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SUMMARY

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. Their emissions are becoming known, particularly in Europe. Once emitted to the atmosphere, trace elements can be transported within air masses and deposited in remote areas. A part of trace elements is accumulated in cultivated and uncultivated soils leading to various undesirable effects, e.g. gradual change in the trace element chemistry of terrestrial ecosystems, and uptake of trace elements in various food chains. The atmospheric deposition of trace elements is well illustrated by changes of their concentrations in samples of various moss species.

Some chlorinated hydrocarbons are toxic chemicals of potential concern because of their stability and their accumulation in soil and the biosphere. Emitted mainly during and after the application of pesticides, chlorinated hydrocarbons can stay in the air for months or even years. They are then subject to atmospheric transport and sink processes. Apart of dry and wet deposition, some chlorinated hydrocarbons undergo photodegradation in the atmosphere, and the reaction products are sometimes less desirable than the parent compounds, e.g. photodieldrin is more toxic than dieldrin. There is a large body of data on the concentrations of chlorinated hydrocarbons in biota, particularly for DDT and its metabolites. Many pesticides are bioavailable in soil and plants. The lipophilic chlorinated hydrocarbons are examples for water insoluble compounds which are largely sorbed by plants from the soil air or the pesticide-enriched air near the soil surface.

There is a need to improve our understanding of the role of indirect changes of trace metal cycles resulting from changing biogeochemical processes. More complete knowledge of the environmental pathways for chlorinated hydrocarbons may aid in the assessment of potentially harmful effects.

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SOURCES AND ATMOSPHERIC TRANSPORT OF TOXIC TRACE ELEMENTS AND CHLORINATED HYDROCARBONS AND THEIR MIGRATION THROUGH INDIVIDUAL ENVIRONMENTAL MEDIA

INTRODUCTION

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

There is little doubt, however, that atmospheric transport may also be 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 potentially toxic concentration levels, which is a function of the character and the recipient as much as of the actual input.

However, while the level of contamination of heavy metals and halogenated hydrocarbons in various biota have been extensively studied, quantitative data on the emissions, concentration levels in air, and ecosystem accumulation and transfer, has 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 EMISSIONS OF HEAVY METALS AND OTHER TRACE ELEMENTS

The concentration of so-called "anomalously enriched elements" in the atmosphere is mainly due to the volatility of these elements at the high temperatures of fossil-fuel combustion, and a variety of other high-temperature industrial processes. Particularly important in this connection is the extraction of non-ferrous metals from sulphides. Estimates of the emissions of the various trace elements from different emission source categories in Europe have been estimated by Pacyna (1985a) and are summarized in Table 1, while the estimates for all countries are presented in Table 2.

It is seen that fossil fuel combustion, particularly solid fuel burned in thermoelectric power plants, is an important source of emissions of many elements. The elements Be, Co, Mo, Sb and Se are emitted chiefly from 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 the recycling of scrapmetal, are the largest emitters of Cd, and As. Lead additives in petrol amounted to 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 element discharge: (1) impurities in fuels, ores, and other raw materials, (2) physical-chemical properties of trace elements, (3) production technology employed, and (4) effectiveness of emission control devices.

The ranges of concentrations of trace element impurities in coals, gasoline and fuel oils used in Europe and the Soviet Union in 1979 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 may be between 500 and 1200 ppm.

Bituminous coal is more contaminated than the other types, while lignite has the lowest amounts of impurities (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. Thus, the 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 residual fuel oil and asphalt (Smith et al., 1975). Generally, the most contaminated crude oils are those from the Middle East and Venezuela (Pacyna, 1982) while crudes from the Far East (Singapore, Indonesia, Africa (Algeria, Gabon, Nigeria), and North America are the lowest in impurities. 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 ($\geq 1000^0$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 effectiveness of air pollution control, are the key factors affecting the Cd and As emissions, particularly from non-ferrous metal smelters. The zinc-cadmium and copper-nickel smelters are the major sources of atmospheric Cd and As, respectively. 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 g x t^{-1}Zn produced (UBA, 1982) to 500 g x t^{-1}Zn produced (Pacyna, 1983). This large difference is probably due to differences in the effectiveness of control devices in various plants in Europe.

Emission of airborne pollutants from electrolytic process for zinc production 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 also 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).

The amounts of trace elements passing through control devices depend on the tendency of various elements to concentrate on fine particles, and the effectiveness of the control devices to capture these particles. 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 3 (Ondov, et al., 1979). Fig. 3 summarizes some average collection efficiencies (and penetrations) of control equipment installed in various European countries.

Many applications of the emission estimates in Tables 1 and 2 require them to be spatially distributed. The spatial distributions of all trace elements considered in Tables 1 and 2 are available in a 150 km x 150 km net grid for Europe. An example for the V emissions is presented in Fig. 4.

Among the metals and metalloids of concern for their potentially harmful effects in the environment, mercury is unique for a number of reasons. Estimates of global emissions of mercury to the atmosphere are variable and necessarily imprecise because of the uncertainty about natural emission rates. Recent estimates of global emissions from natural sources are on the order of 2700 (Pacyna, 1985b) to 6000 (Fitzgerald et al., 1984) tons/y.

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 special 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. On a worldwide basis, these emissions were estimated by Harris and Hohenemser to 1780 t y^{-1}. The anthropogenic emissions of mercury to the atmosphere in Europe in 1979 are presented in Table 4 (Pacyna, 1985c).

It is of interest to compare the anthropogenic emissions of the most important trace elements: As, Cd, Pb, and Hg in Europe to the metal releases from man-made sources in USA and the USSR and from natural sources, shown in Fig. 5. The trace metal emissions from sources in the Soviet Union have been estimated at the Norwegian Institute for Air Research (NILU, 1984) while the numbers for USA come from various US EPA reports (e.g., US EPA, 1977; US EPA, 1979). The data for natural sources in Fig. 5 are taken from a literature review by Pacyna (1985b, 1986), except for the Hg emissions, given by NAS (1978). The natural fluxes of As and Hg emission contribute very significantly to the total releases of these metals. The latter element is discharged mainly from natural sources, such as evasion of gaseous mercury from soils and vegetation, as well as from the ocean, and other water bodies. The predominant source of natural As and Cd appears to be volcanoes, but the natural Cd and Pb contributions to the total emissions of the metals are less significant than the contributions for As and Hg.

The total anthropogenic emissions of the elements in Europe, USA and USSR, are divided into source categories in Fig. 6.

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

There is a very limited information in the literature on the chemical speciation of metals emitted into the atmosphere. Inorganic forms of arsenic dominate in the air over emission areas. Major chemical species of arsenic and other discussed elements evolved during high-temperature processes are presented in Table 5. Trivalent arsenic is the most common form of the metal. Air samples containing arsenic from smelters or coal-fired power plants, consist largely of trivalent arsenic both in the vapor and particulate states. This is very important due to a general rule, that inorganic arsenic exibits greater toxicity than organic arsenic compounds, and the trivalent state more so than the other states. Methylated forms of arsenic are probably of minor significance.

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 from automobiles were studied by TerHaar and Bayard (1971). Lead chlorides and bromides are converted to basic carbonates and sulphate in the atmosphere. The mercury from industries and power plants consists partly of elemental mercury and partly of oxidized forms. Very little information is available with respect to say which volatile compound dominates the evasion process, but it seems that reactive (or oxidized) forms are more abundant in emissions from combustion processes.

Mercury species other than elemental Hg (Hg(0)) and $(CH_3)_2Hg$ can also contribute. Seiler (SNV, 1983) suggests, that Hg emitted as dimethyl mercury is subject to relatively fast degradation to elemental mercury taking place in the air. Brosset (1981a) concludes, that Hg(0) is mobilized to the atmosphere, where it is subjected to atmospheric oxidation processes to yield water soluble forms, subsequently scavenged by wet or dry deposition.

Considering the volatility of the As, Cd, Pb and Hg compounds in Table 5, As(0), As_2O_3, $AsCl_3$, elemental Cd (Cd(0)), and $CdCl_2$ are volatile, $PbCl_2$ is intermediate, and CdO, elemental lead (Pb(0)) and PbO are rather nonvolatile (Gerstle and Albrinck, 1982). The volatile species would be in the vapor state during the high-temperature processes, whereas the nonvolatile compounds would continue to be emitted largely as fly ash, even at the higher temperature.

3 ATMOSPHERIC TRANSPORT

The relationship between the concentration of a volatile metal and the particle size, in high-temperature processes has already been mentioned, when discussing emissions from coal combustion. The volatilization-condensation model relates the bulk concentration of the particles to their diameter, matrix composition, surface layer thickness, and flue gas concentrations. Investigations of surface layer composition suggest that the outermost layer on the surface of emitted ashes is often composed of H_2SO_4, which permits surface condensation of several elements. The condensation takes place on fine particles, preferably in the 0.1 to 1.0 µm diameter range. Additionally, the presence of sulphuric acid on some particle surfaces may be the causative agent in post-combustion crystal 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 very easily transported by air masses 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. It was found that ca 11% of the trace element releases was deposited in the emission area. Pacyna et al., (1984a) have studied the long range transport of several trace elements in Europe. Based on the literature (OECD, 1979), they have inferred the local deposition 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 Pb 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.

Rahn (1976) has compiled information on mass-median diameters of several trace elements (Fig. 7). Trace elements are removed from the atmosphere by dry deposition (sedimentation, interception and impaction) and by wet (precipitation) deposition (rainout, washout). The loss of particles to the surface by interception and impaction is frequently described in terms of 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 less than 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 such extrapolations are highly speculative. Moreover, consideration of the interactions between forest elements with 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 condensating nuclei, and incorporated in 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 air content in the precipitating clouds (Scott, 1978). A large body of measurements show that this ratio is frequently around 1 m^3/ml.

For mercury, the problems are of a different nature. The specification of mercury emitted from various sources, including re-emission of mercury from soil and vegetation, is not well known. It has been suggested that elemental mercury may be converted to water-soluble mercury (II) compounds in the atmosphere, e.g. by reaction with oxidants or radicals, (Brosset, 1981a), but this has only been proposed on the basis of circumstantial evidence. Presumably, the reverse reaction may also be possible. Elemental mercury is practically insoluble in water, and is not affected by precipitation. Uptake by absorption in plants is possible, but quantitative information is lacking (Browne and Fang, 1978). The molecular mercury (II) compounds are quite water-soluble, and should also readily be absorbed in vegetation or into water bodies.

4 MEASUREMENTS OF TRACE ELEMENTS IN AIR AND PRECIPITATION AND VERIFICATION OF EMISSION ESTIMATES

Trace elements associated with aerosols can be sampled on air filters and analysed with suitable instrumental analysis methods, such as atomic absorption spectroscopy, neutron activation analysis or particle-induced x-ray emission spectroscopy (PIXE). Data are available for a handful of sites in Scandinavia and in Northern Europe, mostly for sampling periods of up to one year at irregular intervals from about 1971. Some relevant data are given in Table 6.

Two conclusions can be drawn from these data: (1) the trace element composition of the atmospheric aerosol is remarkably uniform as noted by Peirson et al. (1974), and (2) the concentration decreases only with a factor of 3-10 from the source regions to Southern Scandinavia. There appears also to be a certain decrease in the concentrations for some elements during the period 1972-1985, although this is difficult to quantify on the basis of this rather irregular set of data.

Measurements of trace elements in precipitation is more difficult because of the generally low concentrations. Contamination may be a problem, unless special precautions are taken. In most cases, unfiltered samples have been analysed by atomic absorption or neutron activation analysis. Cawse (1974) found that Al, Se, and Fe were sparingly (8-20%) soluble, as compared with 75-90% of Ca, As, Zn, and Pb, and 50-75% of V, Cr, Mn, Cr, Ni, Cu, Sb and Cs. Some relevant concentration measurements are given in Table 7.

Measurements of Pb, Cd and Zn in precipitation samples from Norwegian background stations show decreasing values for Pb and Zn through the period 1976-1983 (SFT, 1984). No clear trend was found for Cd.

The amount of mercury collected on aerosol filters is only 5-10% of the total mercury concentration in ambient air. Adsorption by amalgamation on silver or gold metal gives concentrations of gaseous mercury in the range 2-10 ng/m^3 (Thrane, 1978; Hanssen et al., 1980; Brosset, 1981b). Moreover, the concentrations of gaseous mercury in air is not correlated with any of the other anomalously enriched trace elements in air. Chemical speciation of gaseous mercury compounds in air has been carried out in connection with the KHM project (Vattenfall, 1983), and the results are discussed by Brosset (1981b, 1983), and by Lindqvist et al. (1985). The chemical speciation is important in connection with precipitation scavenging. The concentration of mercury in precipitation is ~100 ng/l (Brosset, 1981b).

Emission estimates from Tables 1 and 2 and the information on the atmospheric transport from a chapter 4 of this report have been used in various models to calculate trace element concentrations and deposition rates at remote areas over the land and sea. The calculated concentrations and deposition rates were then verified by measurements.

The emission data from Tables 1 and 2 have been used together with the trace element emission survey for the USSR to explain the origin of the arctic aerosol. Pacyna et al. (1985a) applied them in a trajectory model to study source-receptor relationships for trace elements in the Norwegian Arctic. The As, Cd, Pb and V concentrations calculated on the basis of emission survey were generally higher than those measured by 36, 75, 80 and 37%, respectively. Considering the uncertainties involved, this shows a reasonably good agreement between estimates and measurements. Lowenthal and Rahn (1985) used the emission survey in Tables 1 and 2 to explain the origin of sulphates and trace elements at Barrow, Alaska, while Heidam (1985) did a similar study for Greenland.

The emission data from this work were also used to study the long-range transport of pollutants to remote areas of Scandinavia. Pacyna et al. (1984) and Pacyna et al. (1985b) related emission estimates to ambient concentrations measured at Birkenes (southern Norway), Rörvik (southern Sweden) and Virolahti (southern Finland). Estimated concentrations of As, V and Pb were lower than measured but within a factor of two. The differences between predictions and measurements for Pb and V at the Scandinavian sites were partly explained by emissions from local combustion of residual oil and gasoline. Sector statistics was also applied to relate the emission data to average sectoral concentrations for the whole periode of measurements. With this method, a group of elements including As and V was used to differentiate between contributions from emission in eastern and western Europe to the concentrations measured at remote receptors.

Recently, Amundsen et al. (1986) have related the trace element concentrations at Birkenes, measured in 1985 to the emission estimates shown earlier in this report. They found that the main difference between the results from the 1978-1979 measurements at this station reported by Pacyna et al. (1984) and their data is due to a significant decrease of the contribution of some elements from Western Europe to Southern Norway. At the same time the input from Eastern Europe has not been changed.

Ross and Granat (1986) have been studying the deposition of atmospheric trace elements in northern Sweden and concluded that long-range transport from anthropogenic sources in Europe is a main contributor. They related the Cd, Cu, Mn, Pb and Zn emissions from Tables 1 and 2 to the emissions of S (Eliassen and Saltbones, 1983) and compared them to the metal to S ratios measured in the northern Swedish snowpack. An excellent agreement was obtained for both Pb (6% relative difference) and Cd (16%).

Hansson et al. (1983) applied the multivariate statistical method SIMCA to determine the origin of aerosols measured in southern Sweden. They found their results in a good agreement with the emission estimates from this report. Martinsson et al. (1984) also used this inventory to assess the contribution of European emissions to the southern Scandinavian aerosol.

Dulac et al. (1985) and Gomes et al. (1985) used emission data from Tables 1 and 2 to support their findings on the atmospehric pathways of trace elements to the western Mediterranean Sea.

Recently, a few papers appeared in the literature on the significance of atmospheric deposition of trace elements to the Baltic Sea. Andrea and Froelich (1984), studying the As, Sb, and Ge biogeochemistry in the Baltic Sea, used the information on emissions of the above elements from Tables 1 and 2 for the countries which represent the source regions for air pollutants to the Baltic: Belgium, Denmark, Finland, German Democratic Republic, Federal Republic of Germany, Ireland, the Netherlands, Norway, Poland, Sweden and the UK (Rodhe et al., 1980). On the basis of this information they calculated that 11.6% of the As emissions is deposited in the Baltic and can be compared to ca 6% for each of the elements Pb and V. In an independent study, Pacyna (1985d), using the same emission survey and a recent computations of atmospheric annual input of trace elements to the North Sea at Water Research Centre (WRC, 1984), estimated that another 6% of each Pb and As emitted from anthropogenic sources in Europe is deposited in the North Sea.

Most recently the data from Tables 1 and 2 were used by Schneider (1986) to support his findings on source characterization for atmospheric trace metals over the Kiel Bight. He measured the trace element concentrations in the area of the Kiel Bight and postulated on the basis of statistical methods, characteristic ratios for the anthropogenic portion of any element relative to Zn as a reference element. Then these ratios were compared with the corresponding ratios for emissions in the Federal Republic of Germany as reported in Table 2. The comparison of the data revealed a very good relationship between emission characteristics and atmospheric concentrations with only 6% relative difference for Pb and 22% for Cd.

5 CONCENTRATIONS OF TRACE ELEMENTS IN VEGETATION, SOIL AND SURFACE WATER

Determination of the concentration of trace elements in samples of various moss species, particularly Hylocomium splendens, Pleurozium schreberii, or Hypnum cupressiforme, is an elegant measure of the deposition from the atmosphere. Basically, the moss' content gives an integrated value of the deposition during the last 2-4 years. Correlation with values of the deposition obtained from precipitation gauges may be used to transfer the moss concentrations to absolute deposition values (Fig. 8). Since the commonly sampled species grow in sheltered locations, dry deposition measured by this method is limited to the gravitational settling of relatively coarse particles ($d \lesssim 10$ µm). Extensive moss sampling survey data are available for Sweden, Denmark, Finland and Norway. In 1985, moss samples were collected simultaneously in all four Nordic countries. The results will be available later this year.

Samples of peat from ombrotrophic bogs (Hvatum et al., 1983), have been used to show that the deposition of the 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, and 3-10 times higher than in brown coal and other fossil fuels which now constitute the main source of energy in Europe. The accumulated amounts of lead, cadmium and zinc in the upper layers of ombrotrophic bogs correspond to $\gtrsim$ 250 years of deposition at the current level.

Vegetation samples other than moss generally have lower concentration levels, mainly because of the shorter accumulation time for vascular plants and the leaves of deciduous trees, and higher primary production in the case of agricultural crops. Absorption from falling precipitation onto leaf surfaces is the most important uptake process, in addition to dry deposition and root uptake, (Hansen and Tjell, 1981). For organogenic soils, trace element concentrations due to accumulated deposits are as pronounced as in ombrotropic soils. This is amply illustrated by the analysis of samples from the humus layer forest podsoils (Allen and Steinnes, 1980).

For mineral soils, the situation depends on the chemical composition of the parent material, and contributions from pesticides and fertilizers in the case of cultivated soils. Summaries of the trace element concentrations in soils have been given by Bowen (1966).This very general information suggests that, over a sufficiently long time period the concentrations of several trace elements may be significantly increased by atmospheric deposition. This increase is comparable to the increases of some trace element concentrations from application of municipal sewage sludge and from cadmium in commercial phosphate fertilizer.

These considerations refer to cultivated soil with a tillage depth of 20-30 cm. Forest and mountain soils are generally much more affected, because of the importance of the surface soil in nutrient recycling, and because many areas in Norway and Sweden have extremely thin soil cover over granitic bedrock. Most of the deposited trace elements are accumulated in the soil.

Lead, zinc, and cadmium in surface water show concentrations about 1/10th or less of the concentration in precipitation. Lake sediments give an interesting chronology of trace elements which is largely derived from allochtonous material such as leaves and humus brought into the lake. It is possible to quantify the deposition in lake sediments, which depend on the character of the surrounding land and the deposition from the atmosphere. No quantitative cause-effect relationships have been established.

The above information on the level of trace elements in various environmental medias is used to study the element transfers along terrestial and aquatic food-chains. These transfers are represented as compartmental sequences with transfer factors or concentration ratios expressing the relationships at steady state. These have been particularly developed and applied to the behaviour of the radionuclides in the environment, for example, transfers along the soil-pasture grass-cow-milk-man food-chain. The details of the model depend on the availability of data. The aquatic models often proceed in one step from water to aquatic organism with use of the concentration factor. Linear systems models may also be formulated to describe food-chain transfers. The interlinking transfer rate constants must be evaluated. The solution then gives the concentration variations as a function of time.

PART II: CHLORINATED HYDROCARBONS

1 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 posess 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 8 lists some of the compounds and their field of application.

The uncritical, large-scale use of the insecticide DDT, preceeded the general environmental movement in the 1960's and 70'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 countries, including USA and many European countries in the 1970's. DDT continues to be used, however, in many developing countries where it has proven difficult to find suitable substitutes for malaria and other pest control. Persistent chlorinated hydrocarbons still in use as insecticides include, inter alia, toxaphene, chlordane, and lindane.

2 SOURCES OF CHLORINATED HYDROCARBONS

The main source of chlorinated hydrocarbons in the air is the application of pesticides to increase food and forest production. There are several ways for pesticides to enter the atmosphere.

2.1 SPRAY APPLICATION

The major injection of pesticides into the air takes place during the spraying of agricultural crops. The pesticide spray is disseminated into the atmosphere in the form of finely divided droplets or particles of optimum size for maximum control of insects or weeds. This is not always achieved and the spray usually consists of droplets or particles with a wide range of sizes. In addition, the liquid carriers may evaporate under certain conditions, changing the particle size. The influence of drop size on spray drift is shown in Fig. 9, based on studies by Furmidge (1963).

The parameters affecting the quantity of pesticide that reaches a target include particle size distribution, amount of material sprayed, physical-chemical properties of the pesticide as well as height at which the material is released, wind speed, and atmospheric turbulence.

Cunningham (1962) has reported that more than 40% of the original aqueous drop is lost by evaporation before the droplets have fallen 11 m; a very important problem, especially in summer heat. Sometimes evaporation supressants are added to water-pesticide mixtures to diminish the vaporization losses.

2.2 VOLATILIZATION FROM CROPS AND SOILS

Evaporation of pesticide compounds may continue after treating agricultural soils and plant foliage. This adds to the above described releases during spray application and is believed to account for almost 90% of the pesticide contamination in the air (Lewis and Lee, 1976). For example, DDT is lost from soil mainly due to evaporation, and the loss is most intensive immediately after application. Fixation of DDT to soil with high organic content is very strong, and it is not unusual to find that concentraton levels of DDT in soils are virtually unchanged for several years after application (e.g. Kveseth et al., 1979).

There are several factors influencing the evaporation. The fixation is stronger for dry soils, and increases with content of organic matter and clay minerals. Water increases the vapor pressure of the pesticide by competing for adsorption sites. Thus, the mass flow of water moving to the surface of the soil during evaporation contributes to the greater pesticide evaporation from wet than dry soils. Other factors include temperature and humidity of the air, and wind velocity. Pesticides may also be released into the atmosphere when a field is plowed for the next crop.

Pesticides evaporate also from plant surfaces. Pesticide sprays are deposited predominantly on the foliage, and the total surface area of the foliage is often many times that of the soil surface. The pesticides do not penetrate deeply into the leaf surface, and as a result they are exposed to volatilization, dislocation by rain, and photooxidation. One interesting difference of pesticide evaporation from crops and soils is that increased air humidity slightly decreases the former process and increases the latter one.

2.3 EVAPORATION FROM WATER

Surface waters, such as rivers, lakes and oceans, are the main sinks for the majority of air pollutants, among them the pesticides. After deposition, much of the pesticidal material is bound to sediments and only a small part is in a true solution.

The evaporative loss of pesticides from water surfaces is limited to compounds with a moderate vapor pressure and a low solubility. The most commonly studied pesticide in this respect is DDT.

2.4 MANUFACTURING PROCESSES

The production of pesticides is also a likely source of pesticide emissions to the atmosphere. Production of the various products involves the use of many flammable solvents, and occasional fires have been reported (Lewis and Lee, 1976) causing a threat to nearby residents due to pesticide penetration into residential areas.

2.5 STATISTICAL INFORMATION ON THE PRODUCTION AND USE OF PESTICIDES CONSIDERED IN THIS REPORT

There is rather limited information on the use of various pesticides containing chlorinated hydrocarbons in the literature. Lindane (purified γ-isomer of hexachlorocyclohexane-γ-HCH) is widely used in various parts of the world (Mathys, 1984 - personal communication), however, statistical information on its application is scarse. FAO statistics (1979) shows that huge amount of HCH have been used by the countries during the last decade. India used ca $7.7x10^{4}$ 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 $2x10^{4}$ t of technical HCH is produced annually in the Shenyang Chemical Plant alone (Anonymous, 1981). Japan used $5x10^{5}$ 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 hemispehre, 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 $2.9x10^{3}$ t of γ-HCH is 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 was used in 1982 and the γ-HCH content was not less than 99% according to Paulsen (1984, personal information). About 9 t of lindane was 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 three 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 EPPO (European and Mediterranean Plant Protection Organization) area lindane is widely used for desinfection 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. Its use in Europe has been very limited. The same applies to chlordane which again is a complex mixture of chlorinated cyclodiene-like compounds.

Polychlorinated biphenyls (PCB's) are produced by chlorination of biphenyls. However, of the accumulated world production of 1-1.5x10^6 t, it is estimated that only a small part has been released to the environment. Most of the PCB is still in use, with large transformer and electric condensers as the most important "reservoirs". If possible, these amounts are regenerated for further use, rather than destructed. Destruction by incineration requires combustion temperatures in excess of 1200-1400^{0}C and long residence time in the combustion zone. Production of PCB's in Europe has been of the order of 15000-20000 kg/a from 1970-1980. EEC recommendation limits the use to "closed systems".

3 PHYSICAL FORM OF CHLORINATED HYDROCARBONS IN THE ATMOSPHERE

The physical form of the pesticides in the atmosphere depends upon their residence time in the atmosphere, chemical and physical properties (e.g., surface tension, vapor pressure and photoreactivity) environmental factors (e.g. temperature, humidity, wind turbulence) and on the nature and concentration of airborne particles.

There is very little published information on the physical form of pesticides in the atmosphere. This lack of data is largely due to a bias introduced by poor sampling techniques. Many of the early measurements indicated that chlorinated hydrocarbons as pesticide residues in the atmosphere existed predominantly in the form of suspended particulate matter (e.g., Tabor 1965; Antommaria et al., 1965). Later, with the progress made in the sampling techniques, it was found, that several pesticides are present in significant amounts in the vapor state (e.g., Bjorklund et al., 1970). Beyermann and Erkrich (1974) indicated that the mean quantity of gaseous lindane in the air over Mainz, West Germany, was twice as large as the fraction associated with particles. The vaporization loss of pesticides from soil and vegetation suggest that, most likely all of the airborne residues of lindane are in the vapor phase. A part of these gaseous molecules is adsorbed onto suspended particles, and this sorption process is depending on the surface properties of the particle. If the particle is wet, the adsorption will be determined by the water solubility of the pesticide. Since the concentrations of chlorinated hydrocarbons are present in ng x m^{-3} or pg x m^{-3} and the concentrations of suspended particles in µg x m^{-3}, the adsorption becomes low. As suggested by Lewis and Lee (1976), highly carbonaceous material, such as that emitted from coal-burning stacks adsorbs more polychlorinated hydrocarbons than silicate particles, such as airborne soil. Thus, during the transport of anthropogenic pollutants a part of the gaseous pesticides will be adsorbed on the particles, particularly those with a diameter lower than 2.0 µm, but for the more volatile pesticides most of the material may be in the gas phase.

4 LONG-RANGE TRANSPORT OF CHLORINATED HYDROCARBONS WIHTIN THE AIR MASSES

There is an evidence in the literature on the long-range transport of chlorinated hydrocarbons within the air masses, starting with the work by Cohen and Pinkerton in 1966 on the translocation of pesticides by air transport and rain-out. Global transport via the atmosphere was considered to be the only explanation for the presence of pesticides in Antarctica (Peterle, 1968), Barbados (Risenbrough et al., 1968; Seba and Prospero, 1971; Bidleman et al., 1981) and in the air over the North Atlantic as far as 2000 km from the U.S. coast (Harvey and Steinhauer, 1974). DDT and HCH found in the North Pacific have been transported from the Asian continent by the westerly winds, as concluded by Tanabe and Tatsukawa (1980).

Several mechanisms of long-range transport of chlorinated hydrocarbons have been postulated (e.g., Pooler, 1971; Woodwell et al., 1971). The primary mechanism suggested is turbulent diffusion which depends on wind vectors, temperature and topography. Gaseous compounds also undergo the simultaneous process of molecular diffusion, but this is much less significant than turbulent diffusion under most meteorological conditions (Lewis and Lee, 1976). Pooler (1971) studied global circulation problems and found that they play a major role in the long-range transport of airborne pesticide residues. His simplified schematic diagram of the hemispheric circulation pattern is shown in Fig. 10. The mean meridional circulation is the dominant feature in the subtropics, between equator and 30^0 latitude. The equatorward flow is present at low altitudes in the tropical easterlies, and a compensating poleward flow aloft. As indicated in Fig. 10, the subsidence in the subtropical high pressure zones at ca. 30^0 latitude completes the circulation. The level flows from the northern and southern hemispheres meet in the intertropical convergence zone, where the principal exchange of air masses takes place. Poleward of this intertropical zone, the eddy transport by migratory high and low pressure systems, dominates the circulation at higher altitudes. Pooler (1971) indicated that the mean feature of flow at higher latitudes is the eastward motion of the air at all levels, except high in the stratosphere. Thus, the parcel of air may circulate for a long time before it leaves the latitude of origin, and compounds with a long residence time in the atmosphere may be transported over very long distances. This applies to many of the chlorinated hydrocarbons. For example, Atkins and Eggleton (1970) estimated the residence time of lindane to be 17 weeks. Atlas and Giam (1981) calculated the residence time of PCB to be 189 days.

5 REMOVAL PROCESSES

Chlorinated hydrocarbons are removed from the air by various physical and chemical processes. The former group of processes includes removal by precipitation and dry deposition. Atkins and Eggleton (1970) studied the removal of lindane, dieldrin and DDT from the atmosphere and found a weekly removal of lindane of 2.5 per cent by precipitation and 3.3 per cent by dry deposition. The wet removal of dieldrin and DDT was 0.1 and 0.4 per cent, respectively, and dry deposition accounted for 3.5 and 3.4 per cent per week.

The deposition velocities of individual chlorinated hydrocarbons differ by 1-2 orders of magnitude, even at the same sampling site (Bidleman and Christensen, 1979). Mc Clure (1976) observed an increase of the dry deposition velocity (V_d) of PCBs from 0.3 to 3.0 cm x s^{-1} with wind speed for particles > 1.0 µm in diameter. For submicron particles (< 1.0 µm in dia.) this effect is not important (e.g., Sehmel and Sutter, 1974). About 20-30% of the polycyclic aromatic hydrocarbons in the atmosphere is concentrated on the > 1.0 µm dia. particles (Bidleman and Christensen, 1979). Because of the much higher deposition velocities of large particles (Sehmel and Sutter, 1974) the flux of high-molecular weight organics might be expected to be large-particle dominated and hence greatly influenced by wind speed. Other important parameters in this respect include ambient temperature and changes in the atmospheric particulate load. Bidleman and Christensen (1979) concluded that higher ambient temperatures would be expected to reduce the adsorption of organics to aerosols and to increase their re-volatilization. Generally, higher values of V_d were found for the less volatile organic compounds, reflecting a greater degree of attachment to aerosols.

The wet deposition process is often characterized by washout ratios (µg x m^{-3} in rain per µg x m^{-3} in air). For polychlorinated hydrocarbons these ratios are generally low (1.5 x 10^3 for hexachlorobenzene (HCB), 1-5 x 10^4 for HCH). However, Bidleman and Christensen (1979) found that measured washout ratios were significantly higher than those calculated from the equilibrium partitioning of the organic compounds between air and water. They suggested that while PCB and DDT in the atmosphere are partitioned between the vapor and particle phases, they are removed during precipitation by washout or rainout of particles and not by vapor dissolution in raindrops. Similar conclusions for PCB wet removal were forwarded by Murphy and Rzeszutko (1977) and Slinn et al. (1978).

Along a few chemical processes leading to the removal of chlorinated hydrocarbons from the atmosphere, photodegradation is the only mechanism that may compete with physical removal processes. The hydroxy radical plays a major role in the photodegradation of chlorinated hydrocarbons in the atmosphere. It can react with the various pesticides to form peroxides, epoxides and ketones. Ozone, singlet state oxygen and atomic oxygen also react with various organic compounds.

So far, most of the investigations have been performed in the condensed or adsorbed phases of organic compounds, beginning with the photodegradation studies of synthetic pesticide by Wichmann et al. (1946) who discussed the decomposition and volatility of DDT. Later the information on the vapor-phase photolysis of pesticides appeared in the literature (e.g., Nagl et al., 1970; Crosby and Moilanen, 1974). Sometimes the products of photodegradation of pesticides in the air are less desirable than the parent compounds. For example, photodieldrin is more toxic than dieldrin. Many organochlorine pesticides resist photolysis as they resist metabolism (Lewis and Lee, 1976). Others loose their chlorine only slowly. One of the most photosensitive pesticides is chlordane (Baker and Applegate, 1974). Lindane is slightly less photosensitive than chlordane.

6 MEASUREMENTS OF CHLORINATED HYDROCARBONS IN THE AIR

Concentrations of various chlorinated hydrocarbons in the arctic air have been measured during the 5-year program at NILU funded by British Petroleum (Pacyna et al., 1986). Mean concentrations and concentration ranges mesured at Ny Ålesund and Bjørnøya are shown in Table 9 and 10, respectively. It is interesting to note the very significant decrease of the α-HCH concentrations at both stations and the increase of the γ-HCH concentrations after Fall 1982. Since most of the air pollution at NYA and BJO during the summer-fall season is related to emissions in Europe (Pacyna et al., 1985c), it can be suggested that changes in the α- and γ-HCH concentrations at both stations are due to the use of more purified HCH as an insecticide in Europe. Thus, less α-HCH isomer seems to be mixed with more γ-HCH in order to produce and apply pesticides in the European countries after 1982. However, this suggestion is not confirmed due to the lack of statistical information.

The mean concentrations in Tables 9 and 10 are based on episodic concentrations measured during extensive campaigns. The strongest episode was observed during the periode March 6-13 in 1983 when the air masses were carrying pollutants emitted from sources in the northern Soviet Union (Pacyna et al., 1985c). This explains the highest concentrations of γ-HCH, and 5-PCB, at NYA and BJO in Winter/Spring 1983.

The concentration ratio of γ- to α-HCH seems to be a useful tool to distinguish between sources of air pollutants measured in the Arctic. Ratios of γ- to α-HCH ranging from 1:4 to 1:1 were found for the "European" air pollutants, 1:10 to 1:7 for North America and 1:10 to less than 1:100 for the Soviet Union. These ratios were higher in the winter/spring than in the summer/fall seasons indicating that isomerization of γ-HCH to α-HCH is more efficient in the summer/fall season.

The hydrocarbon concentrations at NYA and BJO in Tables 9 and 10 can be compared with the concentrations measured in other parts of the world. Some data for α- and γ-HCH and HCB in the urban air, the air over the areas with enhanced use of pesticides and in clean air (Antarctica) are presented in

Table 11. All these concentrations were measured before the first BP measurement campaign in Fall 1982, and represent mean values for the winter and summer seasons.

The α-HCH concentrations in the Arctic are at the same level as concentrations measured in the USA. The concentrations in Lillestrøm, Southern Norway, were measured in May 1981 and are in the range observed at NYA and BJO in Falle 1982. However, the γ- to α-HCH ratio is 1:3 for Lillestrøm, indicating a contribution of lindane from European or local sources.

Concentration ratios ranging from 1:17 to 1:8, were observed in the air over the Northwest Pacific and the western coast of India (Tanabe et al., 1982), suggesting the use of pesticides of a composition different from that in Europe.

The concentrations measured in the air over the Antarctic Ocean are low and it is difficult to speculate on their origin.

The HCB concentrations in Table 9, 10 and 11 are very similar indicating a very even distribution of HCB over the world. There is not only similarity in the geographical distribution of the HCB concentrations but in seasonal variations as well.

7 *MEASUREMENTS OF CHLORINATED HYDROCARBONS IN SOIL, BIOTA, WATER BODIES AND SEDIMENTS*

There is a large body of data on the concentrations of chlorinated hydrocarbons in biota, particularly for DDT and its metabolites, which have been extensively studied. Although much research has been conducted on insecticides, fungicides, and herbicides, insufficient information is available to assess food chain risk of chlorinated hydrocarbons.

Many pesticides are bioavailable in soil and plants. DDT and lindane in ingested soil were absorbed by sheep and stored in their fat (e.g. Harrison et al., 1970). PCB's and other compounds were absorbed and stored in fat of cattle (e.g. Kienholz, 1980), cow's milk (Bergh and Peoples, 1977), and fat of swine (Hansen et al., 1981). In general, PCB residues in fat reached 5-fold levels in dry feed (Chaney, 1984).

The lipophilic chlorinated hydrocarbons represent the case for water insoluble compounds which are largely sorbed by plants from the soil air or the pesticide-enriched air near the soil surface. Beall and Nash (1971) developed a method to discriminate between movement of chlorinated hydrocarbons through the plant vascular system (uptake-translocation) vs. vapor phase movement. They found that soybean shoots were contaminated by soil-applied dieldrin, endrin, and heptachlor largely by uptake-translocation. Vapor transport predominated for DDT, and was equal to uptake-translocation for endrin. Using this method, Fries and Marrow (1981) found PCB's reached shoots via vapor transport.

Root crops are especially susceptible to contamination by the vapor-transport route. Carrots have a lipid-rich epidermal layer (the "peel") which serves as a sink for volatile hydrocarbons. Depending on the water solubility and vapor pressure of the individual compound, it may reside nearly exclusively in the peel layer of carrots, or penetrate the storage root several mm (e.g. Lichtenstein et al., 1964). The level of chlorinated hydrocarbons in carrot is sharply reduced by increased organic matter in soil, which adsorbs the lipophilic compounds and keeps them from being released to the soil solution or soil air (e.g. Filanow et al., 1976).

Other root crops are much less effective in accumulating chlorinated hydrocarbons in their edible roots, possibly because the surface of the peel is lower in lipids (e.g. Moza et al., 1979).

Following the restrictions on the use of DDT and PCB's after 1970 there has been a general decrease and then a levelling out of the levels of DDT and PCB's in monitored species. The concentration levels in soils and sediments have not changed. Chlorinated hydrocarbons are strongly adsorbed onto the organic fractions of soils, particularly under dry conditions. Thus, the elvel of PCB's in soil from Sweden show seasonal variations which are correlated with runoff intensity. It is not clear whether this is due to material dissolved in the water, or adsorbed to soil particles. Oxidation of sediments in lakes, and in the sea, may be another important mechanism of transfer of chlorinated hydrocarbons to the water and eventually to the atmosphere. Larsson and Södergren (1982) have studied the PCBs transport routes in the aquatic environment. They suggested very efficient transport of PCBs from sediments to the water and fish.

CONCLUDING REMARKS

Burning of fossil fuels, and various other high-temperature processes, lead to increased mobilisation of a number of trace elements which are volatile at high temperatures. Several of these elements are toxic, and therefore undesirable, e.g. lead, cadmium, arsenic. They are present mainly as aerosol particles with a diameter less than 1 µm, and are mainly deposited by precipitation. Accumulation in cultivated and uncultivated soil leads to a gradual change in the trace element chemistry of terrestrial ecosystems which is undesirable in the long term. Undesirable effects are already apparent in the form of high cadmium concentrations in the kidneys of wild herbiuores in Sweden and Norway. However, the sources of trace element emissions in Europe are relatively well known, and can be used to quantify contributions to the deposition through the use of long-range atmospheric transport models. Decreases in the observed concentrations in air, precipitation, and moss samples following reductions in the lead content of gasoline, and improved emission controls, suggest that this approach will serve to pinpoint emissions which must be reduced in order to achieve defined target loadings.

The situation is much more complicated for mercury. After bans on the use of alkylated mercury for seed dressing, and in the paper and pulp industry, atmospheric mercury has become a major source of mercury in freshwater ecosystems, which has reached undesirable concentration levels, particularly in acidified lakes. Although reviewed by Lindqvist et al. (1985) the knowledge of the atmospheric mercury cycle remains incomplete, both with regard to the role (and chemical speciation) of anthropogenic emission and the possibility of chemical transformations in the atmosphere. This is because only a minor fraction of the mercury in the air is available for precipitation scavenging and it is not known precisely which mechanisms determine this fraction. Therefore, both the chemical speciation at the source, and atmospheric transformation reactions should be studied.

Chlorinated hydrocarbons are another group of toxic chemicals of potential concern because of their stability and their accumulation in soil and the biosphere. It seems that a major ecological disaster was averted by the ban on the use of DDT around 1970, but the decrease in the concentrations in biota has been slow for DDT, and even slower for polychlorinated biphenyls. North American studies suggest that atmospheric dispersion and precipitation is an important pathway for PCB in the Great Lakes area, and a similar situation could exist in Scandinavia, although this has not been substantiated. There is good reason to follow the development closely, because PCB's are still produced in Europe, and most of the PCB's produced are still in use in electrical equipment.

Moreover, other chlorinated hydrocarbons are being introduced which may also constitute environmental hazards. More complete knowledge of the environmental pathways for DDT and PCB may aid in the assessment of potentially harmful effects.

More volatile chlorinated hydrocarbons, such as hexachlorobenzene and the hexachlorocyclohexanes, are ubiquitous in the atmosphere, and have been detected both in Southern Norway and at Spitsbergen at comparable concentration levels.

Hexachlorobenzene is formed by thermal reactions with chlorine and hydrocarbons, or by incomplete combustion of chlorinated hydrocarbons. As such, it is of interest as an indicator of incomplete combustion, e.g. in incinerators, which may also be a source of the more toxic chlorinated dibenzodioxines and dibenzofuranes. Atmospheric decomposition by reaction with ozone or hydroxyl radicals may be an important sink process for some chlorinated hydrocarbons.

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Table 1: 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	284	21	101	787	1196	1377	1011	352	4580	1138	122	155	12600	1316
2. Indust.comm.comb.*2	394	29	155	1214	1580	2038	1378	493	7467	1652	154	218	21800	1824
3. Wood combustion	40		25			1500			375	562				4590
4. Gasoline combustion			31				92		1330	74300				
5. Mining			1			192	275		1640	1090		0.2		460
6. Primary n-f metal*3														
6.1 Copper-nickel	2225		225			7850				9250				2500
6.2 Zinc-cadm.	910		570			440				7880		13		48800
6.3 Lead	300		8			120			140	10450				180
7. Second n-f metal*4														
7.1 Copper			.2			61				55	1			660
7.2 Zinc														2630
7.3 Lead			1							387				150
8. Iron, steel metsl			58		15400	1710	14770		340	14660				10250
9. Refuse incineration	11		84	4	53	260	114		10	804	100	32	19	5880
10. Phosphate fertilizer			27			77			77	6		v.s.		230
11. Cement production			15		663					746				
12. Industr. applic.*5	136													
13. TOTAL	4300	50	1300	2000	18900	15500	17600	850	16000	123000	380	420	34500	80000

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

Element	As	Be	Cd	Co	Cr	Cu	Hg*[1]	Mn	Mo	Ni	Pb	Sb	Se	V	Zn	Zr
Country																
Albania	31	0.1	1	3	5	71	31	1	1	92	134	0.4	0.5	43	72	2
Austria	43	0.2	6	22	200	134	1145	182	6	184	1933	1.1	4.5	552	4370	7
Belgium	360	0.5	51	55	642	613	1874	613	25	381	3986	10.9	11.4	908	4736	52
Bulgaria	152	1.4	67	47	181	288	988	218	22	291	2234	7.5	9.7	701	1722	45
Czechoslovakia	86	3.1	23	86	791	323	793	712	44	472	1726	16.8	18.0	943	635	99
Denmark	7	0.1	9	23	50	38	1118	37	6	185	753	12.2	3.8	596	706	5
Finland	127	0.2	23	23	115	246	641	109	7	237	1621	1.2	4.1	565	2460	8
France	228	1.4	85	103	1095	450	3492	1192	34	903	10545	30.3	18.0	2338	6127	51
German Dem.Rep.	133	4.7	36	108	528	376	1244	432	61	549	2084	25.1	24.1	965	746	148
German Fed.Rep.	354	3.9	148	136	2153	1552	4676	2054	60	1013	9308	49.5	46.6	2222	11689	133
Greece	10	0.2	3	17	77	55	125	45	6	273	1303	1.6	3.1	372	121	10
Hugary	34	0.6	8	24	198	509	160	160	10	162	888	3.4	4.6	389	280	20
Iceland*[1]	73	-	81	378	336	514	-	-	84	4130	36300	-	53	10900	264	-
Ireland	2	0.1	1	8	11	13	0.2	8	2	65	456	0.4	1	199	33	3
Italy	93	0.8	54	150	1055	385	2025	925	38	1300	9365	16	24	3952	4420	25
Netherlands	38	0.3	11	38	255	105	1405	253	10	321	2427	9.3	7.9	979	3067	8
Norway	17	v.s.	4	6	40	56	312	45	2	66	803	0.2	1.2	160	1188	1
Poland	656	8.2	207	151	1161	1313	3036	1009	97	653	4568	43.0	37.0	672	4725	254
Portugal	7	v.s.	2	10	27	29	16	20	2	97	525	0.1	1.4	268	39	1
Romania	35	2.4	13	61	619	228	737	554	33	338	1827	12.7	13.1	660	614	76
Spain	302	0.9	124	61	571	565	1069	472	20	510	5534	4.8	10.9	1373	3255	30
Sweden	147	0.1	19	36	195	237	138	172	9	323	2270	0.4	5.4	1003	346	3
Switzerland	1	v.s.	11	5	40	18	4	25	1	51	1083	0.03	0.6	130	50	0.2
Turkey*[2]	62	1.1	17	30	147	427	346	126	15	277	1180	6.0	5.1	419	994	39
USSR*[2]	1064	15.0	280	631	7147	6535	8111	6879	257	6014	43842	80.0	120.0	11262	21281	471
United Kingd.	164	4	51	130	1134	580	2489	1032	60	899	10098	40.0	36.0	2074	3488	150
Yugoslavia	134	0.8	65	40	205	287	851	177	16	284	2423	5.3	7.6	718	2013	29
Luxemburg	0.4	v.s.	1.1	1.3	196	24	49	192	0.4	15	301	0.6	0.2	30	158	0.5
Total	4290	50	1320	2000	18900	15500	48000	17700	850	16000	123000	380	420	34500	80000	1700

*[1] in kg/year
v.s. - very small
*[2] only the European part of the country.

Table 3: 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 4: Anthropogenic emissions of total mercury to the air in Europe in 1979. Unit: ton a^{-1}.

Country	Mining and smelting	Industrial processes	Fossil fuel combustion	Refuse incineration	Total
Albania			0.4		1.4
Austria	1.2		0.5		1.7
Belgium	1.3	3.6	6.8	0.2	11.9
Bulgaria	0.6	0.6	6.7		7.9
Czechoslovakia	0.1	1.9	14.0		16.0
Denmark		0.1	0.7	1.0	1.8
Finland	0.6	0.7	0.7		2.0
France	1.3	7.9	5.2	1.9	16.3
German Dem.Rep.	0.2	2.6	20.9		23.7
German Fed.Rep.	1.7	4.2	16.3	8.1	30.3
Greece	0.1	0.2	1.4		1.7
Hungary		0.7	2.7		3.4
Italy	0.8	7.5	3.6	1.0	12.9
Netherlands	0.6	0.2	1.2	1.1	3.1
Norway	0.3	0.4			0.7
Poland	1.1	2.6	36.6		40.3
Portugal		0.2	0.2		0.4
Romania	0.1	4.0	11.9		16.0
Spain	0.9	2.8	3.8		7.5
Sweden	0.4	2.3	0.4	1.0	4.1
Turkey		0.2	3.6		3.8
USSR	4.2	13.8	65.1		83.1
United Kingdom	0.5	0.7	12.8	5.8	19.8
Yugoslavia	0.6	0.7	3.9		5.2
Europe	16.6	57.9	219.4	20.1	324

Table 5: Major chemical species evolved during fossil fuel combustion and industrial processes.

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, $PbSO_4$ $PbO.PbSO_4$	
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 6: 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	Birke-nes (4) 1985	Velm (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 7: Concentrations of trace elements in precipitation, µg/l.

	West Germany Heinrichs & Mayer (1977)	Chilton England Cawse(1981)	Denmark Hovmand(1979)	Gjärdsjön Sweden Grahn and Roden (1983)	Velen Sweden Granat(1982)	Birkenes Norway Hanssen(1980)	Hälingsland 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	29.09	8
As	-	2	-	-	1	0.8	-.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
Annual of precipitation	1066	672	608	-	-	~1400	681	~500

47
51

Table 8: Main groups of pesticides.

Chlorinated hydrocarbons	Organophosphates	Carbamates
DDT Aldrin Dieldrin Endrin Heptachlor Chlordane Lindane	Methyl parathion Parathion Malathion Diazinon Fenthion TEPP Azinphosmethyl	Carbaryl Zectran

Table 9: Concentration ranges and mean values measured at Ny Ålesund during 5 measurement campaigns (in pg . m^{-3}).

	α-HCH		γ-HCH		HCB		5-PCB		α-chlordane	
Campaign	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Fall 1982	757 1416	1192	0.1 - 9.4	2.1	75 - 169	123	2.3 46.5	15	0.6 - 3.2	1.2
Fall 1983	407 - 695	548	34 - 67	46	158 - 227	186				
Summer 1984	260 - 774	488	24 - 100	47	20 - 201	154	0.9 - 43.0	21	1.7 - 5.4	2.8
Winter/ Spring 1983	151 - 734	485	21 - 102	66	112 - 187	144	32 - 145	62	1.1 - 2.3	1.7
Winter/ Spring 1984	121 787	273	12 - 70	29	29 - 389	151	4 - 51	16	0.6 - 5.1	2.0

Table 10: Concentration ranges and mean values measured at Bjørnøya during 4 campaigns (in pg . m^{-3}).

	α-HCH		γ-HCH		HCB		5-PCB		α-chlordane	
Campaign	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Fall 1982	420 - 1550	774	0.1 - 29	4.2	78.4 - 200	120	6.3 - 37.6	17	0.5 - 1.7	0.8
Fall 1983	277 - 477	326	14 - 32	22	88 - 180	134				
Summer 1984	38 - 305	155	5 - 41	18	42 - 149	57	4.4 - 14	8	0.6 - 2.1	1.3
Winter/ Spring 1983	110 - 469	282	23 - 80	47	87 - 201	124	8.5 - 66	23	1.2 - 3.1	1.7

Table 11: Concentrations of α- og γ-HCH and HCB in various places of the world (in pg . m^{-3}).

Location	α-HCH.	γ-HCH	HCB
1. USA			
Denver, CO (Billings and Bidleman, 1983)	300*[1]		240
New Bedford, MA (Billings and Bidleman, 1983)	1000*[1]		180
Columbia SC (Bidleman, 1981)	370	180	200
College Station, TX (Atlas and Giam, 1981)	420		200
2. NORWAY			
Lillestrøm (Oehme and Ottar, 1984)	875	318	162
3. NORTHERN PACIFIC OCEAN			
- Enewetak Atoll (Atlas and Giam, 1981)	250	15	100
4. WESTERN PACIFIC OCEAN (Tanabe et al., 1982)	1000	100	
5. EASTERN INDIAN OCEAN (Tanabe et al., 1982	500	64	
6. ANTARCTIC OCEAN (Tanabe et al., 1982	25	9	
7. NORTH ATLANTIC (Atlas and Giam, 1981)	390		150

*[1] α and γ-HCH

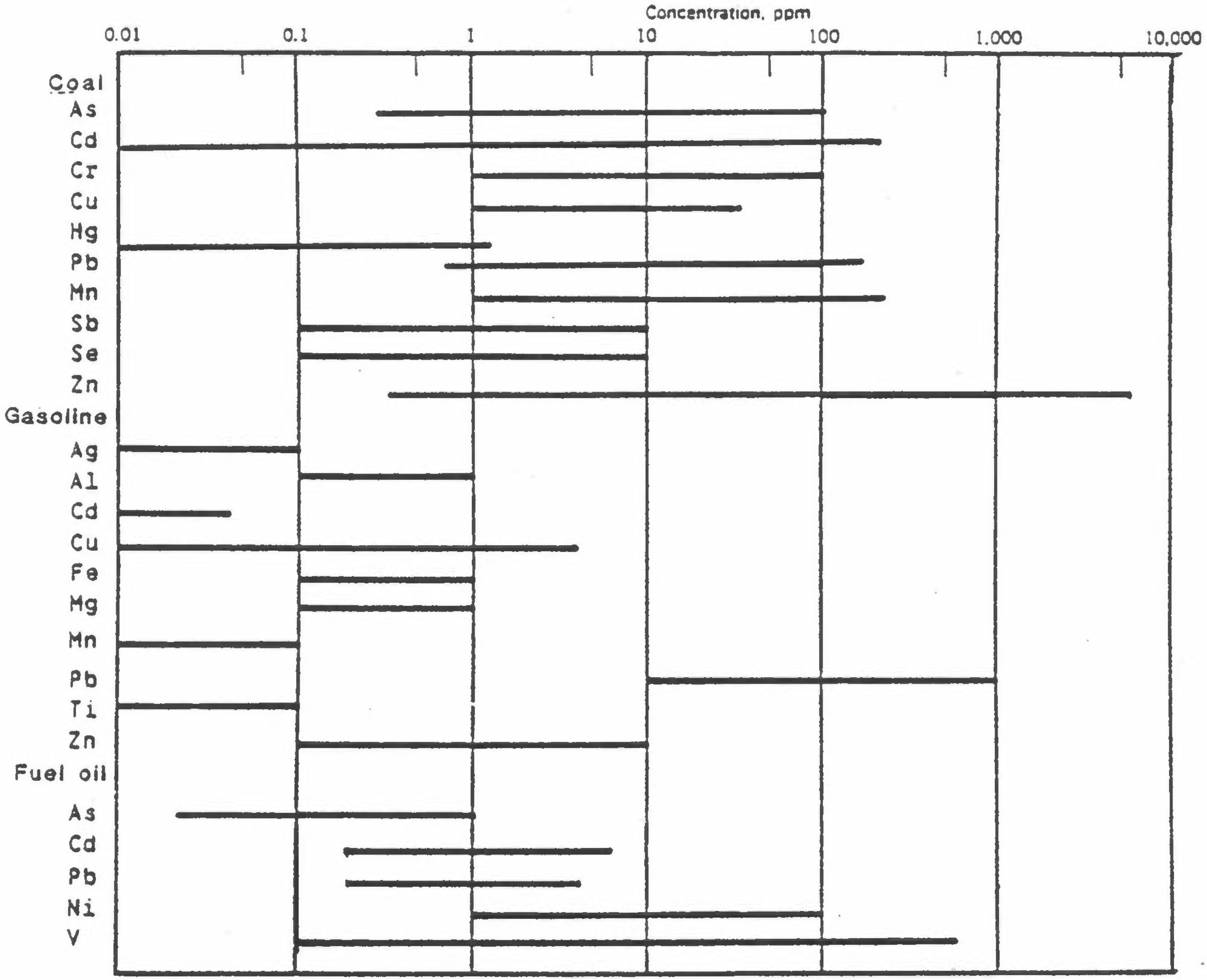

Figure 1: Range of trace elements in fuels.

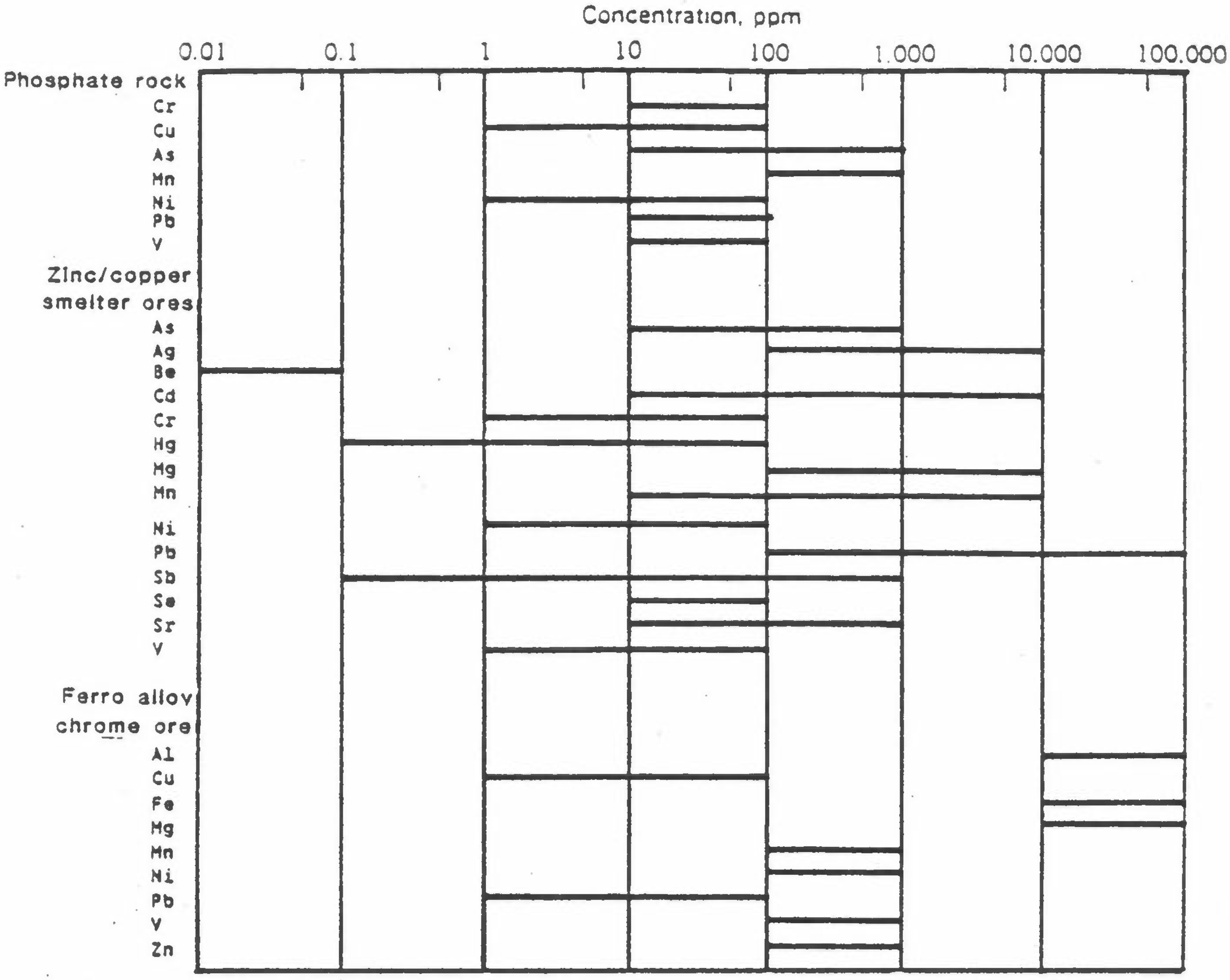

Figure 2: Range of trace elements in industrial materials.

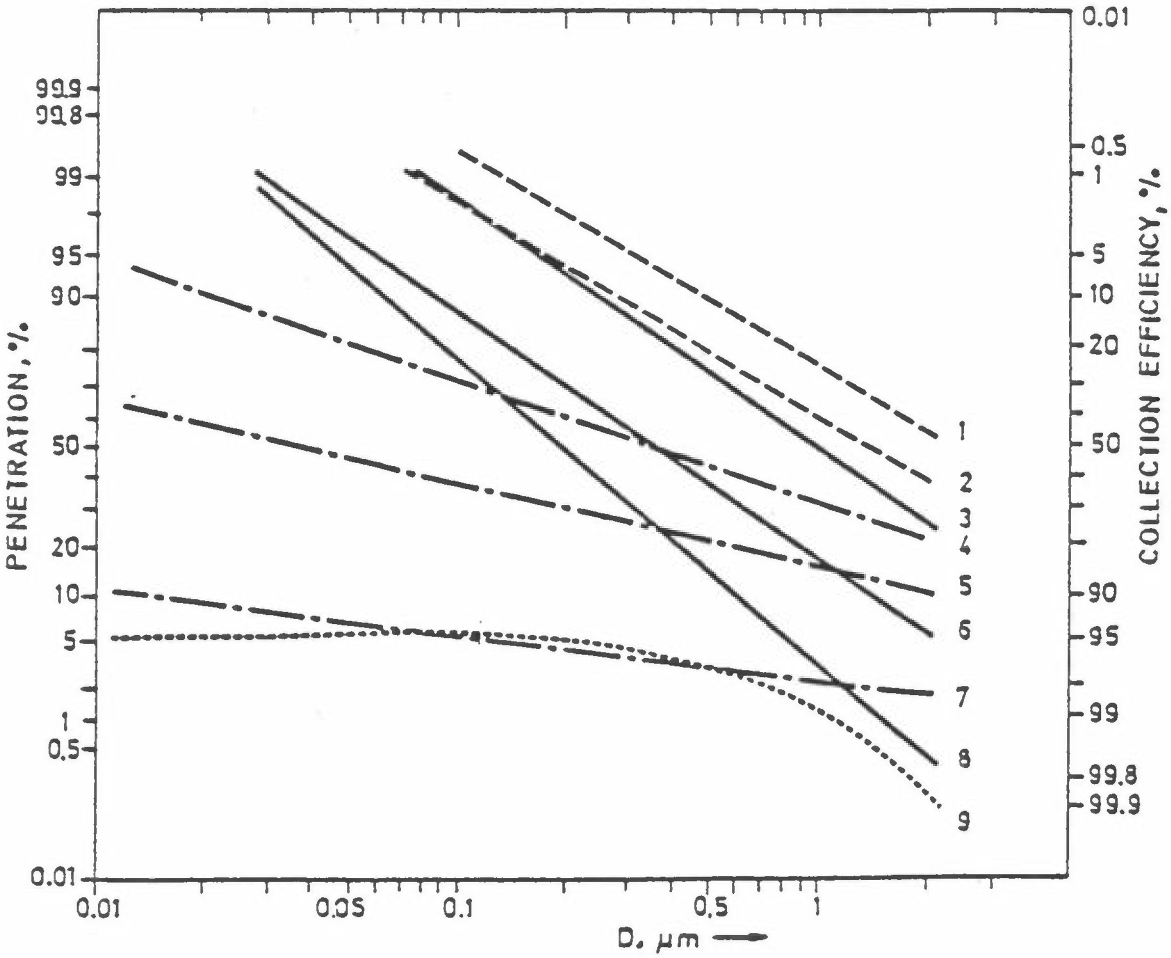

Figure 3: Average collection efficiencies and penetrations of control equipment for various particle sizes.
1 - High efficiency cyclone.
2 - Multicyclone.
3 - Low efficiency scrubber.
4 - Low efficiency electrostatic precipitator.
5 - Medium efficiency electrostatic precipitator.
6 - High efficiency scrubber.
7 - High efficiency electrostatic precipitator.
8 - Venturi scrubber.
9 - Fabric filter.

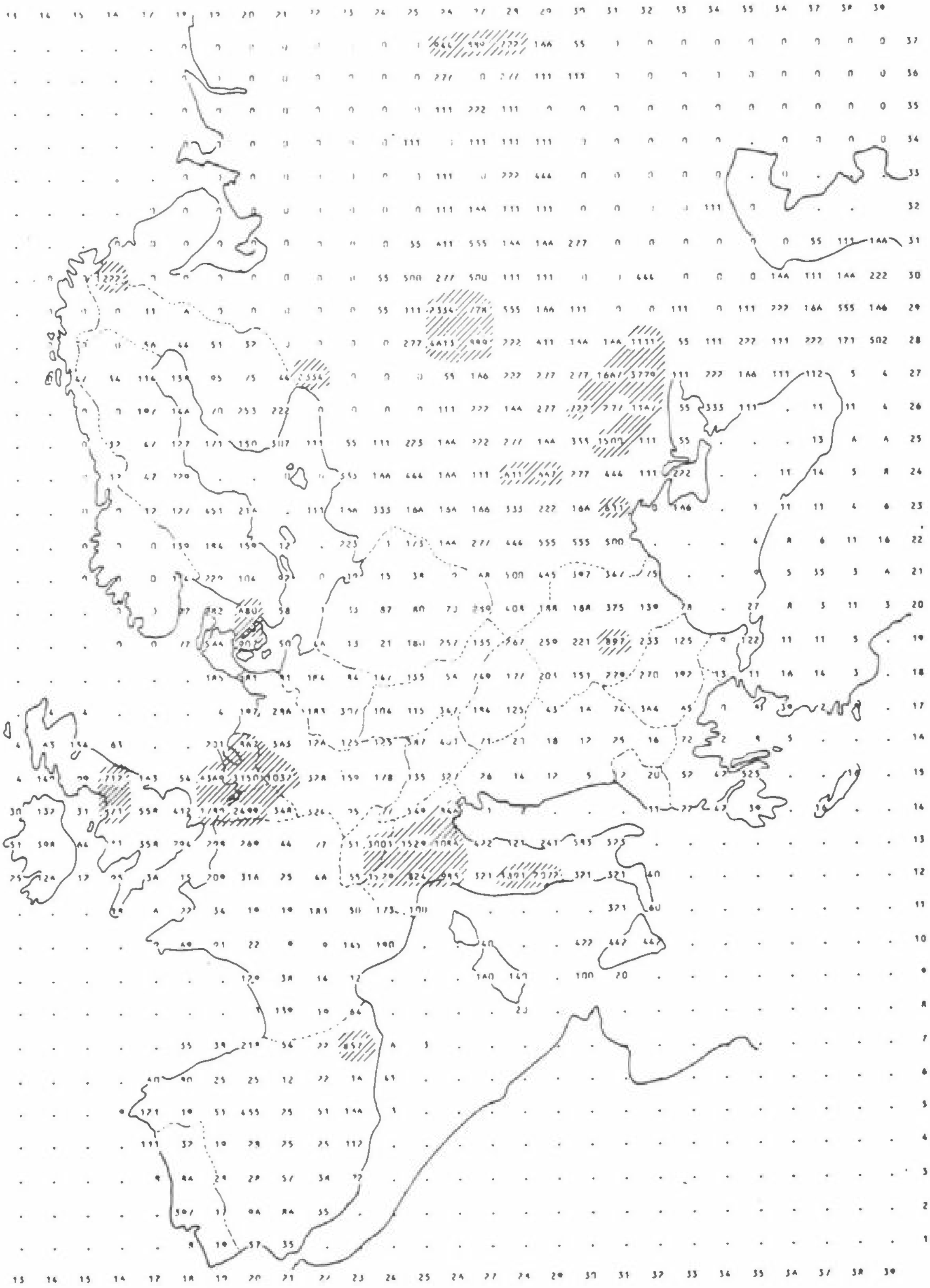

Figure 4: **Spatial** distribution of vanadium emission in Europe in 1979 in 10^2 kg/year. The shaded areas represent locations with emissions higher than the average for the grid area.

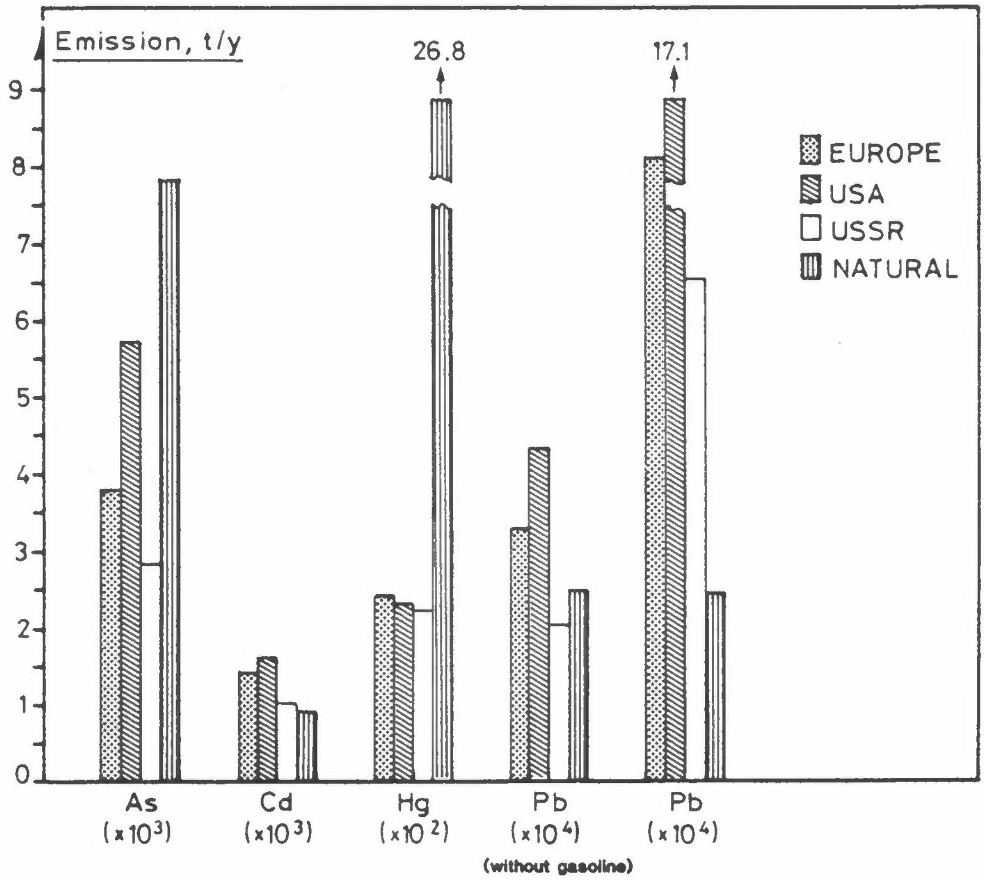

Figure 5: Total atmospheric emissions of As, Cd, Hg, and Pb in Europe, USA, USSR, and from natural sources.

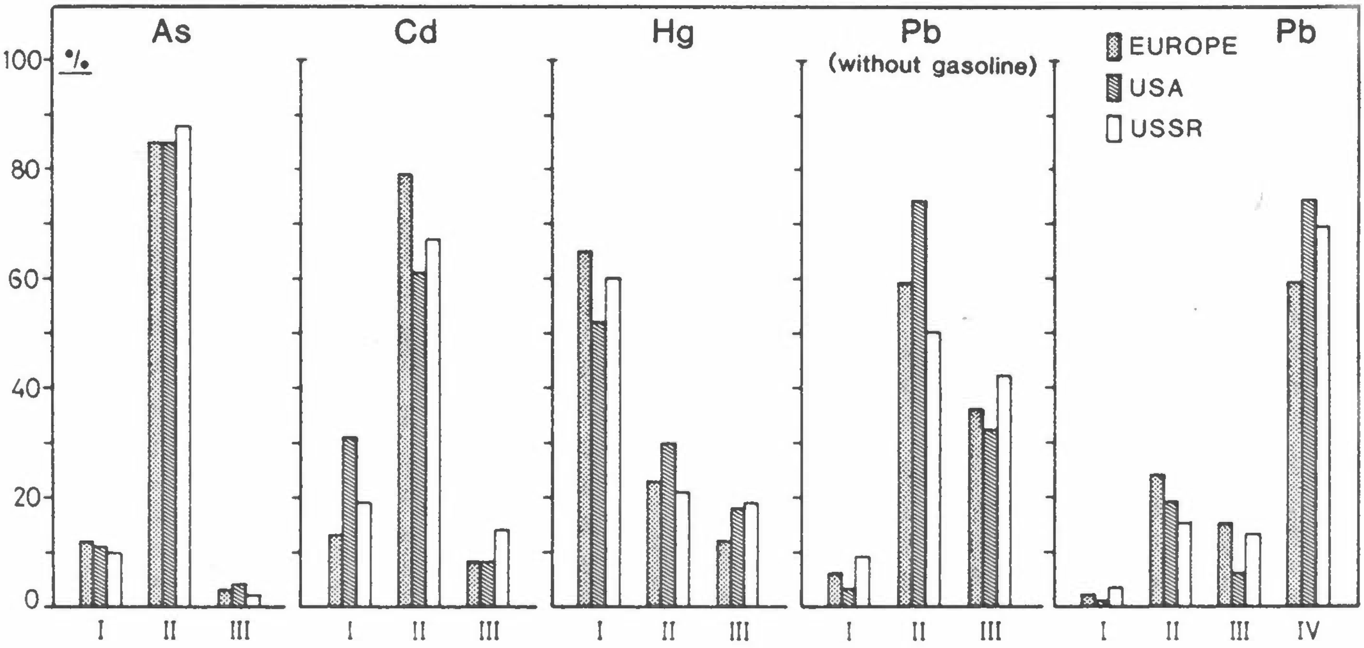

Figure 6: Atmospheric emissions of As, Cd, Hg, and Pb from fossil fuel combustion (I), non-ferrous metal production (II), and other anthropogenic sources (III) in Europe, USA, and USSR.

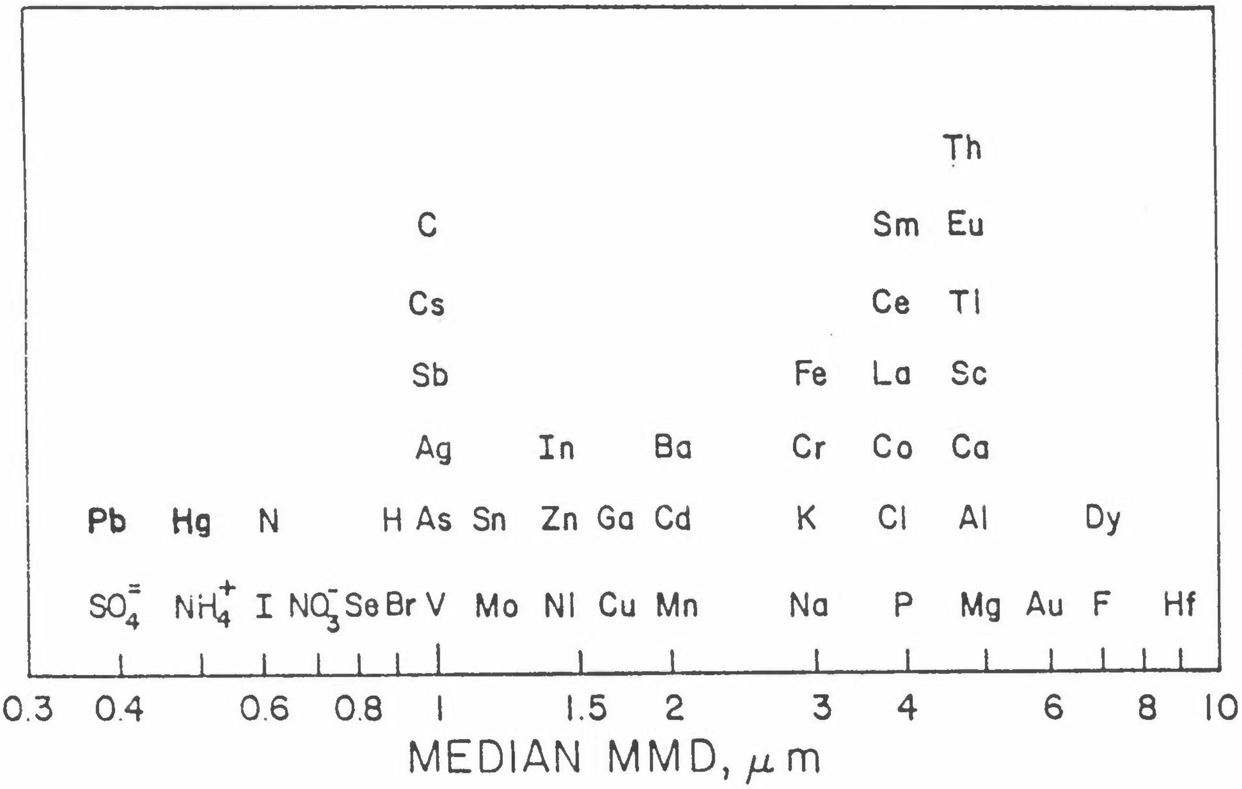

Figure 7: Mass median diameter of trace elements. Mean values. (After Rahn, 1976).

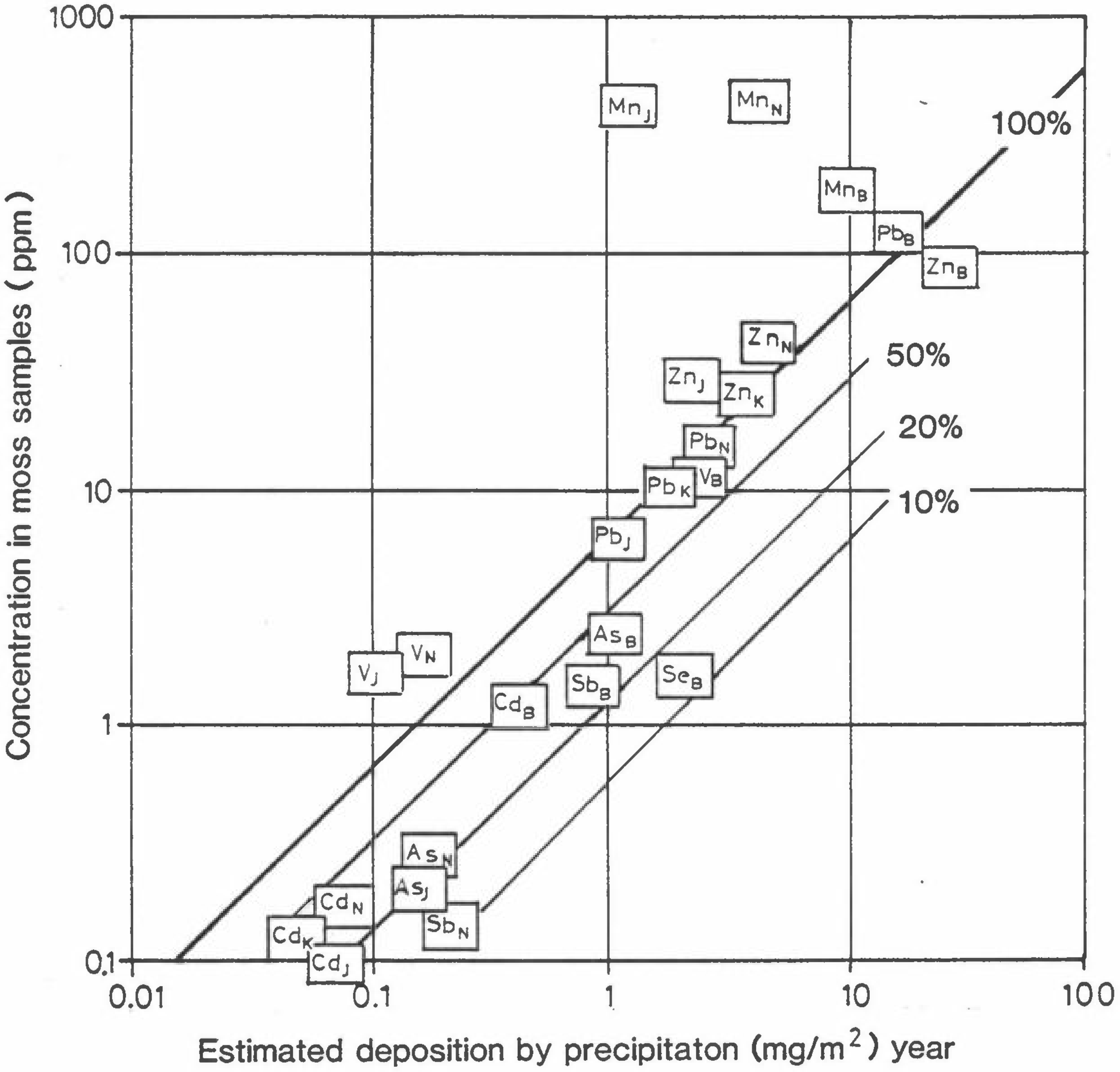

Figure 8: Comparison of trace element concentrations in moss samples and estimated deposition from precipitation samples.

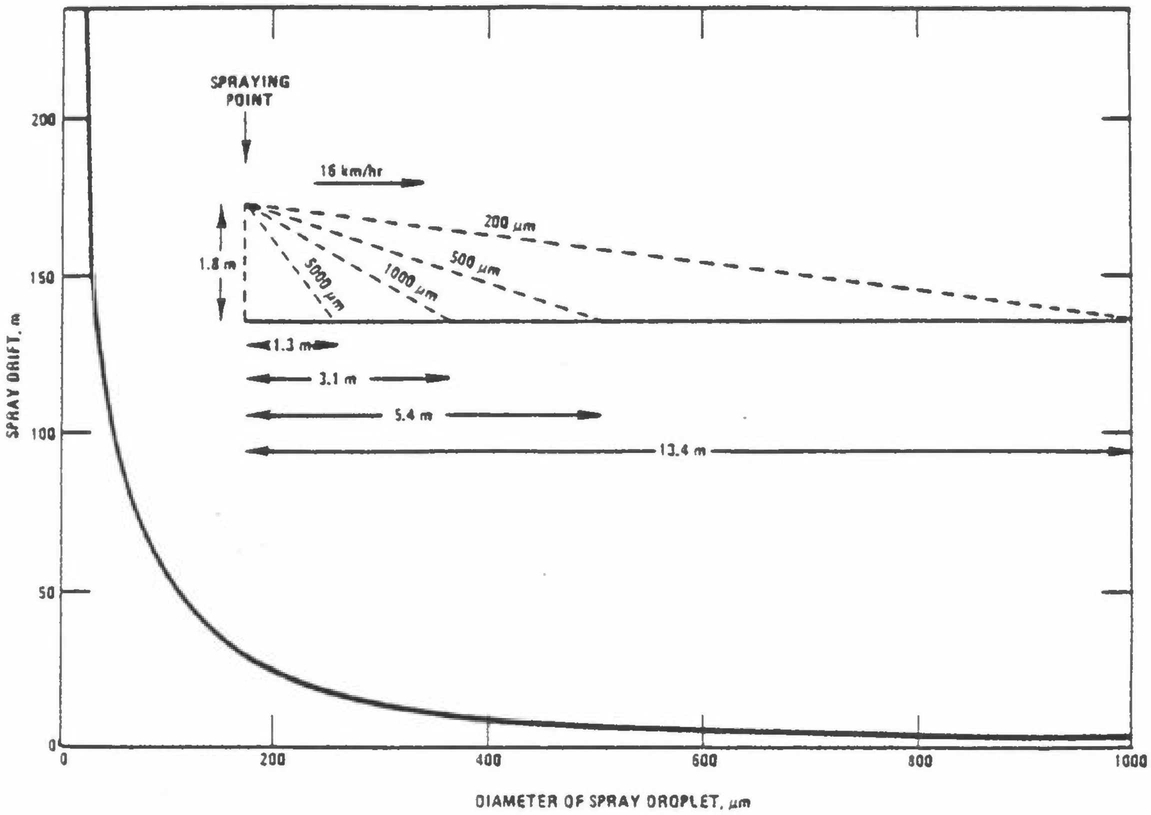

Figure 9: Spray drift as a function of diameter of spray droplets (after Furmidge, 1963).

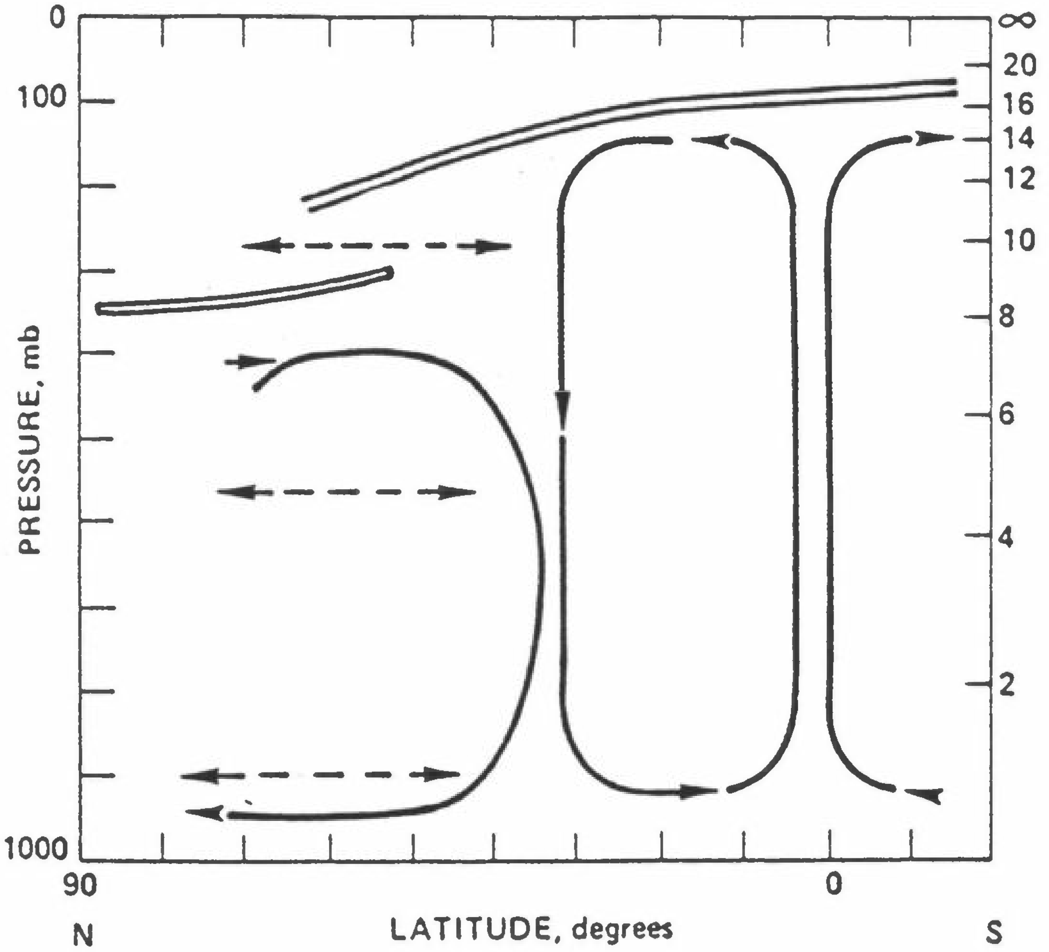

Figure 10: Hemispheric meridional circulation pattern (adapted from Pooler, 1971).

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TITTEL
Sources and atmospheric transport of toxic trace elements and chlorinated hydrocarbons and their migration through individual environmental media.

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TITLE

ABSTRACT Emission sources of heavy metals and chlorinated hydrocarbons are reviewed together with their atmospheric transport and migration in the environment. Concentration levels of these pollutants are presented for air, precipitation, vegetation, soil and surface water.

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