DIAGNOSIS AND PROGNOSIS OF THE DISTRIBUTION OF CONTAMINANTS IN THE GEOSPHERE

Uri Mingelgrin and Ahmed Nasser
Institute of Soils, Water and Environmental Sciences, Volcani Center, ARO, P.O.B 6, Bet Dagan, Israel

Abstract: Only in the late 1970's did the industrialized countries begin to comprehend the enormity of the damage brought about by pollution of the geosphere. Although the harm caused by the use of DDT and other organochlorine pesticides was already noted by Rachel Carson in her 1962 seminal book 'Silent Spring', the first major institutional move to stop pollution and reclaim polluted land was in 1978, when the Love Canal neighborhood was evacuated and the U.S. Superfund program initiated. The geosphere contains huge quantities of pollutants deposited in the past and more are still emitted today. This time-bomb threatens to release its toxic content into groundwater, surface water and the atmosphere and to contaminate the biota. Although the distribution of pollutants in the geosphere is hard to estimate since there is a continuous exchange of pollutants between the geosphere, biosphere, atmosphere and hydrosphere and pollutants undergo a myriad of both chemical and physical transformations, the state of the geosphere is undoubtedly worrisome. It is estimated that about 500,000 km^2 of the pre-2002 EU (16% of the land area) and about 35% of the land area of the countries that were then candidates for joining the EU are polluted to some degree. The prognosis is, however, better. Throughout the world, major efforts are being made to reduce pollution and remediate contaminated areas, and indeed signs of recovery are evident. In the U.S, for example, both the total amount of pesticides used and the quantity applied per unit area is declining steeply. The amount of herbicides added per unit area of corn, decreased by 25% and of insecticides by 60% in the decade between 1991 and 2001.

Key words: geosphere; global contaminants distribution; leading contaminants; organic pollutants; trace metals

I. Twardowska et al. (eds.),
Soil and Water Pollution Monitoring, Protection and Remediation, 3–23.

1. INTRODUCTION

The pollution of the geosphere is continuing relentlessly ever since the beginning of the Industrial Revolution, but only in the 1970s did decision makers begin to comprehend the severity of the damage it caused. One of the first to raise the alarm was Rachel Carson, who already in 1962, in her book Silent Spring, warned of the harm caused by the use of pesticides and in particular the persistent DDT and other organochlorine compounds. It took, however, more than a decade for authorities anywhere to take action. The first major institutional move to remediate polluted land and to stop the deterioration in soil and water quality which came perilously close to the point of no-return, was in 1978, when the Love Canal neighborhood in the city of Niagara Falls, New York was evacuated and the Superfund program was initiated. A ditch at the site where construction of a never-completed canal has begun by William T. Love was turned into a disposal site for municipal and industrial chemical waste. In 1953, the company that then owned and operated the site, covered the ditch with earth and sold it to the city of Niagara Falls for one dollar. Twenty five years after the Love Canal ceased to serve as a dump, over 80 compounds, 11 of them presumed to be carcinogenic, percolated upward, after their containers rotted and released their contents to the surface in yards and basements, including that of a public school built on the banks of the hazardous waste-filled ditch.

In response to the Love Canal environmental catastrophe, the U.S. Congress established a series of acts aimed at remediating polluted lands, halting ongoing pollution of the geosphere and preventing future pollution. U.S. EPA (United States Environmental Protection Agency) that came into being only eight years earlier was responsible for carrying out its mandates. The first act was named CERCLA (Comprehensive Environmental Response, Compensation and Liability Act) and was followed by SARA - The Superfund Amendments and Reauthorization Act. These acts established, for the first time anywhere, a government trust fund devoted to the remediation of polluted sites, the size of which was US$8.5 billion. It took Europe a few more years to join the fight against the pollution of the geosphere. The earliest inventories of POPs (persistent organic pollutants) were compiled in Europe only in the 1980s.

2. THE GLOBAL DISTRIBUTION OF POLLUTANTS IN THE GEOSPHERE

Despite the numerous measurements taken throughout the globe, an exact mapping of the global distribution of major pollutants is not possible. The distribution of pollutants in the geosphere is hard to estimate since it is ever changing. There is a continuous exchange of pollutants between the geosphere, biosphere, atmosphere and hydrosphere and pollutants undergo a myriad of biological, chemical and physical transformations. The complexity of the dynamics of pollutants distribution is exemplified in Figure 1 (Fernandez and Grimalt, 2003). Notwithstanding the uncertainty in defining its precise condition, the state of the geosphere is undoubtedly worrisome.

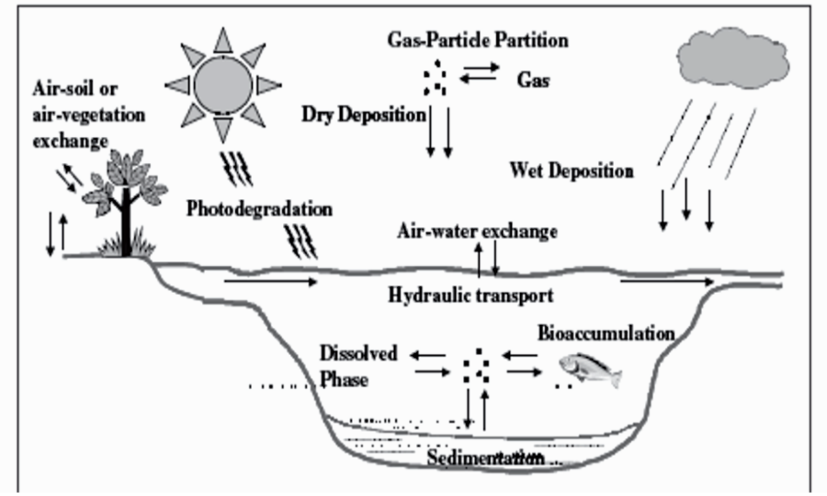

Figure 1. Main environmental processes governing long-range transport of pollutants (adapted from Fernandez and Grimalt, 2003).

It is estimated that 16% of the area of the countries that belonged to the European Union in 2002 (about 500,000 km^2) and 35% of the land area of the countries that were candidates for joining the EU at that time are polluted to some degree. The European Environment Agency estimated that there are about 1,500,000 sites that require soil remediation throughout the EU (Pollution Online, 2002). The precise number of polluted sites depends strongly on the definition of the maximum allowed levels of pollutant concentrations and on the thoroughness with which pollution is sought out. Thus, in the Netherlands, 350 sites were declared as requiring remediation in 1981, while in 1995 – 300,000 sites were designated as requiring remediation at a cost of 13 billion Euros. It is not likely that within a fifteen year period pollution spread to such an extent. It is much more likely that the immense increase in the number of polluted sites arose from the tightening of regulations regarding soil pollution and from soil analyses becoming mandatory or at least voluntarily performed in more cases.

2.1 Models

The fate of pollutants in the geosphere is not easily quantified. They may undergo, each pollutant to a different extent and through different pathways, numerous processes such as sorption, degradation, plant uptake, vertical transport and volatilization, and the interrelation between these processes is complex and non-linear. The major tool for overcoming the enormity of the task of defining the global distribution of pollutants is modeling. Predictive models are intended to forecast the future fate and distribution of pollutants from presently available data (or define the present state from past-collected data). However, even in the ideal case, models produce a good approximation of the most likely future scenario (or scenarios) but not yield an exact determination.

The limited predictive capacity of models is an unavoidable outcome of a few factors. Firstly, the measured data which serves as input for any given model's calculations is always incomplete. Data being collected by different research groups are likely to be measured at different spatial and temporal scales, making the integration of these data to a uniform input base rather complicated. Secondly, our understanding of the processes that pollutants undergo in the different compartments of the geosphere and of the myriad of interactions with biotic and abiotic entities is incomplete. This lack of complete knowledge results in the adoption of various approximations, (namely the construction of different models), each being suitable to a limited set of uses or conditions. Important processes which are not fully understood are often described by their effects, or in other words, the model employs empirical parameters. Such parametrization further limits the scope of the model, making its predictions less accurate as the environmental conditions for which the predictions were made become less similar to those of the systems in which data used for the definition of the model's parameters were collected. Different modeling approaches lead to predictions that at times vary significantly from each other. Finally, with all the breathtaking advances in computing capacity, present day computer power is still inadequate for the incorporation of all relevant interactions and processes in a single executable model, thus necessitating the adoption of rather crude approximations.

Nevertheless, a careful use of models, performed by personnel aware of the limitation of the specific model they chose to utilize, can give a reliable estimate of the present and future distribution of pollutants in the geosphere. Correctly used models serve as cost-effective tools for environmental impact assessments and make it possible to regulate the use of agricultural chemicals, identify areas which are potentially vulnerable to surface and groundwater contamination from non-point source pollution, or support ecosystem restoration goals. Environmental simulation models may serve as relatively inexpensive alternatives to costly field monitoring strategies. Even if modeling cannot yet completely substitute for laboratory or field measurements, it can serve as a complimentary assessment method, allowing more efficient use of data obtained from field and laboratory studies.

For example, according to EC Directive 91/414/EEC, the European Union requires information on Predicted Environmental Concentrations (PECs) in soil, groundwater, surface water and air of bioactive substances and their toxicologically and environmentally significant metabolites as supporting data in applications for authorization of the use of plant protection products. PEC values are used to determine whether additional studies (e.g. field or lysimeter studies) are required to assess the mobility of the product in soil and its potential for leaching into groundwater. Validated models are indispensable tools for predicting environmental concentrations in soil, groundwater and surface water. The EU is using a modification of the EPA version of the PRZM model developed by an industry/academic/EPA consortium named the Forum for International Co-ordination of Pesticide Fate Models and their Use. It goes by the acronym FOCUS (1997). FOCUS has developed standardized scenarios, intended to cover a range of conditions simulating those existing throughout the EU, for performing first-tier assessments of the exposure of groundwater and surface water to organic pollutants. These scenarios are due to become an essential part of the process of authorization of pesticides for use in the EU.

In the Netherlands, the model PESTRAS (Pesticide Transport Assessment) model was developed for use in assessing the fate and behavior of organic pollutants in soil. Processes like adsorption-desorption kinetics, the formation and behavior of reaction products, vapor diffusion in the gas phase and the volatilization of pesticide from the soil surface are included in that model, which is coupled to a model for soil water flow. Later on, the PEARL (Pesticide Emission Assessment at Regional and Local scales) model, simulating the behavior of pesticides in soils, was developed. Important features of that model are: (i) object oriented design, (ii) model and data are accessed through a user-friendly Graphical User Interface, (iii) data and scenarios are stored in a relational database, and (iv) easy link with external programs, such as Geographical Information Systems and inverse modeling tools. The PEARL model is now the official tool in Dutch pesticide registration procedures. It is a one-dimensional, multi-layer model that describes the fate of a pesticide and its relevant transformation products in the soil-plant system and considers the processes of transient state soil water flow, potential evapotranspiration, interception of water, water uptake by plant roots, evaporation of water from the soil surface, lateral discharge, heat flow, pesticide application, dissipation of pesticide from the crop canopy, convective and dispersive transport of pesticide in the liquid phase, diffusion of pesticide through the gas and liquid phases, equilibrium sorption and non-equilibrium sorption, first-order transformation kinetics, uptake of pesticide by plant roots, and volatilization of pesticide at the soil surface.

Environmental-fate and transport models vary in their complexity from simple indexing models to highly sophisticated stochastic models, which take into account a large number of relevant parameters and the dependence of their value on local conditions. Among the many index models that exist, noteworthy are LEACH and VOLAT (Laskowski et al., 1982), travel time(Jury et al., 1984), attenuation factor (AF) and retardation factor (RF) (Rao et al., 1985), mobility and degradation index (MDI) (Mahmood and Sims, 1986), leaching potential index (LPI) (Meeks and Dean, 1990) and mass-fraction models (Zee and Boesten, 1991; Beltman et al., 1995). These models are widely used for ranking the pollution hazard of chemicals, and in combination with geographical information systems (GIS) they can be used for regional-scale preliminary assessments of groundwater vulnerability to nonpoint-source pollutants (Khan and Liang, 1989; Hoogeweg and Hornsby, 1995; Hollis, 1988-1990; Loague et al., 1996). Kleveno et al. (1992) compared the AF model with the considerably more detailed PRZM model (Carsel et al., 1984) and found that the AF compared well to PRZM in estimating the relative mobility of pesticides in heterogeneous soils and under conditions of variable recharge. The latter model is the only significant pesticide model acceptable for regulatory purposes in the US. Nearly all geospheric transport models are deterministic and employ the one-dimensional flow approximation for flow in the unsaturated zone. Such models generally do not consider horizontal flow and do not produce a full 3-dimensional description of the flow process. Description of numerous models can be found in Jury and Ghodrati (1989), Jarvis et al. (1995) and Vanclooster et al. (2000).

2.2 Leading Contaminanats

Pollutants that are of more than local interest as far as contamination of the geosphere is concerned, must possess a number of characteristics, the more important of which are toxicity, persistence and a capacity to disperse, which in turn depends on the pollutant's leachability (or water solubility), volatility and tendency to sorb on particulate matter that has the potential to be air-borne.

The contaminants that have the highest impact on the geosphere may be classified as follows:

Trace elements – Concerning the global pollution of the geosphere, probably the most significant trace elements are the metals Hg (mercury), Cd (cadmium) and Pb (lead).

Organohalogens – These are organic substances containing halogens, especially chlorine and to a lesser extent bromine or fluorine. The more common groups in this family of compounds are:

- Halogenated aliphatic hydrocarbons. Probably the most important member of this group is TCE (trichloroetane or trichloroethylene) which is used heavily as a solvent or a degreasing agent in various industries and in dry cleaning.
- Halogenated aromatic hydrocarbons, such as dioxins. Dioxins are a group of several hundred substances that belong to two related sets of compounds: chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs).
- Chlorinated phenolic compounds, such as polychlorinated biphenyls (PCBs; Figure 2).
- Organohalogenateded pesticides, such as aldrin, dieldrin, andrin and DDT.

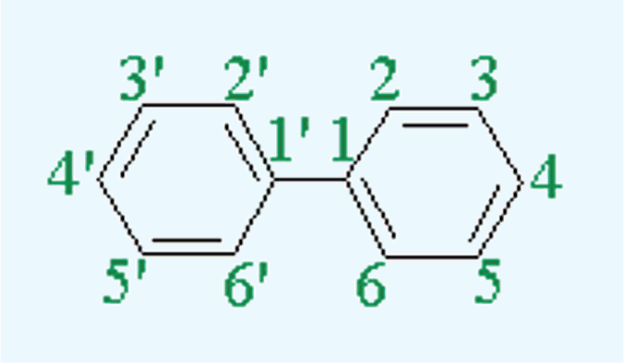

Figure 2. Schematic representation of PCBs.

Polyaromatic hydrocarbons (PAHs) - This is a group of over 100 organic compounds composed of several fused benzene rings (e.g., anthracene and pyrene). Some PAHs are persistent and carcinogenic and they are formed during the incomplete combustion of organic substances such as coal, oil, gas or garbage.

The United Nations, through its Environmental Program (UNEP), drafted the Stockholm Convention on persistent organic pollutants (POPs) which was adopted in 2001. The POPs listed in that convention as being of major environmental concern are given in Table 1.

Table 1. POP list adopted by the Stockholm Convention on persistent pollutants.

Aldrin	Heptachlor
Chlordane	Hexabromobiphenyl
Chlordecone	Hexachlorobenzene
DDT	Hexachlorocyclohexanes
Dieldrin	Mirex
Dioxins	PCBs
Endrin	PAHs
Furans	Toxaphene

2.3 Global Cycles of Persistent Pollutants

The global distribution of persistent pollutants, both POPs and toxic trace elements is not stationary. Neither is it determined by a process in which pollutants are added at a given location by man-made activity on the one hand and removed by natural processes such as leaching, evaporation or degradation on the other. Pollutants rather undergo a continuous cycle of redistribution, while an anthropogenic, freshly produced fraction may at any time be added into that cycle and another fraction is removed by both natural and anthropogenic processes.

The global spread of persistent organic pollutants has become one of the main environmental problems of the last decade (Fernandez and Grimalt, 2003). POPs can reach remote locations, far away from the source of pollution by a number of mechanisms. These include transport through the atmosphere in the gaseous state or in aerosols, and through the hydrosphere and the geosphere, in solution or attached to suspended particles, (for example, due to erosion). The presence of pollutants in remote areas is to a large extent due to transport in the atmosphere as a gas and hence, the more volatile the compound, the higher the probability for it to be found further away from its source. This phenomenon is sometimes termed the global distillation effect. The concentration of some POPs in polar regions and at high altitudes, where low temperatures result in condensation and consequently deposition, was reported to reach levels exceeding human consumption guidelines (AMAP, 1998).

Following is a brief discussion concerning some of the more important POPs. Dioxins are considered to be the most highly toxic group of xenobiotic compound. The tetrachloro dioxin congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD; Figure 3) is harmful in food and water at sub-ppt levels, and in fact, the term dioxin is used at times to refer to this congener. CDDs and CDFs are not commercial products, but are rather inadvertent byproducts of human activities such as industrial or municipal waste incineration or burning fuels (e.g., wood, coal or oil). Other activities, including chlorine bleaching of pulp and paper and certain processes employed in the chemical industry can also generate small quantities of dioxins. So can cigarette smoking. Natural processes, for example lightning-induced forest fires, can produce CDDs and CDFs as well and accordingly, dioxins were detected in the geosphere in locations where anthropogenic products are not likely to be present. Thus, traces of dioxins at the ppt level were found in buried clay deposits, both in Europe and in the U.S. Recent assessments confirm that anthropogenic emissions are the major source of dioxin released to the environment, but there is insufficient data to quantify the contribution of natural sources to the dioxin content in the geosphere.

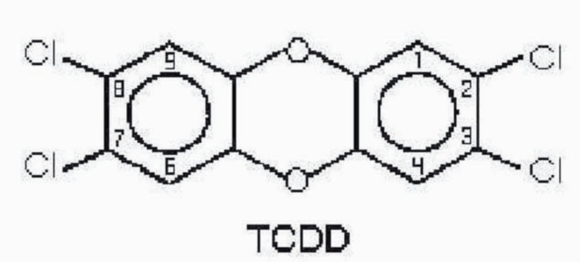

Figure 3. Structure of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

The global cycle of dioxins consists of suspension and formation of wind-born aerosols of particles (or droplets) that either contain dioxins or have them sorbed on their surfaces, and of evaporation of dioxins from soils and surface waters to the atmosphere. From there, redeposition back to land and surface water occurs. Adsorption to sediments and bioaccumulation are the primary removal mechanisms from surface water, until resuspension occurs again.

PCBs are probably the most important persistent organic pollutants. These compounds are dielectric liquids, resistant to both chemical and biological decomposition. Their major use is in transformers and other electric components. Due to their widespread use and persistence, PCBs were detected throughout the globe, from livers of seals in the Antarctic to mother’s milk in Europe. Deleterious effects in humans attributed to PCB uptake were detected, among other locations, in Taiwan and Japan. These effects included malformations in babies whose mothers were exposed to PCBs (Gladen et al., 2003). Their relatively low solubility in water provides a modicum of protection against acute poisoning (McFarland and Clarke, 1989), but the likelihood of long term accumulation of PCBs and their ubiquitous nature, make this family of compounds probably more hazardous than the considerably more toxic dioxins.

Studies on the distribution of PCBs in soils and the sub-soil (as well as in tree leaves) that were conducted in England, Scotland and Italy (Cousins et al., 1999), confirmed the widespread occurrence of PCBs in the geosphere. The work performed in the British Isles focused on sites in agricultural research farms far removed from potential PCB sources, thus ensuring that the PCB detected originated from aeolian deposition. In Italy, samples were taken in locations of varying proximity to PCB sources, including two remote Alpine valleys. As expected, there was a gradient in PCB concentration in soils, the concentration declining as the distance from PCB sources increased. However, even in the more remote locations both in Italy and the U.K., PCBs were detected. At all these remote locations, PCBs concentrations were similar, even if relatively low. This observation suggests the existence of a mechanism, most likely wind born, for a more or less uniform spread of PCBs throughout much of the globe, with peaks near contaminant sources. The above studies indicated that the leaching of PCBs downward in the unsaturated zone is rather slow, PCB concentrations at the soils' surface being a few orders of magnitude higher than at 20 cm depth. A similar vertical distribution was found in soils of Norwegian forests (Krauss et al., 2000).

Another pathway of PCBs dissemination was demonstrated in studies conducted in France and Canada. Domestic sewage was shown to contain considerable concentrations of PCBs, much of it apparently originating from aeolian deposition. Secondary treatment removed much of the PCBs' content, totally eliminating many of the congeners, especially the more hydrophobic ones. However, much of the removed PCB content remained in the sludge, sometimes resulting in a high enough concentration of PCBs to be of ecological and human-health significance (Blanchard et al., 2001; Pham and Proulx, 1997). Thus, irrigation with effluents or application of sewage sludges to soils, a common practice in many countries, may constitute a significant source of PCBs reaching the geosphere.

In summary, the major mechanism for PCBs mobility is a cyclical evaporation from soil and water surfaces and winds lifting PCBs into the air along with water vapor and dust, eventually redepositing them with rain and snow, condensed from the gas phase or adsorbed to settling particles. Because of their considerable environmental mobility, once emitted to the environment PCBs enter a global pool in which they remain susceptible to redistribution (Iwata et al., 1995; Tanabe, 1998). As a result of this high mobility and their substantial persistence, the concentrations of the PCBs tend to equalize throughout the globe (Tanabe et al., 1994). Accordingly, monitoring data indicate that the polar regions may become a sink for PCBs (Muir et al., 1992).

Munthe and Palm (2003) composed the final report on The Atmospheric Cycling of Mercury and Persistent Organic Pollutants, submitted to EUROTRAC-2 (A EUREKA Environmental Project). Hg was chosen for study since, of all the trace elements, it is of the highest global concern. It is toxic and its high volatility and the large number of species in which it is found in the environment dictate a world-wide distribution in all environmental compartments, including the hydrosphere, atmosphere and geosphere. Being an element and hence stable, Hg poses a long term risk to the global environment.

The major anthropogenic sources of mercury are emissions from combustion. Electric power plants, non-ferrous metal production plants, steel and pig iron foundries, cement kilns and waste disposal sites (especially waste incinerators) are prominent examples of mercury emission sources. In addition, considerable amounts of Hg are emitted from chlor-alkali plants, gold production installations, battery production plants and manufacturing of measuring and control instruments, electrical lighting, wiring devices, and electrical switches. About three-quarters of the total Hg emissions were attributed to combustion of fossil fuels, specifically of coal. Figure 4 summarizes the anthropogenic emission of mercury in 1995. Asia, and especially Japan, China, South and North Korea and India, is by far the largest source of mercury emission, China contributing more than 25% to the total global emissions.

Yet, Europe and South Africa are also significant contributors of mercury to the environment.

The environmental mobility of mercury is strongly dependent on the chemical speciation and physical mode (gas state, adsorbed etc.) in which the element is present. The major chemical form of mercury emitted to the atmosphere is gaseous elemental mercury, contributing around 50% of the total emissions. Bivalent mercury that exists as different nonionic organic species and as a cation is also commonly emitted into the environment. Atmospheric (and to a lesser extent effluent) emission of Hg sorbed on particulate matter contributes about 10% of the total mercury emitted. Identifying the chemical speciation of mercury emitted into the environment from a given source is crucial for the assessment of environmental and human health risks as well as for the estimation of transport and fate of the emitted mercury.

The exceptional volatility of mercury makes it the leading metal as far as global spread is concerned, but other metals such as Cd and Pb, are of major environmental concern. Since they are less volatile, these metals display a higher tendency to concentrate in areas that are relatively close to their source. The less volatile metals do spread through the environment, sorbed or embedded in particulate matter.

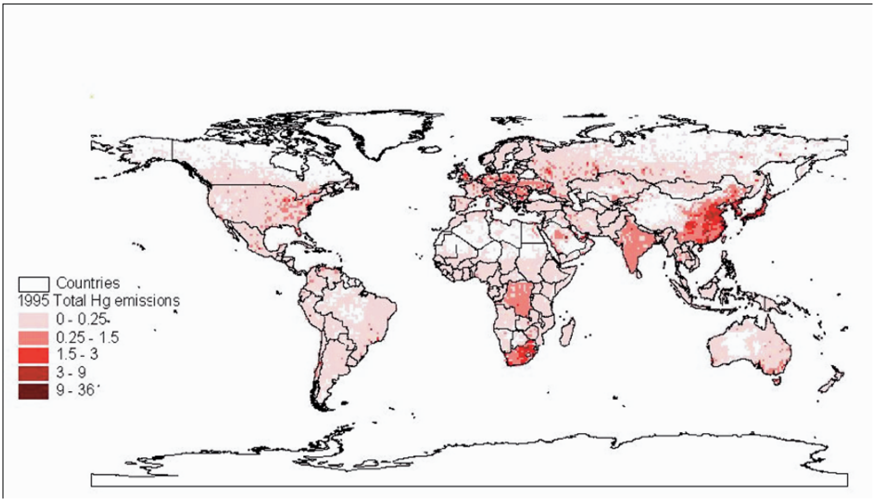

Figure 4. Anthropogenic emissions of total mercury (tons) in 1995 (Munthe and Palm, 2003).

Yet, the fact that in the case of Hg, only 10% of the atmospheric emission is in particulate form, indicates that atmospheric deposition of metals other than Hg is a less important source of geospheric pollution in locations that are situated far away from the pollution source.

Metals can be transported vertically as well as horizontally in the liquid phase, both as solutes and attached to suspended particles. The transport of metal ions, especially downward through the unsaturated zone, is enhanced by the formation of neutral and anionic complexes with various ligands, prominent among which are the soluble components of the organic fraction of soils or of soil additives such as sludge (Mingelgrin and Biggar, 1986; Vulkan et al., 2002). Figure 5 presents a paper electrophoresis chromatogram of the water soluble Cu species extracted from a sewage sludge. This chromatogram demonstrates the abundance of water soluble copper species present, most of them neutral or negatively charged.

Not only is enhanced transport via attachment to soluble species important to the downward movement of metal cations, but it is also relevant to the distribution in the geosphere of organic contaminants. Figure 6 demonstrates that the vertical transport of the pesticide atrazine was strongly enhanced by irrigation with an effluent. Sewage effluents are richer in potential carriers (e.g., dissolved organic matter, including detergents) than the high quality water used as the reference irrigation water in the study (Graber et al., 1995) in which this data was generated.

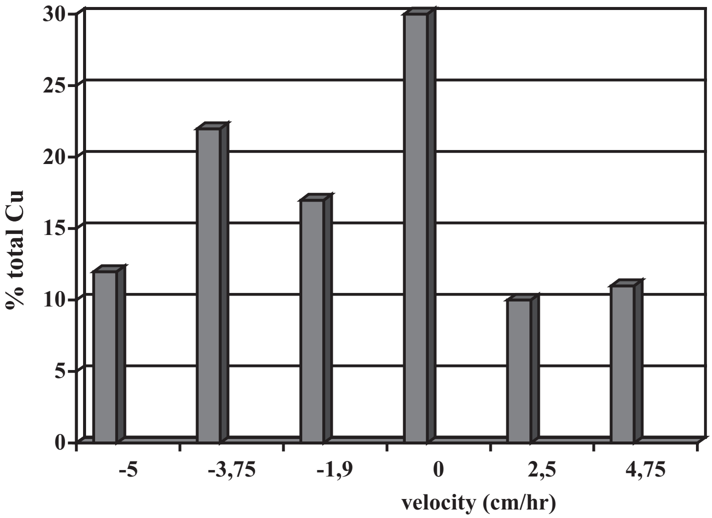

Figure 5. Paper electrophoresis chromatogram of copper species in a Davis sludge saturation extract (Mingelgrin and Biggar, 1986).

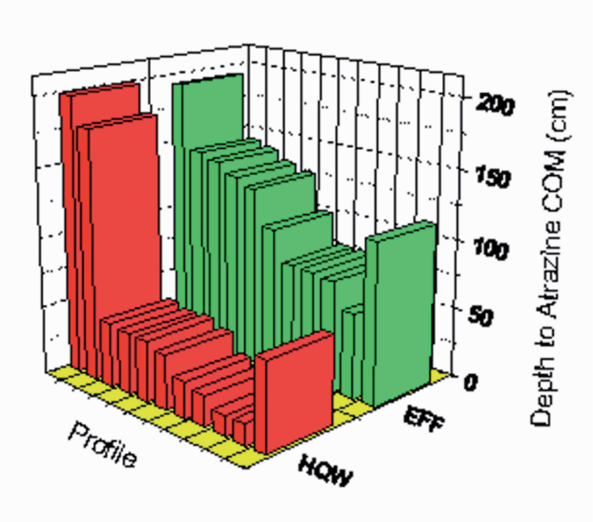

Figure 6. Atrazine transport under irrigation with sewage effluent (EFF) and high quality water (HQW) (Graber et al., 1995). COM refers to center of mass.

2.4 Case Studies

Meijer and co-workers (2003) conducted a survey on the global distribution of PCBs and HCB (hexachlorobenzene) in the soil's upper horizon. That team measured the concentrations of the investigated pollutants in 191 surface (0-5 cm) soils. Differences of up to 4 orders of magnitude were found for PCBs' concentrations between sites. The lowest and highest PCB concentrations (26 and 97,000 pg/g dw) were found in samples from Greenland and from mainland Europe (France, Germany, Poland), respectively. The authors estimated the total global load of PCBs in soils to be 21,000 ton.

PCB concentrations in soils were strongly influenced by proximity to the source of the pollution. The concentrations also increased with soil organic matter content, since PCBs, being rather hydrophobic tend to sorb to, and thus accumulate in, the organic fraction of the soil. Most (>80%) of the estimated PCB load in soils is found in the major "global source region", namely in the northern hemisphere at temperate latitudes (30-60 degrees N), or in the organic matter-rich soils just north of that region. The distribution of PCB consumption throughout the globe is given in Figure 7 and the good correlation between the concentration of PCBs in soils and between their consumption is evident.

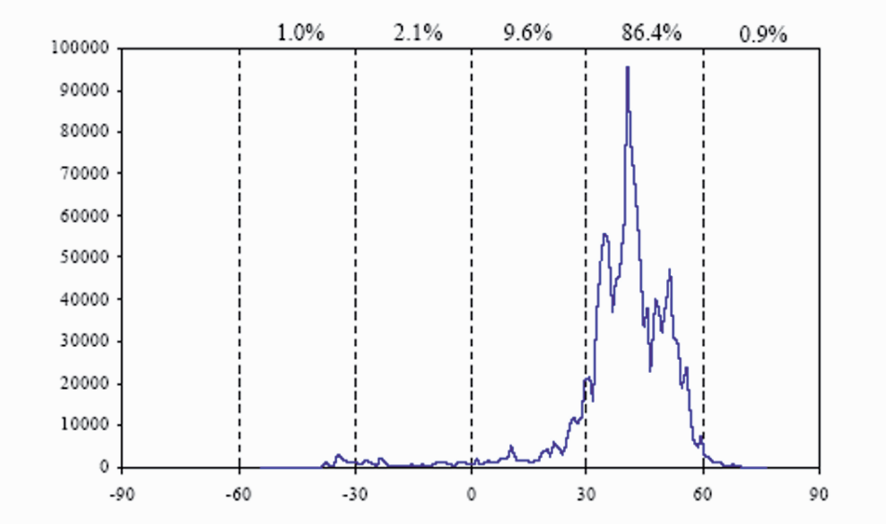

Figure 7. Estimated cumulative consumption of PCBs by latitude (in tons/degree) (Munthe and Palm, 2003).

The findings of the above study indicate that a gradient in PCBs concentration has developed throughout the globe, the concentration declining as the distance from the pollution source increases. Yet, significant concentrations of the pollutants were found at remote sites.

Thus, this comprehensive study confirmed the results of other investigations concerning the global distribution of PCBs (e.g., Section 2.3) that suggest a tendency of the concentration of PCBs to become similar throughout the globe, with the exception of peaks in concentration in the vicinity of the sources of pollution.

Accordingly, recent studies demonstrated that organochlorinated pollutants, including PCBs and organohalogenateded pesticides, are found in measurable concentrations all over the globe, even in areas far from the sources of pollution. For example, although they inhabit a remote location, albatrosses in the Midway Islands contained DDT, PCBs and dioxins in the adult birds, chicks and eggs at concentrations nearly as high as the concentrations found in bald eagles in the North American Great Lakes (e.g., Auman et al., 1997).

Fernandez and Grimalt, 2003, tried to define the global distribution of POPs, while minimizing the influence of local pollution foci. To that end they studied remote sites, specifically high altitude mountain regions. These authors measured the concentration of numerous POPs in water, soil, air and lake sediments in selected locations throughout Europe and the Tenerife Island. PAH concentrations in the sediments were particularly high in Eastern Europe (Tatra Mountains). In all other studied locations, the concentrations were similar, yet much lower then in the Tatra Mountains (Figure 8). Concentrations in soils and air samples showed a similar trend, demonstrating that air-borne particulate matter and the air gas phase are the main transport media for PAHs. Accordingly, atmospheric deposition is the main mechanism of geospheric pollution far enough from the source of pollution. In contrast, the concentrations of the organochlorinated compounds measured in that study did not display an orderly geographic distribution or a distinct relationship between their concentrations in the different environmental compartments (Figure 9). Fernandez and Grimalt (2003) did, however, discern an altitude-dependent concentration gradient for the organochlorinated compounds which was more evident for the less volatile PCBs, suggesting a condensation phenomenon from the gas phase.

2.5 Prognosis of the State of the Geosphere

Pollutants have been reaching the geosphere for many years now, both directly as a result of local anthropogenic activity and after being carried, at

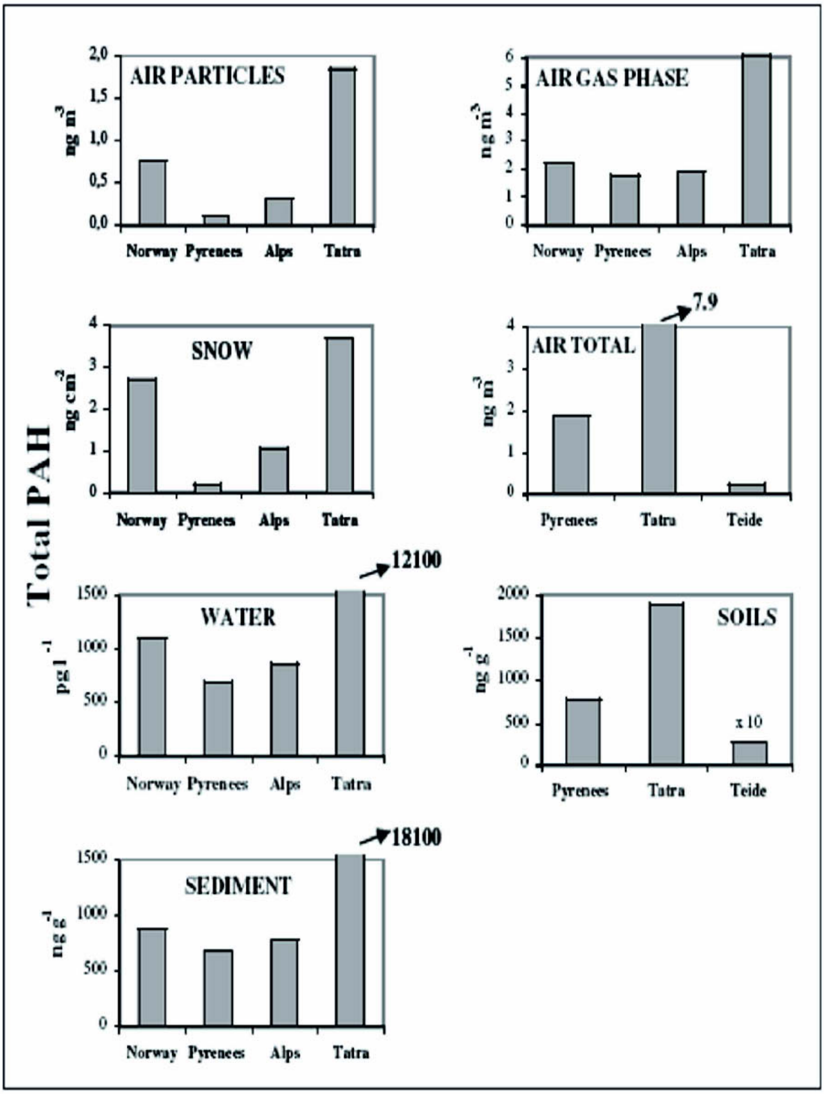

Figure 8. Total PAH levels (sum of 23 compounds from fluorene to coronene) at selected high altitude regions (Fernandez and Grimalt, 2003).

times for long distances, through the hydrosphere or the atmosphere. The geosphere, and in particular its upper horizons, has thus turned into a depository of a myriad of contaminants and their degradation products. Consequently, the state of the geosphere, as far as its load of pollutants and the resultant damage to the ecology and to human health, is bad and in numerous locations pollution has reached the level of a veritable environmental disaster. The prognosis for the future quality of the geosphere is, however, guardedly good. Throughout the world, major efforts are being

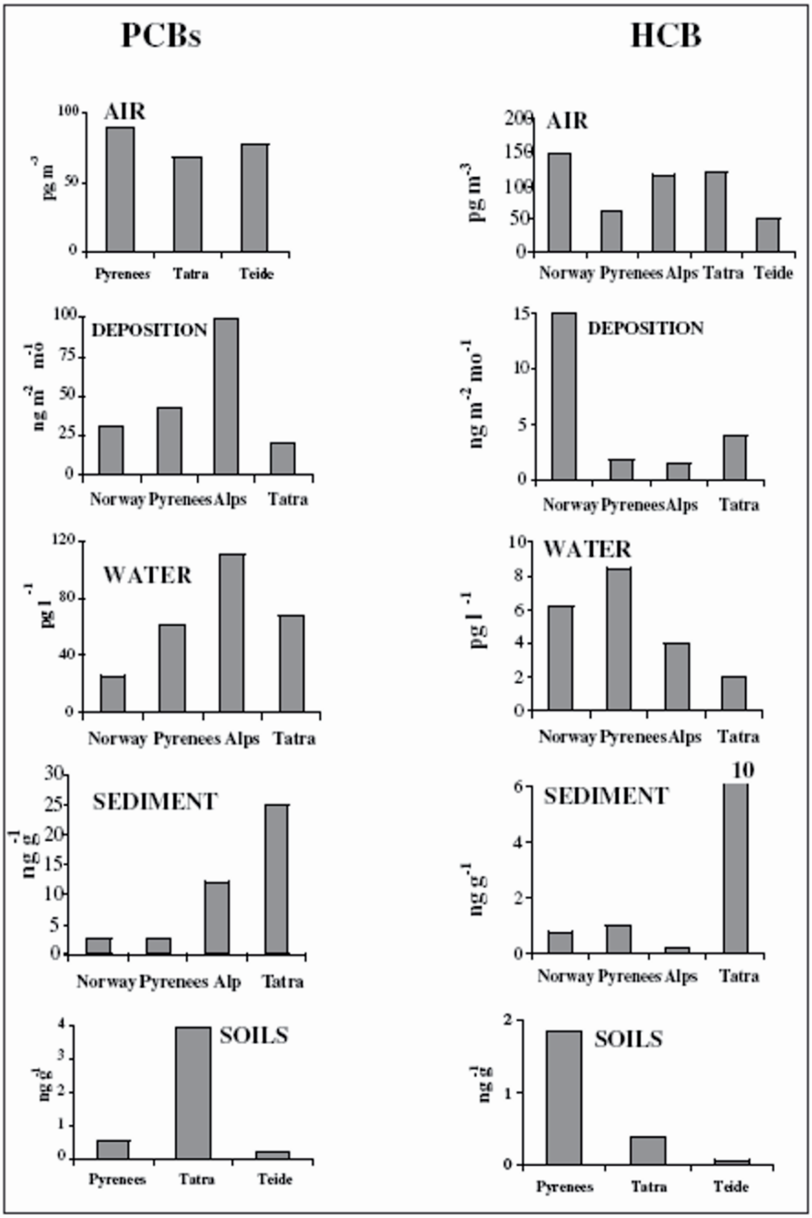

Figure 9. Concentrations of PCBs (sum of 7 congeners) and HCB at selected high altitude regions (Fernandez and Grimalt, 2003).

made to reduce pollution and to remediate already contaminated areas. Sampling and analytical procedures both ex- and in-situ have greatly improved in recent years. One interesting example (Terry et al., 2001) is the development of a technology to detect the elusive DNAPLs with the aid of hydrophobic dyes. Similarly, remediation protocols are becoming more technically efficient and economically affordable, thus making it feasible to remediate a wider range of polluted areas. And indeed, signs of recovery are evident.

Various indicators of environmental pollution point at a reduction in the extent of contamination of the geosphere. This turning of the tide is particularly evident in the more developed countries, but it also holds true on a global scale. Dioxins, for example, are only one of several families of contaminants for which fish advisories have been withdrawn by several states in the U.S. One reason for this is that many pulp and paper mills have changed their bleach kraft processes in a way that reduced the levels of dioxins in their effluent. The number of advisories for dioxins that were issued in the U.S., fluctuated between 1993 and 1997, with the highest number of advisories (65) being in effect in 1997. Since then, the number of advisories declined. Likewise, federal efforts to enforce regulations addressing PBTs (persistent, bioaccumulative, and toxic compounds), have yielded a considerable reduction in PBT emissions. The U.S. EPA estimated that in 1999 alone, the amount of PCB waste released in the U.S. was reduced by 129 million pounds as compared to the previous year and the amount of PAHs released declined by four million pounds (EPA, 2000). The amount of soils contaminated by dioxin, lead or arsenic was reduced by 573 million pounds in that year (EPA, 2000).

The amount of persistent pesticides used globally, and in particular of pesticides that are highly toxic to non-target organisms, is on the decline. New pesticides are more effective against their target pests and at the same time less harmful to other organisms. In the U.S., both the total amount of pesticides used and the quantity used per unit cultivated area are being reduced sharply. In corn production, for example, the amount of herbicides added per unit area declined by 25% and the amount of insecticides by 60% between 1991 and 2001. The fraction of pesticides listed in the United States that is defined as highly toxic to mammals, declined by more than 50%. Current trends in plant protection practices further reduce the risk pesticides pose to the environment. These trends include the development of precision agricultural procedures, whereby sensors such as remote sensing devices, enable the optimization of application time and dose at a high spacial resolution. The broader acceptance of integrated pest management, in which biological and other non-chemical plant protection methods are integrated into the pest control regime, and the fast expansion of organic agriculture are also welcome trends from the environmental point of view.

The above optimistic prognosis should not divert our attention from local foci of pollution still active. The high cost of adopting pollution-preventing measures, led many firms and municipalities to resist the efforts of environmental agencies to impose the cessation of emission of pollutants. This is true even in countries in which awareness of the harm done by the emitted pollutants is very high, let alone less environmentally conscious countries. Likewise, the cost of soil remediation, which despite of recent advances is still very high, leads many firms to disavow their responsibility to past and present contamination and to fail to disclose emissions that would require cleanup.

Countries that are experiencing an intensive process of industrialization tend to neglect, in the midst of that process, environmental concerns. Strict international supervision is at times necessary to keep these sources of pollution to a minimum. A case in point is China, in which environmental pollution has reached a critical level in some places. Yet, the fact that the Chinese government has declared already in 2002 the launching of a massive 700 billion yuan ($84 billion), 5-year environmental protection plan to combat the worsening pollution, suggests that this large country is also approaching the stage of receding environmental pollution.

REFERENCES

AMAP 'Arctic Pollution Issues, 1998: A State of the Arctic Environment Report', Arctic Monitoring and Assessment Programme, Oslo, p. 188.

Auman H. J., Ludwig J. P., Summer C. L., Verbrugge D. A., Froese K. L., Colborn T. and Giesy J. P., 1997, PCBs, DDE, DDT, and TCDD-EQ in two species of albatross on Sand Island, Midway Atoll, north Pacific Ocean. *Environ. Toxicol. Chem.*, 16, 498–504.

Beltman W. H. J., Boesten J. J. T. I. and S. E. A. T. M van der Zee, 1995, Analytical modeling of pesticide transport from the soil surface to a drinking water well. *J. Hydrol.* **169**, 209–228.

Blanchard M., Teil M. J., Ollivon D., Garban B., Chesterikoff C. and Chevreuil M., 2001, Origin and distribution of polyaromatic hydrocarbons and polyclorobiphenyls in urban effluents to wastewater treatment plants of the Paris area (France), *Water Res.,* **35**, 3679–3687.

Carsel R. F., Smith C. N., Mulkey L. A., Dean J. D. and Jowise P., 1984, User's Manual for the Pesticide Root Zone Model (PRZM) Release 1, EPA-600/3-84-109. US Environmental Protection Agency, Athens, GA.

Cousins I. T., Gevao B. and Jones K. C., 1999, Measuring and modeling the vertical distribution of semivolatile organic compounds in soil. I: PCB and PAH soil core data, *Chemosphere*. **39,** 2507–2518.

EPA U.S., 2000, First Annual 1999 Accomplishments Report, EPA's Agency-wide Multimedia Persistent, Bioaccumulative, and Toxic Pollutants Initiative. EPA 742-R-00-003, (2000).

Fernandez P. and Grimalt J. O., 2003, On the global distribution of persistent organic pollutants, *Chimia*, **57**, 514–521.

FOCUS, 1997, Leaching models and EU registration. DG VI. European Commission, Doc. 4952/VI/95, Brussels, pp. 123.

Gladen B. C., Doucet J., and Hansen L. G., 2003, Assessing human polychlorinated biphenyl contamination for epidemiologic studies: lessons from patterns of congener concentrations in Canadians in 1992, *Environ. Health Perspect*., **111**, 437–443.

Graber E. R., Gerstl Z., Fisher E. and Mingelgrin U., 1995, Enhanced transport of atrazine under irrigation with effluent, *Soil Sci. Soc. Am. J.,* **59**, 1513–1519.

Hollis J. M., 1988-1990, Assessments of the vulnerabiliy of aquifers and surface waters to contamination by pesticides. Research Report of the Soil Survey and Land Research Centre for U.K. MAFF.

Hoogeweg C. G. and Hornsby A. G., 1995, Pesticide risk assessment in a watershed using GIS. Applications of GIS to the modeling of non-point source pollutants in the vadose zone, *ASA-CSSASSSA Bouyoucos Conference, Mission Inn, Riverside, CA*.

Iwata H., Tanabe S., Ueda K. and Tatsukawa R., 1995, Persistent organochlorine residues in air, water, sediments, and soil from Lake Baikal region, Russia. *Environ. Sci. Technol.* **29**, 792–801.

Jarvis N. J., Bersgtrom L. F., and Brown C. D., 1995, in: *Environmental Behaviour of Agrochemicals*, edited by T. R. Roberts and P. C. Kearny, (Wiley, New York), pp.196–220.

Jury W. A., and Ghodrati R., 1989, in: *Reactions and Movement of Organic Chemicals in Soils*, Soil Science Society of America, Special Publications, **22**, pp. 271–304.

Jury W. A., Spencer W.F., and Farmer W. J., 1984, Behavior assessment model for trace organics in soil: III. Application of screening model. *J. Environ. Qual.* **13**, 573–579.

Khan M. A. and Liang T., 1989, Mapping pesticide contamination potential. *Environ. Mgmt.* **13**, 233–242.

Kleveno J. J., Loague K., and Green R. E., 1992, Evaluation of a pesticide mobility index: impact of recharge variation and soil profile heterogeneity. *J. Contam. Hydrol.* **11**, 83–99.

Krauss M., Wilcke W. and Zech W., 2000, Polycyclic aromatic hydrocarbons and plolychlorinated biphenyls in forest soils: depth distribution as indicator of different fate, *Environ. Pollut.,* **110,** 79–88.

Laskowski D. A., Goring C. A. I., McCall P. J., and Swann R .L., 1982, in: *Environmental Risk Analysis for Chemicals*, edited by R. A. Conway (Van Nostrand Reinhold, New York,, pp.198–240.

Loague K., Bernknopf R. L., Green R. E. and Giambelluca T. W., 1996, Uncertainty of Groundwater Vulnerability Assessments for Agricultural Regions in Hawaii: *Review. J. Environ. Qual.* **25**, 475–490.

Mahmood R. J. and Sims R.C., 1986, Mobility of organics in land treatment systems. *J. Environ. Eng.* **112** (2), 236–245.

McFarland V. A and Clarke J. U., 1989, Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: consideration for a congener-specific analysis, *Environ. Health Perspect.*, **81**, 225–239.

Meeks Y. J. and Dean J. D., 1990, Evaluating ground-water vulnerability to pesticides. *J. Water Res. Planning Mgmt.* **116** (5), 693–707.

Meijer S. N., Ockenden W. A., Sweetman A., Breivik K., Grimalt J. O., and Jones K. C., 2003, Global distribution and budget of PCBs and HCB in background surface soils. *Environ. Sci. Technol.*, **37**, 667–672.

Mingelgrin U. and Biggar J. W., 1986, Copper species in aqueous sewage sludge extract, *Water, Air Soil Pollut.,* **28**, 351–359.

Muir D. C. G., Wagemann R., Hargrave B. T., Thomas D. J., Peakall D. B., Norstrom R. J., 1992, Arctic ecosystem contamination. *Sci. Total Environ.* **122**, 75–134.

Munthe J. and Palm A., 2003, editors, The Atmospheric Cycling of Mercury and Persistent Organic Pollutants. Final Report, submitted to EUROTRAC-2 (A EUREKA Environmental Project), MEPOP, International Scientific Secretariat, GSF - National Research Center for Environment and Health Munich, Germany.

Pham T. T. and Proulx S., 1997 PCBs and PAHs in the Montreal urban community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St Lawrence River, *Water Res.*, **31**, 1887–1896.

Pollution Online, April 19, 2002; http://www.pollutiononline.com.

Rao P. S. C., Hornsby A. G., and Jessup R. E., 1985, Indices for ranking the potential for pesticide contamination of groundwater. *Soil and Crop Sci. Soc. Florida Proc*. **44**, 1–8.

Tanabe S., 1988, PCB problems in the future: foresight from current knowledge. *Environ. Pollut.* **50**, 5–28.

Tanabe S., Iwata H. and Tatsukawa R., 1994, Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Total Environ.* **154**, 163–177.

Terry W., Griffin P.G. and Watson K. W., 2001, A comparison of field techniques for confirming dense non-aqueous phase liquids (DNAPLs); http://www.containment.fsu.edu/cd/content/pdf/203.pdf.

Vanclooster M., Boesten J. J. T. I., Trevisan M., Brown C. D., Capri E., Eklo O. M., Gottesburen B., Gouy V., and A. M. A. van der Linden, 2000, A European test of pesticide-leaching models: methodology and major recommendations, *Agric. Water Man*age. **44**, 1–19.

Vulkan R., Mingelgrin U., Ben-Asher J. and Frenkel H., 2002, Characterization and time dependence of transition metal speciation in the solution of a sandy soil amended with sewage sludge, *J. Environ. Qual.* **31**, 193–203.

Zee van der S. E. A. T. M. and Boesten J.J.T.I., 1991, Effects of soil heterogeneity on pesticide leaching to groundwater. *Water Resource. Res.* **27**, 3051–3063.