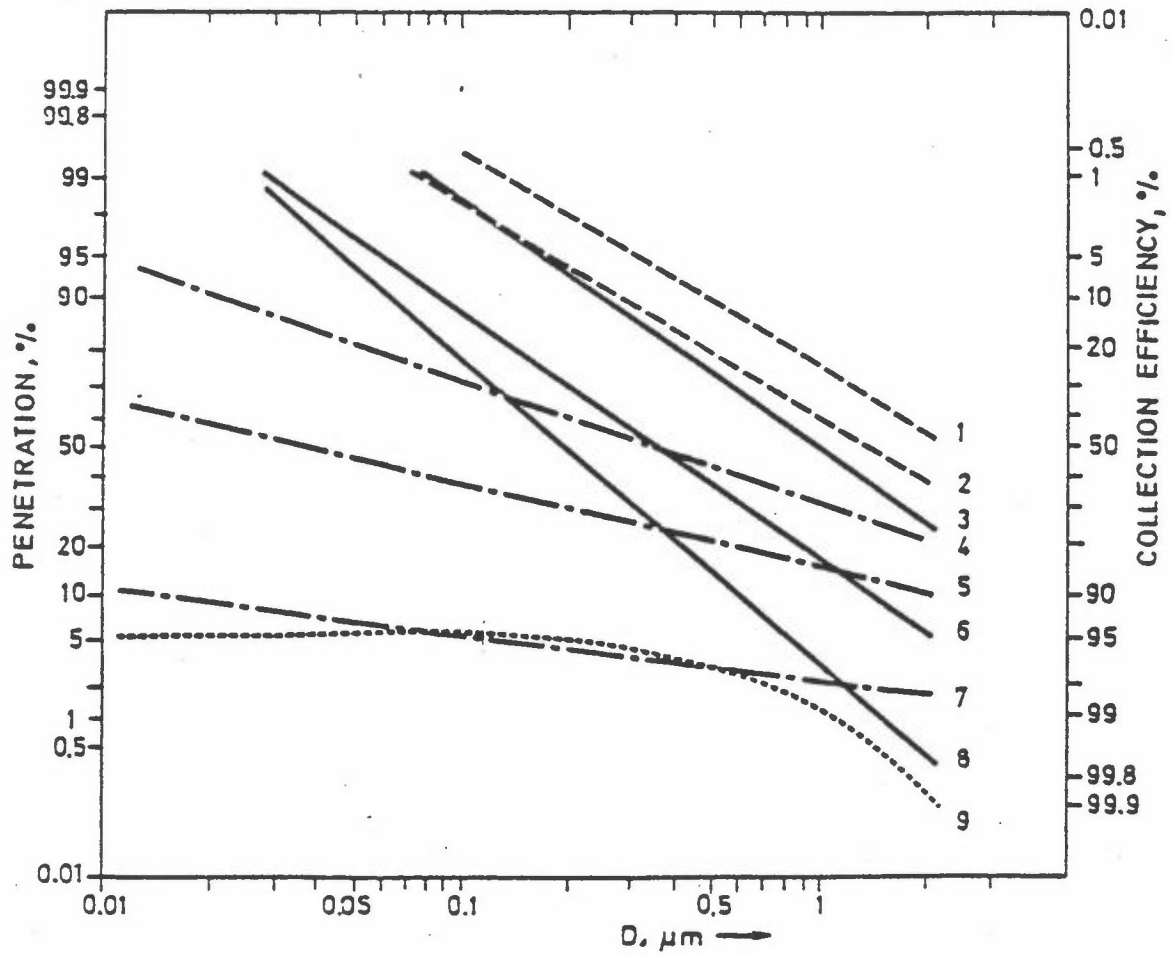


Figure 3: Average collection efficiencies and penetrations of control equipment for various particle sizes.

- 1 - High efficiency cyclone.
- 2 - Multicyclone.
- 3 - Low efficiency scrubber.
- 4 - Low efficiency electrostatic precipitator.
- 5 - Medium efficiency electrostatic precipitator.
- 6 - High efficiency scrubber.
- 7 - High efficiency electrostatic precipitator.
- 8 - Venturi scrubber.
- 9 - Fabric filter.

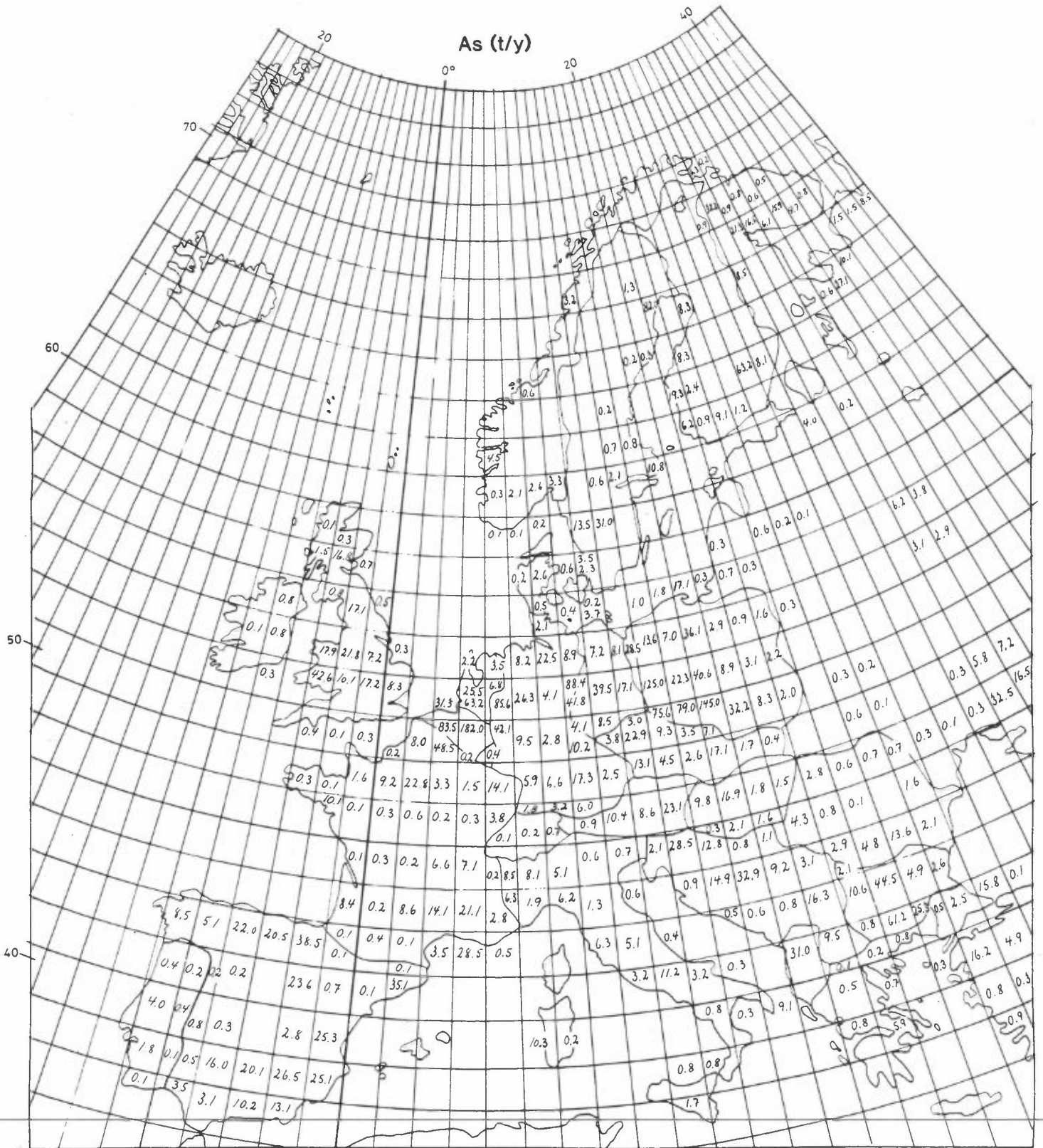


Figure 4: Spatial distribution of arsenic emissions in Europe in the $1 \times 1/2^0$ grid net (in t/y) after Pacyna (1985a).

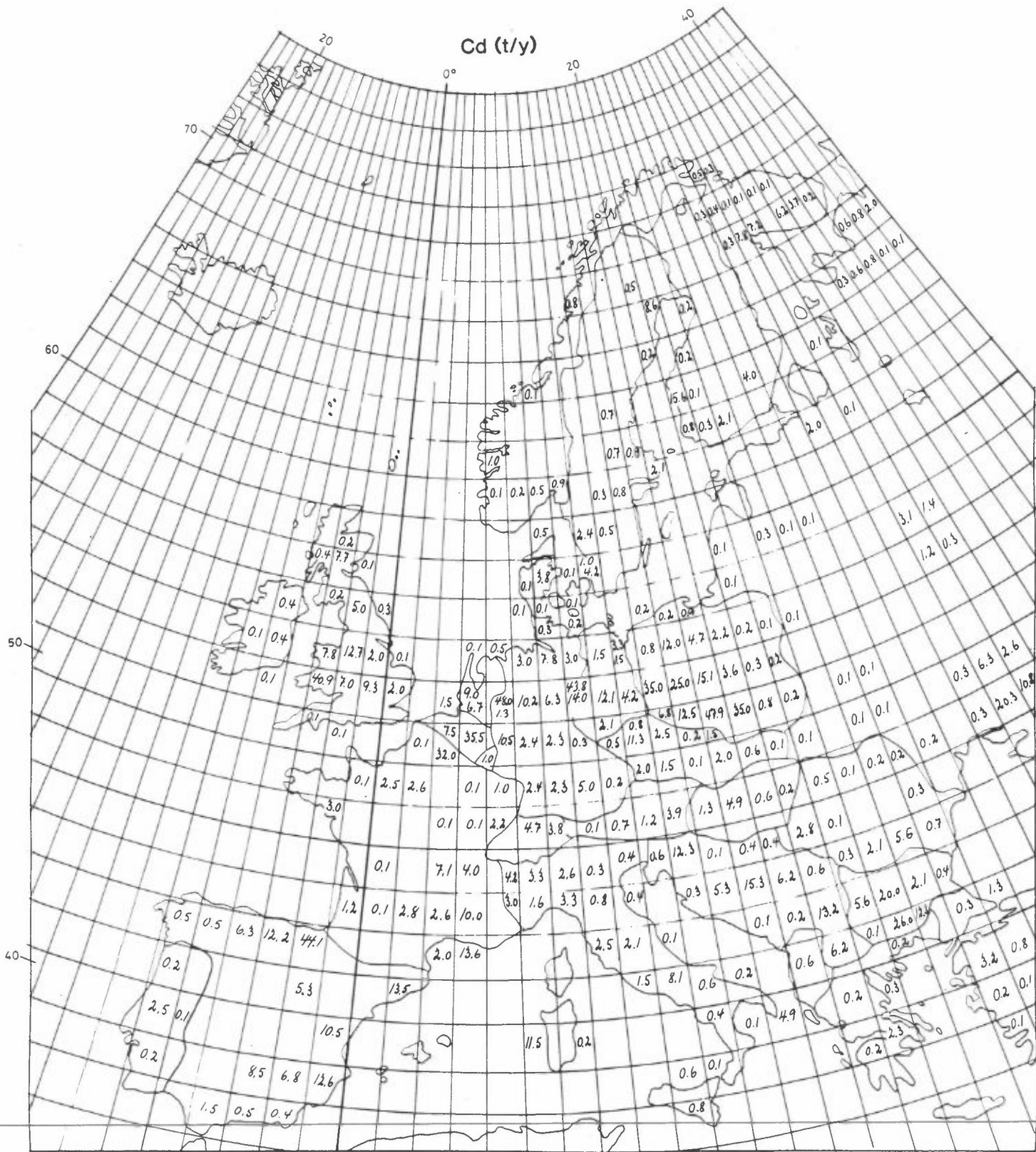


Figure 5: Spatial distribution of cadmium emissions in Europe in the 1 x 1/2° grid net (in t/y) after Pacyna (1985a).

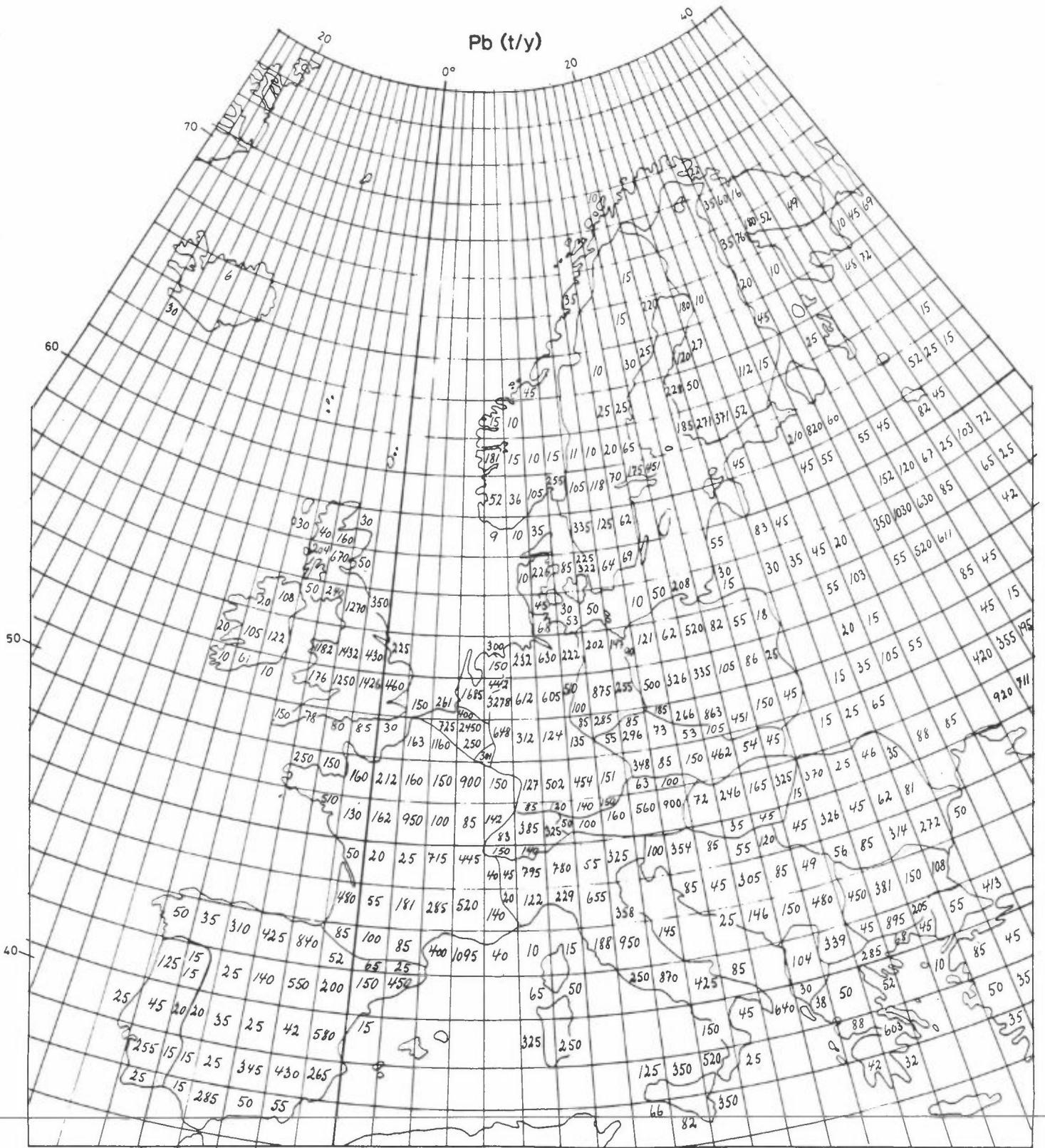


Figure 6: Spatial distribution of lead emissions in Europe in the $1 \times 1/2^\circ$ grid net (in t/y) after Pacyna (1985a).

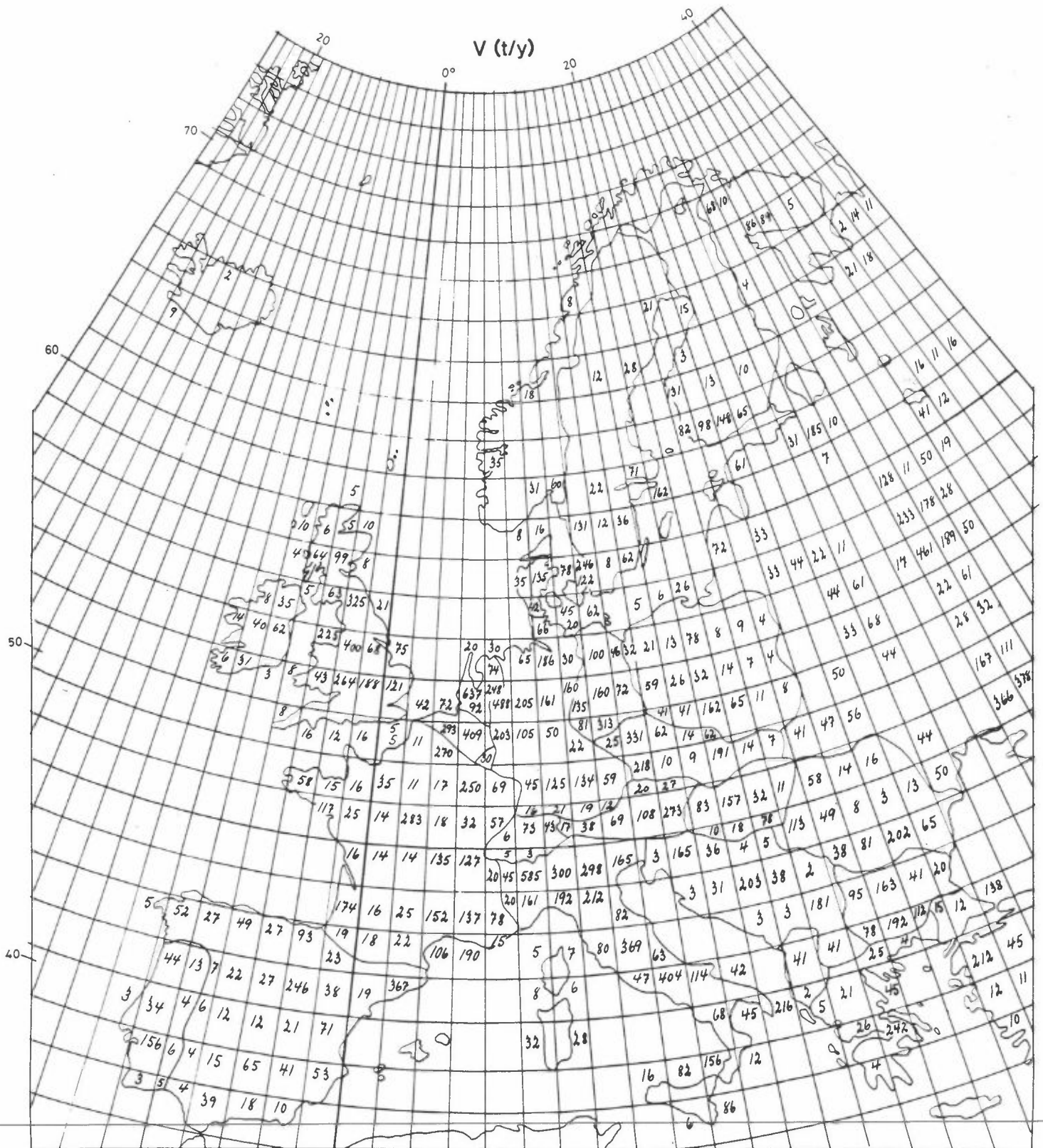


Figure 7: Spatial distribution of vanadium emissions in Europe in the $1 \times 1/2^\circ$ grid net (in t/y) after Pacyna (1985a).

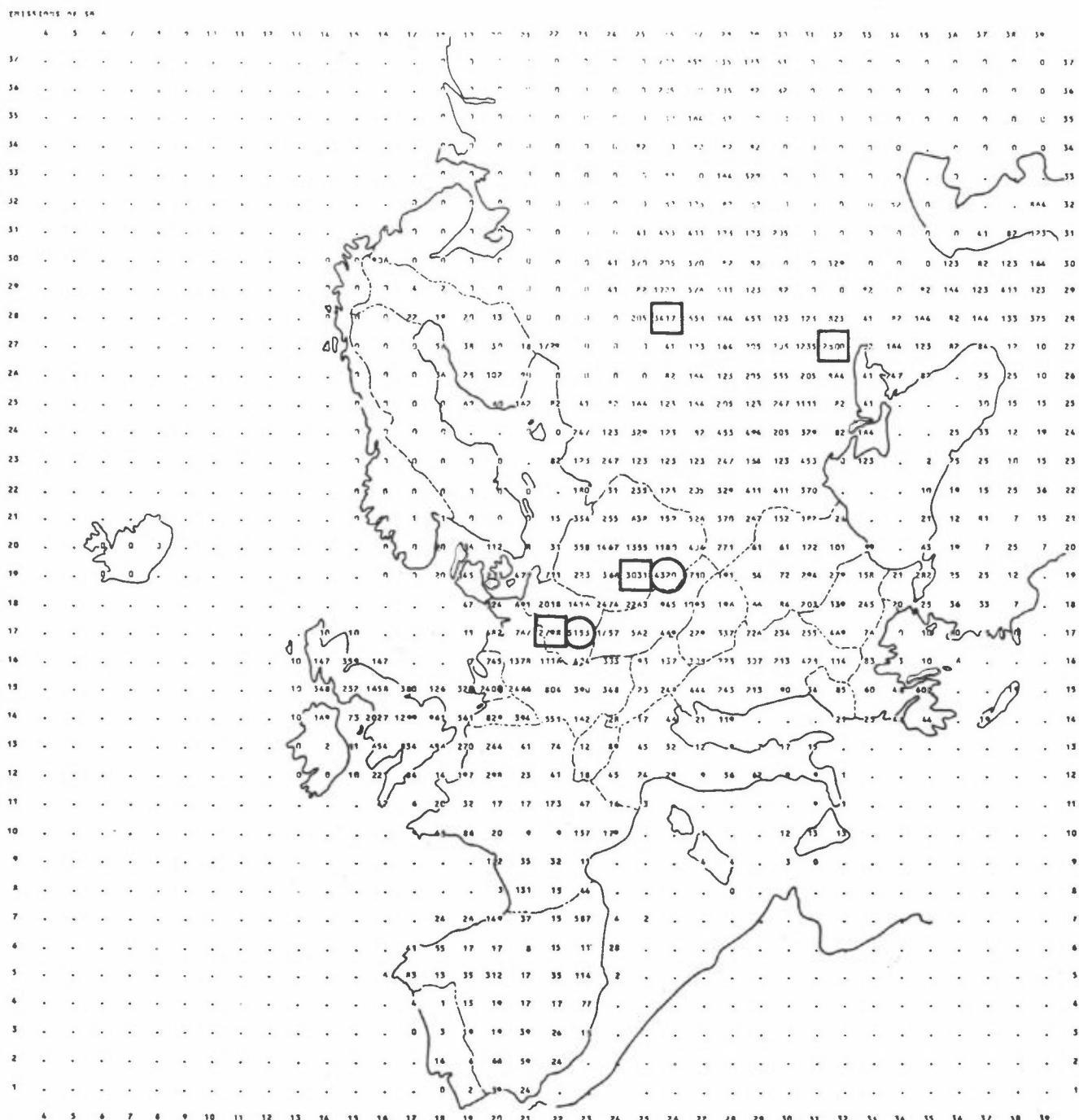


Figure 8: Spatial distribution of antimony emissions in Europe in the EMEP grid of 150 km x 150 km (in kg/y) after Pacyna (1983).

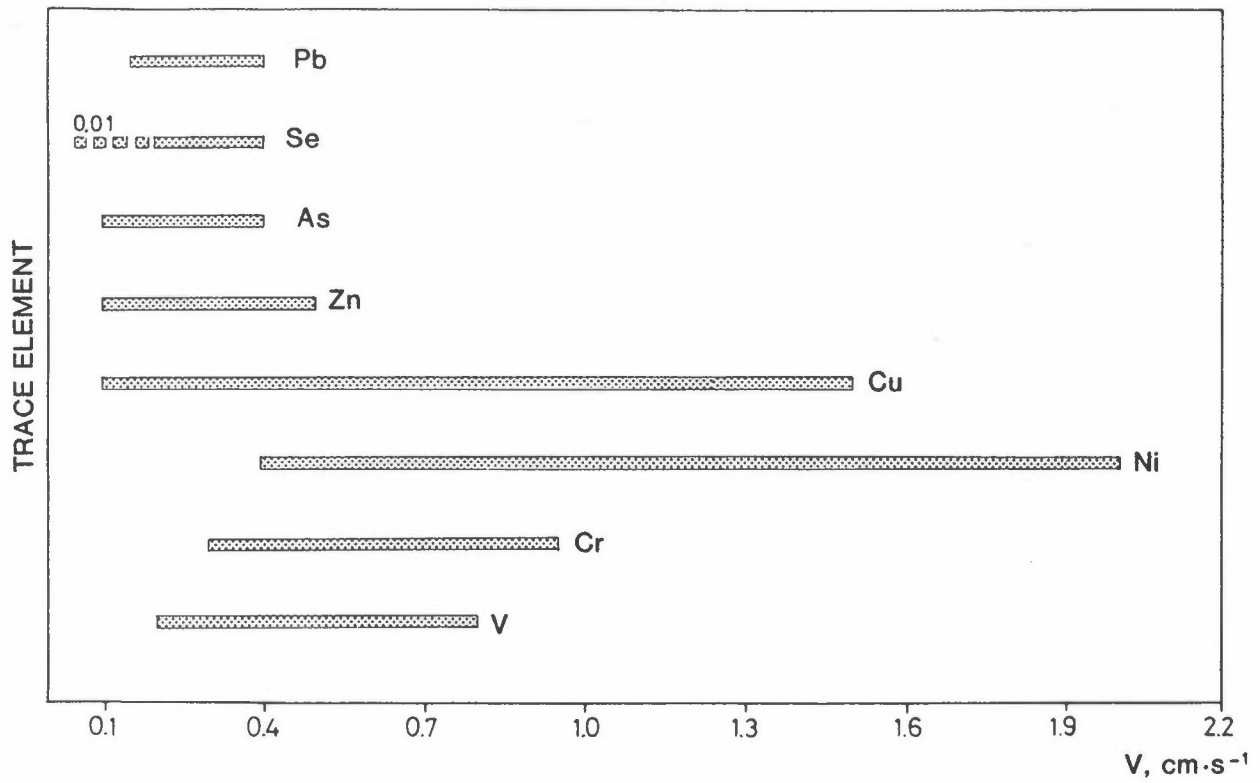


Figure 9: Average deposition velocities of trace elements (in cm/s).

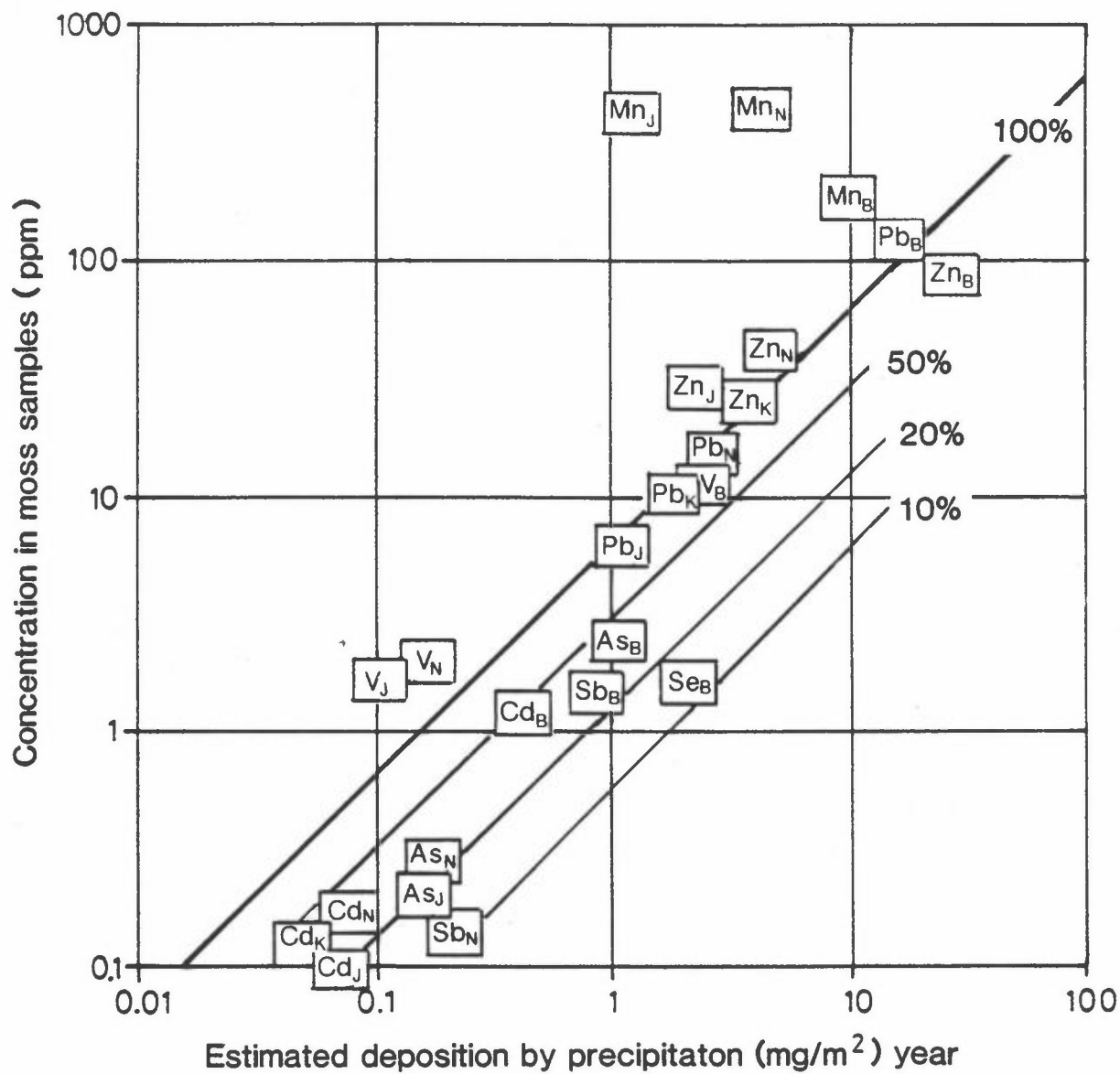


Figure 10: Comparison of trace element concentrations in moss samples and estimated deposition from precipitation samples.

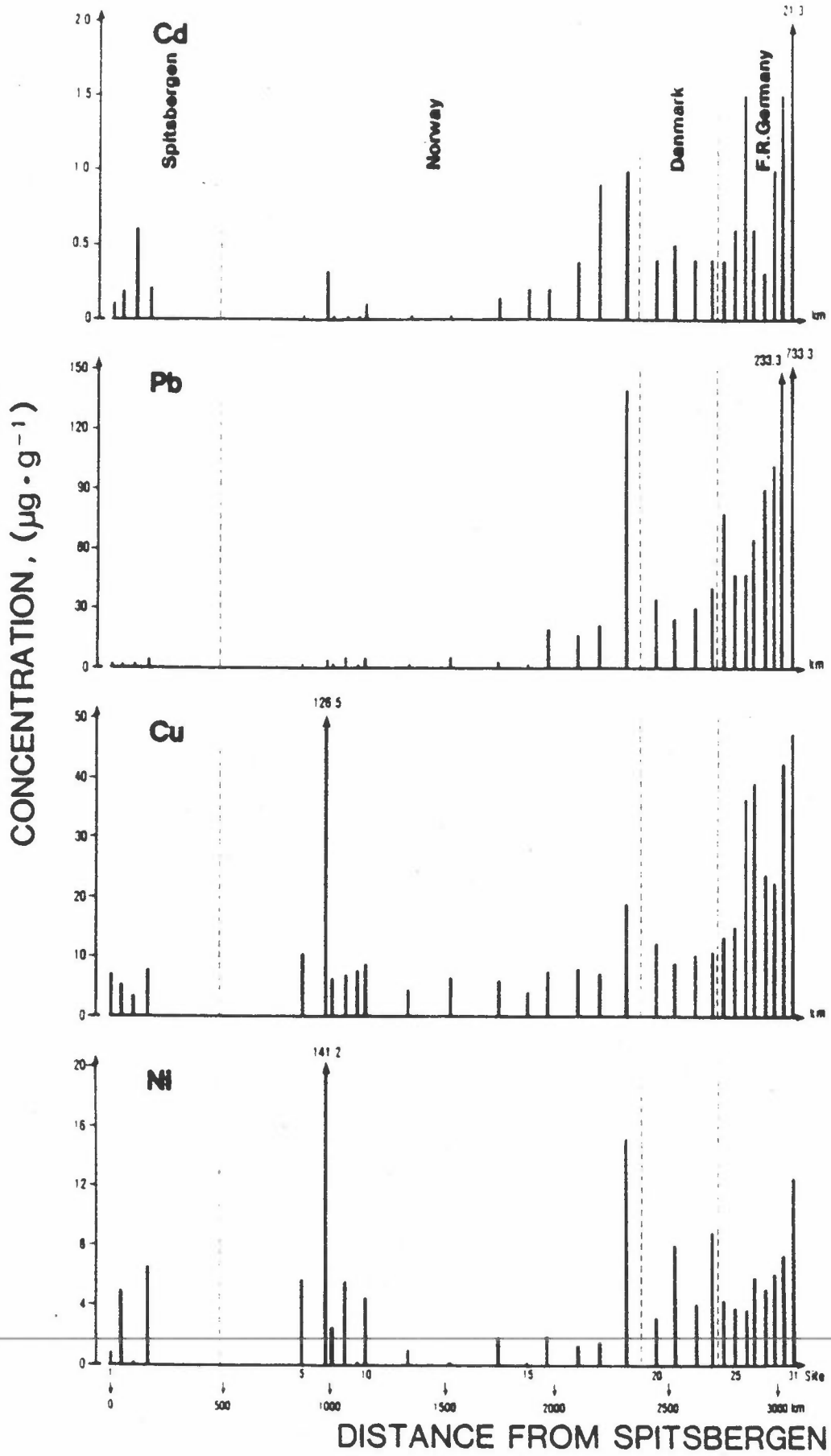


Figure 11: Concentration of heavy metals in moss samples taken as a transect from Fed. Rep. of Germany to Spitsbergen (Ottar, et al., 1986).

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3 STIKKORD (à maks. 20 anslag) Environmental cycle Heavy metals Chlorinated hydrocarbons			
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TITLE
ABSTRACT (max. 300 characters, 7 lines) Toxic trace elements and chlorinated hydrocarbons represent a special class of environmental contaminants, because of their strong bioaccumulation and persistence. Atmospheric transport and deposition by precipitation scavenging and dry deposition is an important source of these substances in terrestrial and aquatic ecosystems. It was concluded that available data create a basis for systematic approach to describe the environmental cycle of the heavy metals and the chlorinated hydrocarbons.

* Kategorier: Åpen - kan bestilles fra NILU A
 Må bestilles gjennom oppdragsgiver B
 Kan ikke utleveres C