Time Delayed Responses of Chemicals in Soils

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ABSTRACT

In areas were agriculture is practised the input of chemicals often exceeds the amount removed with the crop. As a result an accumulation of chemicals and leaching of chemicals to the groundwater takes place. Removal times from the soil may vary upto tens of thousands of years. This retention is caused by strong adsorption/precipitation processes of the soil constituents (capacity controlling parameters). However, the properties of the soil as well as redox and pH conditions may change with time for instance by changes in land-use. Because chemicals exhibit a non-linear behavior towards those changes this may result in a sudden release (Stigliani et. al., 1991; Salomons, 1993).

EXAMPLES OF THE ACCUMULATION OF METALS, NUTRIENTS AND PESTICIDES IN SOILS

The use of chemicals in agriculture is widespread in Europe and the US. Numerous reports on groundwater pollution by agricultural chemicals are available in the literature (Hallberg, 1989; Leistra and Boesten, 1989). The use of organic chemicals in four European countries is presented in figure 1.
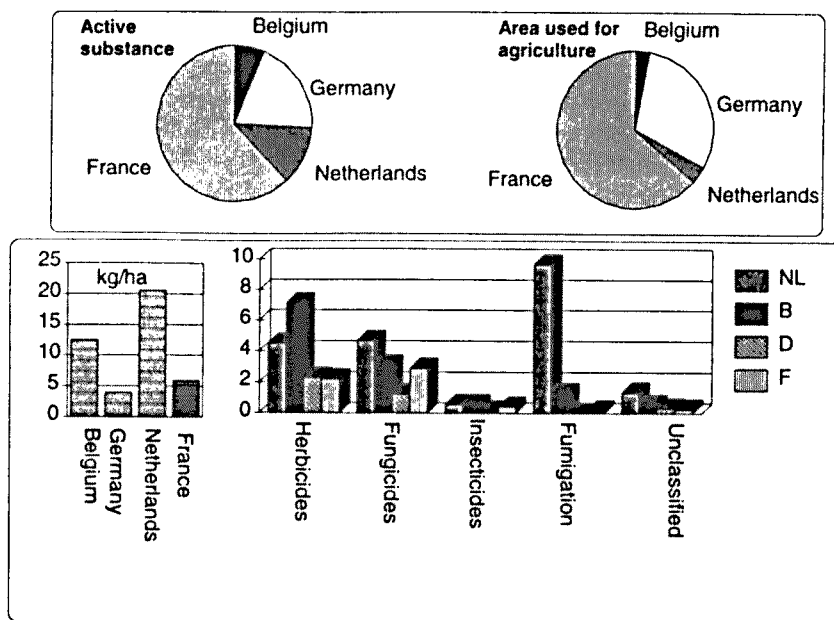

Figure 1. Use of organic chemicals in Germany, France, Belgium and the Netherlands (Salomons and Stol, 1993)

The highest total amount is used in France which also has the highest area in use for agriculture. More important however, from the view point of potential impact on the environment, is the use of organic chemicals per hectare. In this comparison Belgium and the Netherlands have the highest usage of organic chemicals per hectare. Fumigation of the soil (in particular in potato growing areas) accounts for the huge use of organic chemicals in the Netherlands. In the Netherlands numerous restrictions on the use of organic chemicals in agriculture will be put into force and it is expected that in a few years time application will be halved.
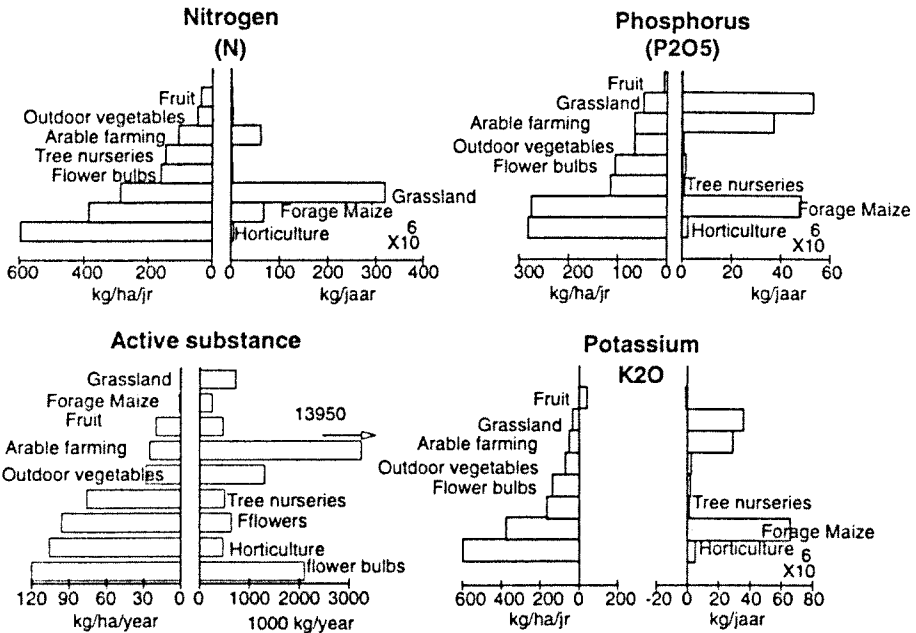

Figure 2.   Accumulation (application minus removal by crop) of nutrients in different farming systems (Salomons and Stol, 1993)

In figure 2 the use of organic chemicals (expressed as active substance) and of nutrients in Dutch agriculture is shown. The growing of flower bulbs, flowers and cultivation of crops green houses use the highest amounts of active substance. Expressed in kg/ha/year the application of organic chemicals is as high or higher then the application of fertilizers. The data given in figure 2 refer to the applied amounts minus removal by crop. They do not take into account degradation.

Nutrients also show an excess if the application is corrected for the amounts removed by crop. There is one exception: the application of potassium fertilizer in fruit growing area. Here potassium use is limited because excess potassium causes a certain kind of disease in apples. The growing of forage maize accounts for a large input of nutrients into the soils. This excess use of nutrients is not because of the high nutrients requirements of maize. The forage growing areas in the Netherlands are used as a "dumping area" for excess animal manure from the animal husbandry industry.

The excess chemicals is degraded in the soil (organic chemicals), accumulated and partly transported to the groundwater. The accumulation in the soil is highly dependent on the properties of the chemical and the nature of the soil itself. To make some intercomparison possible we calculated the time needed to remove different chemicals from a one meter soil column by natural leaching. The soil chosen was a sandy soil because of its low retention properties.
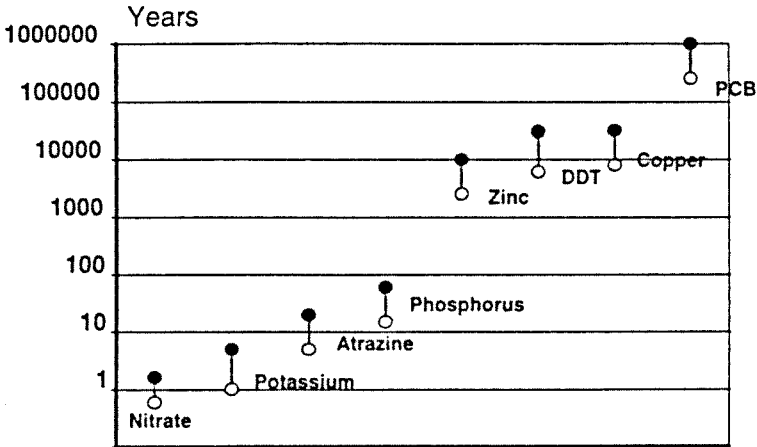

Figure 3. Time needed to remove by natural leaching chemicals from one meter of sandy soil (Salomons, 1993)

For strong hydrophobic compounds like PCB's and DDT or some heavy metals the time needed is in the order of thousands to tens of thousands of years. This long retention time of those chemicals puts severe boundaries on the allowable inputs in the soil from fertilizers and atmospheric deposition to prevent a further increase in the upper part of the soil.

NON-LINEAR BEHAVIOR OF HEAVY METALS

Redox changes

Chemical conditions in the environment can conveniently be depicted in so-called Eh-pH diagrams (figure 4).One of the impacts of mankind on the environment could be referred to as "messing-around" in the Eh-pH diagram. Draining of peat lands, flooding of soils or storage of dredged material on land are examples of man-induced changes in redox conditions.

Redox potential (Eh) depends on the availability of oxygen in soils, waters, and sediments, and upon biochemical reactions by which microorganisms extract oxygen for respiration. One can think of the redox potential as a kind of "chemical switch" (non-linear) mechanism determining the observed sequence by which the chemicals are utilized by microorganisms.
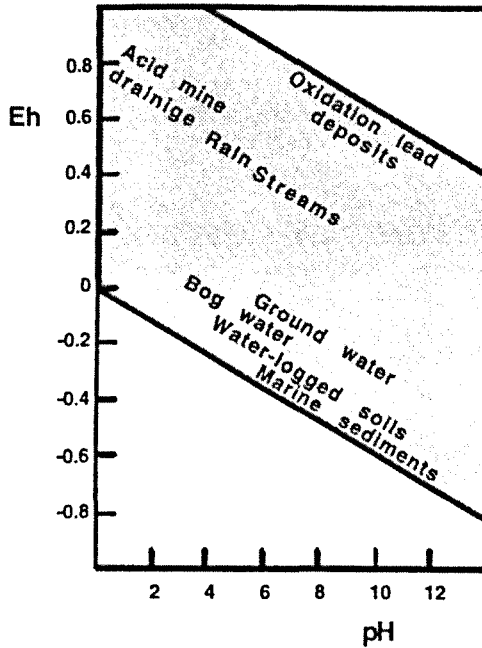
Figure 4. Major environments in terms of their Eh and pH range (Based on Garrels and Christ, 1965).

The Eh-pH diagrams can also be used to show the stability of heavy metal compounds and provide an easy way to illustrate the result of changes in environmental conditions.
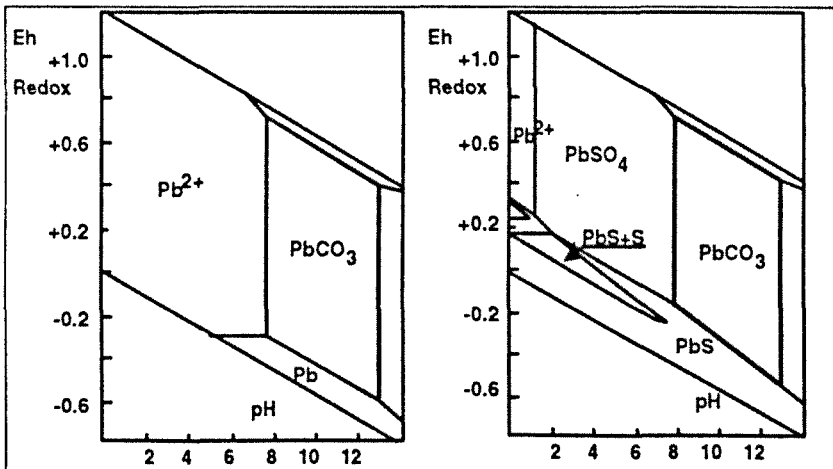

Figure 5. The Eh-pH diagram for lead in a freshwater environment and for a marine environment.

Redox conditions influence the mobility of metals in two different ways. Firstly, there are direct changes in the valences of certain metals. For example, under reducing conditions Fe^{3+} is transformed to Fe^{2+}. Similarly, manganese and arsenic are subject to direct changes in valence. Since the reduced ions are more soluble, increased concentrations of these metals have been observed in reducing environments such as ground waters and pore waters of sediments. Redox changes effect metals also indirectly. As an example a Eh-pH diagram for lead is shown in figure 5. The dominant stable phase is lead carbonate which becomes unstable if the environment becomes more acid. Lead carbonate has a rather high solubility product and when this mineral occurs in surface waters high dissolved lead concentrations are expected.

On the other hand under reducing conditions (low redox) sulfate reduction will take place and leadsulfide becomes a stable phase. Leadsulfide has an extremely low solubility and concentrations of lead in pore waters of sediments is low. The formation of metalsulfides is important for those depositional areas where sulfate is present: estuarine and marine environments. On the other hand, an increase in the redox will cause lead sulfide to become unstable with a subsequent rise in dissolved lead concentrations. This change is not gradual but rather sudden and an example of a non-linear response. The change from lead sulfide occurs when polluted (anoxic) sediments are dredged from harbors and dumped either on land or in waterways. In these oxygenated environments lead sulfide is not stable and will be oxidized.

Indirect effects also occur when chemicals are associated with components which are subject to redox changes. This is the case for phosphorus and most metals which are (at least partly) associated or adsorbed to iron and manganese hydroxides (Förstner, 1986). These phases are not stable with a lowering of the Eh (figure 6) and are converted to ironsulfides or ironcarbonates depending on the chemical conditions. When this occurs the metals associated with iron and manganese hydroxides are mobilized.
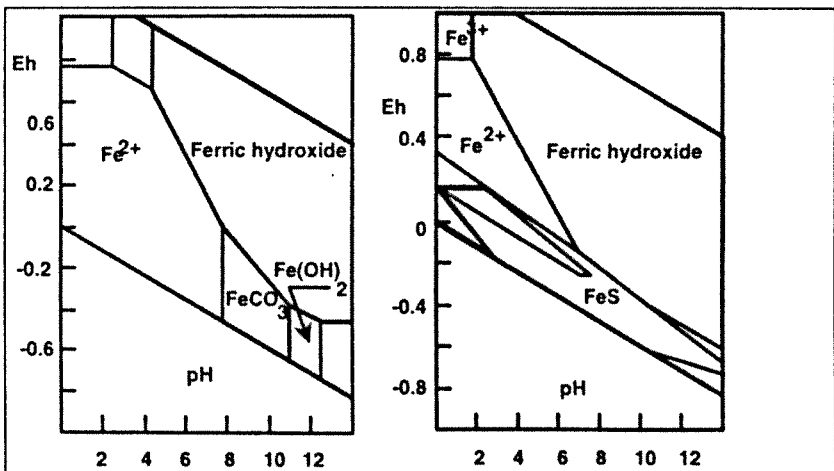

Figure 6. The Eh-pH diagrams for iron in a freshwater environment and in a marine environment.

Precipitation processes versus adsorption processes

The Eh-pH diagrams only refer to metal compounds. However, in a number of cases no compounds are formed but the metals are absorbed to iron-manganese hydroxides, clay particles and the organic matter. It is important to know whether dissolved metal concentrations are determined by precipitation-dissolution reactions (formation of metal compounds) or by adsorption processes. With precipitation-dissolution processes the concentrations will not depend on the total metal content in the sediment/soil, and an increased input in the system will not affect the dissolved concentrations (Figure 7). On the other hand when adsorption is the main process for binding the metals, the increased input will cause an increase in metal concentrations in the pore waters.
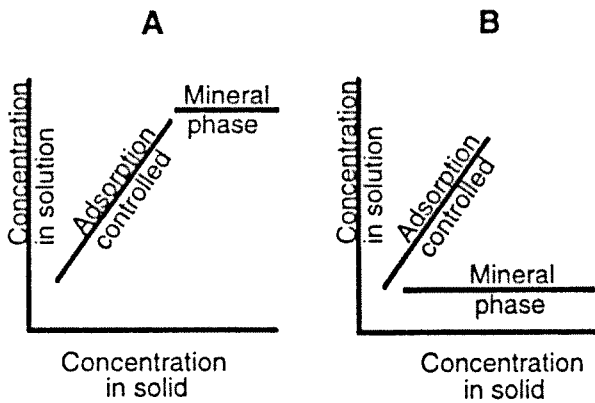

Figure 7.   Relationship between dissolved metal concentrations and the concentration in the sediments.

In figure 7 a summary is given of concentrations of heavy metals in pore waters of contaminated anoxic sediments in relation to the total concentrations. Two situation are possible:

- the metal compounds has a higher solubility compared with the adsorbed form (figure 7 A)
- the metal compound has a lower solubility compared with the adsorbed form (figure 7 B)

Metalsulfides which occur under reduced conditions in sediments and soils have a low solubility and we have situation 7 B. Direct evidence for presence of sulfides has been obtained from microprobe studies.

For lead in surface waters or in mine waste we may have the situation of figure 7 A. This especially the case if leadcarbonate is directly introduced in the water system or present in waste dumps as happens in certain cases of lead mining. This situation is unfavorable

since the high solubility of leadcarbonate may cause high dissolved lead concentrations and make the water unfit for drinking water. Whether such a situation persists depends on the presence of adsorbing substances like clays, organic matter or Fe/Mn hydroxides in the system. If this is high, leadcarbonate is converted to adsorbed lead with a lower solubility

However, if the suspended matter concentrations (surface waters) are low or the amount of adsorbing substances is low (waste dumps), the dissolved lead concentrations will be determined by the solubility lead carbonate mineral. This may result in high dissolved lead concentrations.

Storage of contaminated dredged spoil on land causes an increase in the mobility of heavy metals in the surface layers of the dump site. Under reducing conditions most metals occur as sulfides with a low solubility. Under oxygenated conditions the sulfides become unstable and the metals become adsorbed to the sediment/soil particles with an increase in overall solubility (see figure 7 B). As a result an increased accumulation of metals in crops takes place (Nijssen and van Driel, 1988)

Changes in redox conditions also take place when dredged material removed from harbours and discharged in surface waters. Figure 8 shows the results of an experiment in which dredged material was suspended in river- and in seawater for extended periods of time to simulate the dumping of dredged material in a highly energetic environment. In both cases the dredged material contains cadmiumsulfide which is unstable in surface water and a remobilization of cadmium is expected. However, a drastic difference is observed between a freshwater and a marine environment. In both cases the cadmiumsulfide decomposes. In the marine environment only a partial readsorption takes place because the chloride ions form very strong cadmiumchloride complexes and thus prevent readsorption. Chloride is hardly present in the riverwater and a nearly complete readsorption and consequently low mobilization of cadmium takes place.
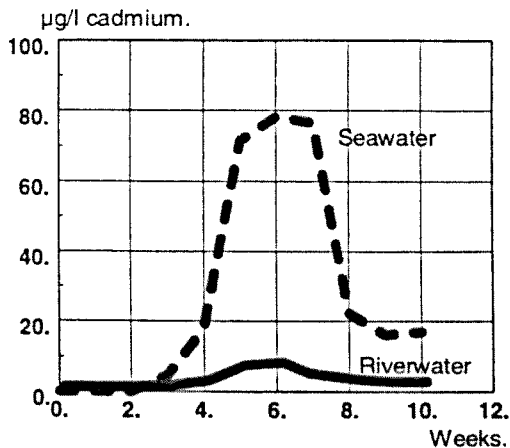

Figure 8. Release of cadmium from dredged material suspended in seawater and in riverwater.

Adsorption of metals: influence of the pH

The adsorption of metals is highly dependent on the pH and increases from near nil to near 100% as pH increases through a critical range 1-2 units wide (Salomons and Förstner, 1984). This means that a small shift in pH causes a sharp increase or decrease in dissolved metal levels. The pH depends to a large extent on the buffering capacity of the system. If the buffering capacity is slowly consumed as may happen trough continuous input of acid from acid rain or acid mine drainage a certain threshold will be exceeded and metals will start rather suddenly to desorb from the sediments or the soils. The onset of the adsorption or the desorption is characteristic for each metal. This rather sudden change is again an example of a non-linear response of the system.
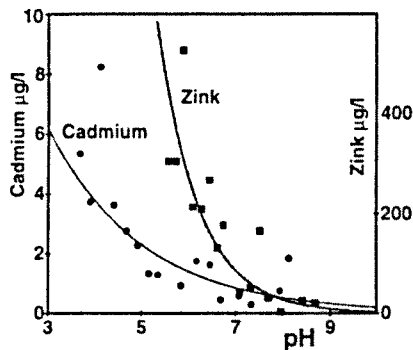

Figure 9.   The relationship between the pH and cadmium and zinc in the soil solution for soils in the Netherlands.

Figure 9 gives as an example the relationship between pH and dissolved metal concentrations in a set of soils from Western Europe. These soils had different degrees of metal contamination, however figure 9 shows that pH is an overriding factor in determining the concentrations in solution. Also quite clear from these data is the non-linear response of the metals towards pH changes. If buffering capacity in the form of calciumcarbonate is present (e.g. liming by farmers) the pH will remain above about 6 and metals will have low concentrations in the pore waters of the soil. Once the buffering capacity is gone (in itself a non-linear phenomenon) the pH decreases and the metal concentrations in the soil solution increase rapidly.

This non-linear response has also ecotoxicological significance. A nice example has been observed by us in the river Rhine and its distributary the river IJssel (Salomons, 1989). Travel time from the river Rhine to measuring point in the river IJssel is only a few days. However, over this time period the pH increase about 0.5 units. As a result the distribution of cadmium over the suspended matter and the solution changes due to increased adsorption. The decrease in dissolved cadmium causes a decrease in uptake by the bivalve Dreissena polymorpha. In this case it is a positive benefit (detoxifying), however in a river or lake subject to acidic inputs the reverse would occur.
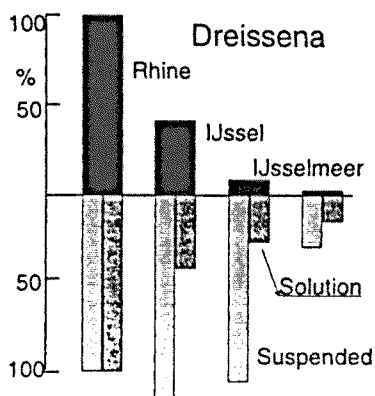
Figure 10. Relative concentrations of cadmium in Dreissena Polymorpha in the river Rhine, in its distributary the river IJssel and in the IJsselmeer (a lake which is fed by the IJssel). The concentrations of cadmium in solution and in the suspended matter are shown below the X-axis. Concentrations in the river Rhine are given as 100 %.

Redox and pH changes

Redox conversions occur at many places in the hydrological cycle. An important case is mining which takes place both at the large scale (commercial mines) or on a smaller scale. In particular for metal mines the oxidation of pyrite, cause environmental problems with regard to acid-mine drainage. The rate determining step in acid-mine drainage is the production of ferric sulfate, which is a powerful oxidant. At high pH pyrite is oxidized chemically, but at pH values between 3.5 and 4.5 the ferrous-ferric oxidation is accelerated by a factor of 200 by the bacterium Metallogenium, a further drop in pH (2-3.5) causes an increase in the iron oxidation by 10^5 to 10^6 by Thiobacillus ferroxidant.
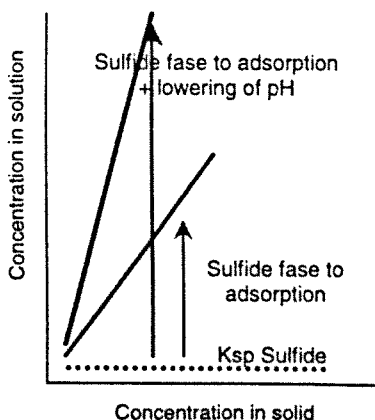

Figure 11. The increase in concentrations when metalsulfides become unstable in an oxygen rich environment

The metals in mine waste are present as sulfides. In the mine waste dumps therefore, the remobilization of metals is the result of two processes:

- the oxidation of the metal sulfides
- the low pH caused by the oxidation of pyrite

The earlier case, where oxidation of metal sulfides (dredged material) also causes a release, is a minor problem compared with mine waste. Now the lowering of the pH and the much lower adsorbing capacity of the mine waste compared with sediments causes a much more significant increase in dissolved metal levels (figure 11).

Oxidation of pyrite takes place almost immediately after the waste dumps of access to oxygen. Some results on the time frame involved in acidification of waste dumps and resulting drop in pH is shown in figure 12. These results refer to waste dump of a gold mine in Indonesia where waste dump contained several percent of pyrite. Over a period of less than one year the waste dump started to generate acid with an increase in metal levels. In this particular case the waste rock contains abundant amounts of manganese and zinc.
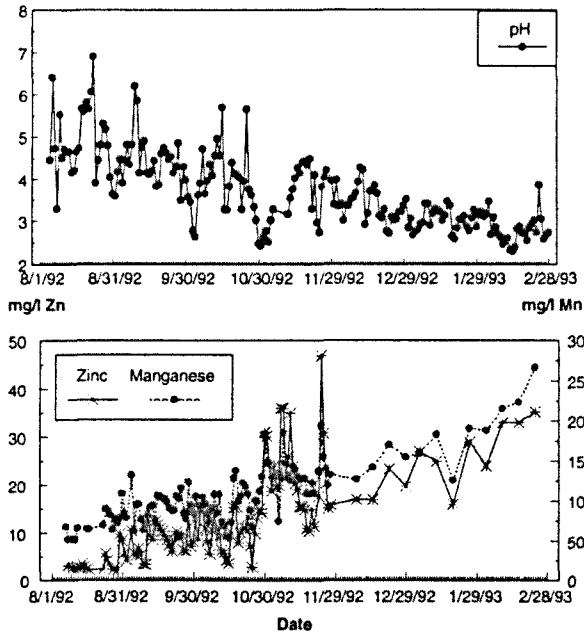

Figure 12. Change in the pH and resulting concentrations in manganese of a stream draining a waste rock dump (Kalimantan, Indonesia).

Oxidation of pyrites also plays an important role in the negative environmental impact caused by draining of wetlands (or acid-sulfate soils). It is well documented that wetlands can serve to protect adjacent water bodies from inputs of sulfuric and nitric acids (acid rain). As these acids pass through the wetlands, sulfuric acid is reduced to insoluble sulfides and nitric acid is reduced to molecular nitrogen via the denitrification reaction.

When wetlands dry out, the system may switch from one dominated by anaerobic chemical reactions to one controlled by aerobic reactions. Interestingly, Lake Blåmissusjön in northern Sweden, known as "the most acidic lake in Sweden", was not acidified by acid deposition, but rather, as a result of drainage (for agricultural purposes) of the watershed soils surrounding the lake. Acidification occurred because the waterlogged soils were rich in pyrite, a compound containing sulfur in the reduced chemical form (S^{2-}). After drainage, oxidizing conditions prevailed, causing oxidation of the sulfur to sulfuric acid, which subsequently washed into the lake and acidified it.

EXAMPLES OF THE BEHAVIOR OF DIFFUSE POLLUTANTS IN SOILS

Arsenic accumulation

In general the input arsenic in the soil is derived from:

- atmospheric deposition
- sewage sludge
- animal manure
- fertilizer

A summary of the inputs for the Netherlands is presented in table 1.

Sludge	0.69
Compost	0.5
Chemical Fertilizer	1.9-3.6
Manure	13-15
Deposition	8

Table 1.   Inputs of arsenic to agricultural land in the Netherlands (tonnes/year) (Stoop and Rennen, 1992)

These sources of arsenic have caused an increase in the arsenic content of agricultural soils in comparison with soils from non-agricultural areas (nature).

	Mean concentrations	Range
Marine Clay Soils	12.6	3.1-29.5
River flood plains Rhine	67.1	7.3-205
River flood plains-Meuse	30.5	4.1-90.7
Peat soils	12.2	1.7-21.4
Löss soils	8.3	6.1-11.7
Sandy soils	7.8	1.7-24.5
Forest soils		1.2-8.6

Table 2.   Mean arsenic contents (μg/g) in a number of agricultural and non-agricutlural soils in the Netherlands (Stoop and Rennen, 1992).

Soils which are effected by river sediments (e.g. polders and river flood plains) have much higher arsenic contents (table 2). River flood plains from the Rhine contain upto 70 μg/g of arsenic (Salomons and de Groot, 1978; Japenga et al., 1990).

For certain agricultural areas however, the main source of arsenic is the use of sodiumaresenite as a defoliant for potatoes. In the Netherlands maximum values of 20 kg/ha have been used. On a worldwide basis 80-90 % of the arsenic produced is used in agriculture and accumulates in the soil (Nriagu and Pacyna, 1988).
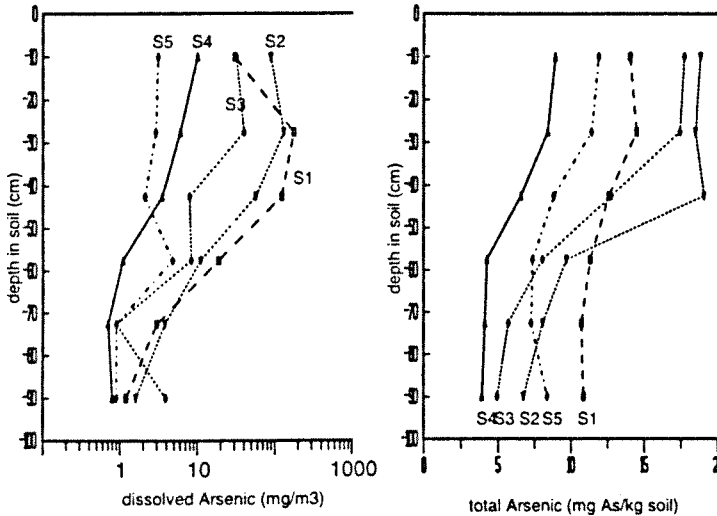

Figure 13. Concentrations of arsenic in the soil pore waters and in the soil itself for a number of soils which have been subject to use of defoliants containing arsenic.

In figure 13 some examples of the accumulation of arsenic in agricultural (sandy) soils, which in the past have been used for potato growing and where arsenic containing defoliants were applied, are presented (Bril, 1993). The highest concentrations are found in the upper part and reaches values upto 20 mg/kg, deeper in the soil column values are 5 to 10 mg/kg.

The concentrations in the soil pore waters are high and show already some evidence of leaching. Concentrations of dissolved arsenic are upto several hundreds of μg/l (note that the X-axis is logarithmic).

Although the concentrations in the upper part of the soil are 2-3 fold increased compared with the subsoil and do not exceed current environmental standards for agricultural soils, the concentrations in the soil solution are quite high and exceed standards for water quality in the Netherlands. Based on these field data and laboratory experiments predictions were made for the leaching of arsenic for the coming 100 years. The predictions are based on the model of Bril and Postma (1993). The results show that after about 50 to 100 years the arsenic will reach the groundwater table (groundwater table in the Netherlands is generally quite high).
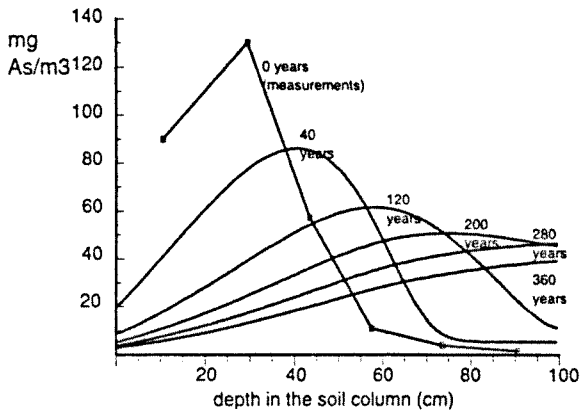
Figure 14. Calculated profiles of dissolved arsenic in the soil for 40, 120, 200, 280 and 360 years after present.

Combined inputs of acid and metals and changing land use

The soil is subject to atmospheric deposition. Although the quantities may be small it is one of the contributors to the continued accumulation of chemicals in the soil. For heavy metals and for a number of organic chemicals the release to the ground water and removal by crops is rather low. Therefore even if the inputs decrease, the accumulation (although at a lower rate) will continue.
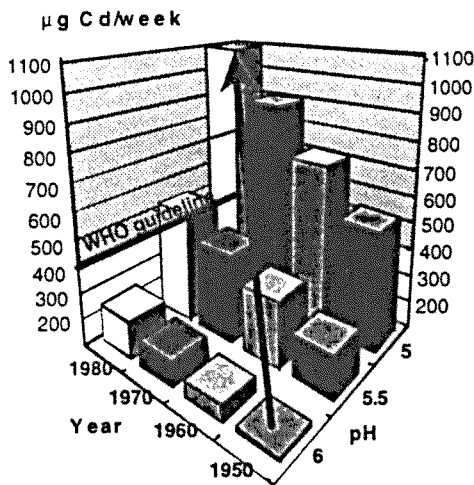

Figure 15. Estimated cadmium uptake by humans as a function of pH for the years 1960, 1970 and 1980 (Drawn after data from Stigliani and Joffe, 1992)

Calculation performed for cadmium accumulation in the agricultural soil in Western Europe shows a continuous increase with some leveling off for later years (Stigliani et al., 1993). Soils, at least in Western Europe, Canada and the US are also subject to acid inputs from the atmosphere. In interpreting these kind of predictions on metal

accumulations and their impact on the environment, one should also consider the effects of acidification. Metal concentrations in the soil solution depend to a large extent on the pH (see also figure 9). The increase in dissolved cadmium and the change in speciation due to pH changes will both cause a greater bio-availability of cadmium. The two effects of increased cadmium in the soil and greater uptake due to pH change by crops can be combined to determine their potenital impact on human intake (Stigliani and Jaffe, 1993). The results shown in figure 15 show that cadmium concentrations which at a certain time cause human uptake below the WHO limits will exceeds the WHO limits when the acidity of the soil increases.

These theoretical calculations show that it is necessary to take the whole system into account for predicting environmental impact. In this particular case, however it is known that farmers apply lime to raise the soil-pH for maintaining crop productivity (Mahler and McDole, 1987), thus the situation of increased uptake may not occur for human consumption.

The combined effect will have a greater impact on non-limed natural areas, where the increased bio-availability will effect the soil biota, vegetation and accumulation in the food chain. The situation shown in figure 15 is highly relevant for forests and for those cases (in Europe) where agricultural land use is changed to forestry. In the latter case liming, as it is being practiced by farmers will stop and after a number of years the pH of the soil will decrease (Johnston et al., 1986) and a non-linear response with regard to the pH (van Breemen et al. 1983) and subsequently to the release of metals may occur.
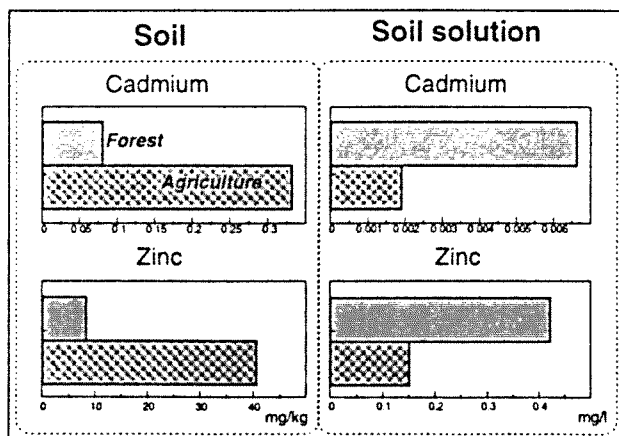

Figure 16. The mean concentrations in the soil and in the soil solution of agricultural and forest soils in the Netherlands (Römkens, unpublished data)

Present agricultural soils have higher concentrations of heavy metals compared with forest soils (figure 16). These high concentrations are caused by agricultural practise and by-products in fertilizer or the application of sewage sludge. Despite the higher concentrations the concentrations in the soil solution are much lower. On the other hand the forest soils have the highest concentrations of cadmium and zinc in the soil solution. These differences are simple due to differences in pH between the agricultural (limed) and

the more acidic forest soils. When agricultural land is converted to forest we may expect even higher concentrations in the soil solution then in the present forest soils. The concentrations in the new forest soil will also depend strongly on the organic matter content. In soils with a low organic matter content high concentrations of dissolved metals (e.g. cadmium in figure 17) are expected to develop.
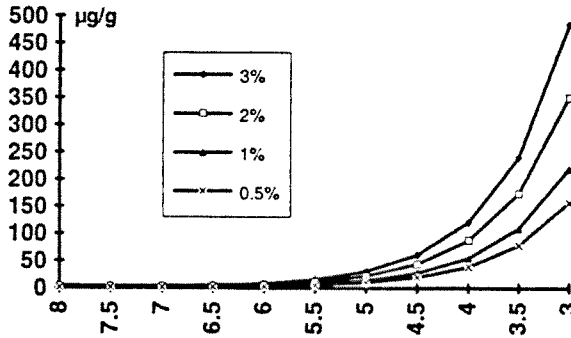
Figure 17. Concentrations of cadmium in the soil solution as a function of pH and four different organic carbon levels in the soil (theoretical calculations)

HOW TO PREDICT LONG-TERM MOBILITY AND COPE WITH STORED POLLUTANTS

The various issues discussed in the previous sections show that there is a need for long-term measures to deal with the accumulation of pollutants in soils and sediments. Non-linear behavior of heavy metals are caused by changes in the master variables or capacity controlling properties of sediments and soils.

CCP	Important parameters	Major biogeochemical cycle
Cation Exchange capacity	clay minerals, organic matter	Carbon cycle
pH	carbonate content	Calcium cycle
Redox potential	Iron, manganese oxides, sulfides	Iron, manganese and sulfur cycle
Organic matter	Organic matter	Carbon cycle
Structure	Organic matter and inorganic minerals	Carbon cycle
Salinity (complexing capacity of the soil solution)		Carbon cycle (DOC)

Table 3.   Inter linkage between Capacity Controlling Parameters and major biogeochemical cycles

The capacity controlling parameters are those parameters which determine the extent of retention of metals by sediments and soils. Important are the clay content and the organic matter content which due to their small grain sizes provide large amounts of surface area for adsorption of metals and in the case of organic matter for organic micro-pollutants. In addition these components are often covered with iron and manganese hydroxides which again provide surfaces for adsorption. The capacity to adsorb can be approximated by the cation exchange capacity. The extent of the adsorption depends on the pH (figure 9) which is a master variable for describing the behavior of metals. The pH depends on the buffering capacity of the system and may stay constant over long periods followed by a strong change in pH once the capacity is exhausted. Another master variable, which determines the chemical forms of the metals, is the redox as was exemplified for the case of lead (figure 5). Research into the behavior of heavy metals up to now was mainly confined to the effects of the master variables and capacity controlling parameters on mobility and bio-availability.

As a result most regulators and scientists have assumed in their decisions and research that these properties are constant and a sediment or a soil is a static systems. Of course this is true if we consider the short term, say about 1 to 5 years. In the long term these capacity controlling parameters are not constant and are effected by changes in land use, changes in the hydrology. These changes effect cycles of elements like nitrogen, carbon and sulfur and hence the capacity controlling parameters. Not only that these capacity controlling properties are not constant and that the soil-sediment system is dynamic, the changes often show a non-linear behavior.

If one wants to control for instance diffuse pollution and prevent non-linear responses it is necessary to assess and manipulate those factors which determine the capacity controlling parameters and master variables. This implies that it is necessary to study in detail the major biogeochemical cycles of sulfur, nitrogen, carbon and also of calcium, iron and manganese
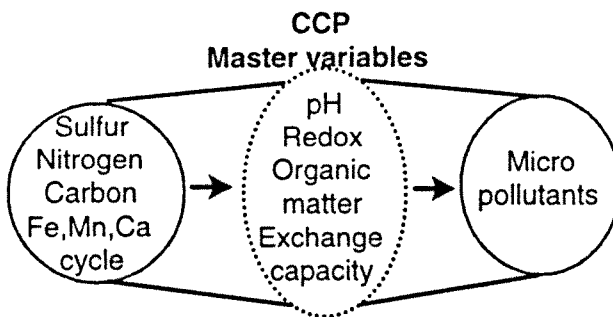

CCP
Master variables

Figure 18. The interlinkage between the major biogeochemical cycles, master variables & capacity controlling parameters (CCP) and the mobility of micro-pollutants.

The various examples given show that a mono-disciplinary approach will not lead towards a better understanding of long-term behavior of chemicals in the environment. On one side we have the scientists which have studied and know "nearly everything" about the

intricate interactions of chemicals with organic matter, adsorbing surfaces in the soils etc. On the other side we have the geochemists and biogeochemists who study the cycles of the major elements like carbon, nitrogen and sulfur. Element cycles which determine the capacity controlling parameters. It is necessary to bring these disciplines together with their own pieces of the puzzle to solve potential problems with continuous diffuse build-up of pollutants in soils and sediments and changes in major element cycles.

ACKNOWLEDGMENTS

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