Some recent developments and approaches in soil protection research

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Abstract

Evaluation of soil quality takes a key position in research directed towards the scientific foundation of soil protection. When interest is focused on quality in relation to soil pollution, contaminant behaviour in the soil system constitutes the central theme. An important aspect is contaminant mobility, both with respect to its transport to other environmental compartments and to its uptake by organisms.

Behaviour of compounds in soil is governed by a large number of variables which can be compound-related and soil-related. A few of such variables which attain increasing interest in present Dutch soil research are briefly described. These are compound speciation and factors affecting 'bio-availability'. Moreover, attention is given to problems associated with heterogeneity, which play a role in soil at various scales.

Introduction

Alterations in human society, which developed during the past half century in an increasingly accelerated way, laid a concurrently growing burden upon the environment. This burden is not only brought about by the production and disposal of huge amounts of waste products resulting from a growing population and from changing living conditions. Also technological developments, in industry and in agriculture, have contributed to a considerable extent.

These developments have forced to the establishment of rules and measures aimed at environmental protection. In the Netherlands, as in many other industrialized countries, first attention in this respect has been paid to the environmental compartments water and air. Legislation for soil protection is well on its way now.

Environmental legislation requires, or will at least benefit from, the availability of standards in order to allow a critical evaluation of existing situations and intended activities. In case of pollution such evaluation must be based on the effects resulting from the presence of contaminants in the system. Appreciation of soil quality with respect to contaminant presence should thus also be based on an evalu-

ation of the resulting effects. In most cases this implies that total content values of a contaminant in soil do not supply sufficient information. Usually it is the active form, amount, or concentration of the contaminant which governs its effect. This means that proper evaluation of contaminant presence in soil requires a quantitative judgement of contaminant behaviour in soil and that soil quality evaluation can usually not be based on single value interpretation.

It depends on the soil phase via which the effect of interest predominantly exerts itself whether the contaminants' presence or activity in either the gaseous, the liquid or the solid phase of soil should deserve major attention. Because of the continuous dynamic equilibria between the soil phases they usually all three have to be considered.

Compound behaviour in soil is governed by an extensive number of varying conditions and properties. These may as well be related to the compound as to the system under consideration. The complexity involved requires that quality criteria for soil preferably should follow sliding scales instead of being based on fixed values. With respect to compound properties, the featuring in cationic or anionic form, for example, in many cases is deciding as to adsorptive bonding. Thus compound speciation plays a dominant role in interaction evaluation for soils. Also system parameters such as pH and redox values next to soil composition are greatly influencing contaminant behaviour. In addition, effects of contaminants to living organisms are to a great extent dependent on the so-called bio-availability of the compound. Sometimes this is strongly related to behaviour-controlling system parameters, but in many cases also specific properties of organisms play a role. Finally, soil properties and conditions are ever varying. This holds for the microscale of soil particles, for the soil profile scale and for the field scale.

In the following, chemical speciation of compounds, bio-availability and soil heterogeneity are elaborated somewhat further. They constitute essential topics with respect to soil quality evaluation, at the same time representing highlights in current Dutch soil research. The topics chosen necessarily reflect the authors' interests to a certain degree.

Compound speciation

The total amount of contaminant in soil may be distributed over various chemical forms: precipitated as a mineral, adsorbed onto the solid phase, dissolved in the soil solution and, in the case of a volatile compound, present in the gaseous phase of the soil. The contaminant present in these forms will exhibit different mobility and reactivity in the system, availability for plant uptake and toxicity for organisms.

During recent time much attention has been given to the development of chemical speciation models which can compute the distribution of a compound over different forms as a function of system parameters. Speciation calculations can be incorporated in models describing compound transport.

Here attention will be given to chemical speciation including complexation, sorption and precipitation reactions as the most important physico-chemical processes in soil.

Several computer codes are available which describe chemical speciation. Well known examples in this respect are MINEQL (Westall et al., 1976) and GEO-CHEM (Sposito & Mattigod, 1980). These models are applicable to soil-water and sediment-water systems when a good system description is available. This means a good choice of components and species present, and selection of proper formation constants (log K values) for all species involved. The models also need input data such as total amount of components, concentration of free components (e.g. pH or pe), or partial pressure of gas species.

Some applications of chemical speciation computations concerning heavy metals, cyanides and sorption behaviour are treated below.

Important reactions governing speciation of heavy metals in soil solution and ground-water or surface water are hydrolysis, formation of chloride complexes and complexation with organic compounds. The latter may be of synthetic nature like EDTA, of natural origin like acetic or citric acid, or dissolved soil organic matter (e.g. fulvic acids). Although several attempts have been made to model heavy metal complexation with fulvic acids proper computation of the speciation is not yet possible.

On the other hand extensive research has been done on heavy metal complexation with synthetic chelates, such as EDTA, DTPA and NTA. This work was aimed at the improvement of heavy metal solubility in soil with respect to plant uptake or at merely estimating availability to plants. For polluted soils and sediments it may be expected that such chelates increase mobility of heavy metals (Salomons & Förstner, 1984). Besides this, chelates may be used in order to remove heavy metals from polluted soils or solid wastes. For optimizing the extraction of heavy metals it may thus be useful to model the processes involved, such as metal dissolution, desorption and complexation. This can be achieved by calculating free-metal activity and metal chelate concentrations at different pH values (Keizer et al., 1986).

An evaluation of the reactivity of cyanides to soil compounds in relation to solubility in the soil, with respect to leaching and to toxic effects of organisms following a certain exposure, also requires knowledge about different cyanide species and their respective concentrations in soil. Extraction of cyanide-polluted soil at different pH values and subsequent determination of total compound concentrations (CN, Fe, Ca), pH and redox potential value in the soil extracts provides information about the solubility of iron cyanides in the soil by calculating free component (CN^-, Fe^{3+}, Ca^{2+}) activities. Distribution over different species can then be computed (Keizer, 1984). Fig. 1 presents results of calculated cyanide speciation at different pH values, assuming iron oxide and iron cyanide as controlling phases. The huge influence of pH above 7 on the cyanide speciation becomes apparent this way.

Sorption processes may be included in various ways in the chemical speciation models, depending on the type of sorption. Then the sorbed amount of a certain compound is treated as a species present in solution. Equations to describe compound sorption (e.g. Langmuir, Freundlich) can easily be incorporated in the speciation models. So heavy metal (e.g. cadmium and copper) sorption data can be described very well with a pH-dependent Freundlich sorption equation (Lexmond, 1980; Chardon, 1984; Keizer et al., 1986).
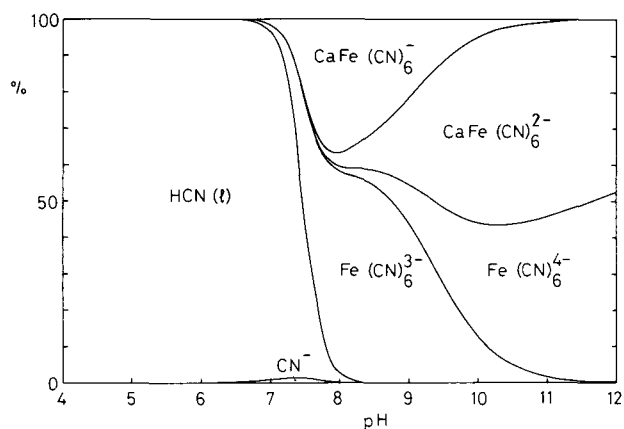
Fig. 1. Computed distribution (%) of dissolved cyanide species assuming equilibrium with iron oxide and iron cyanide; ionic strength = 0.05 mol/l and pe + pH = 15. Values for formation constants are the same as used by Keizer (1984).

Speciation models can also be extended to incorporate electro-chemical surface complexation. Recently a new and relatively simple electrochemical model has been introduced for sorption of compounds on metal oxides (Bolt & van Riemsdijk, 1982; van Riemsdijk et al., 1986).

Bio-availability

The significance of contaminants present in soil for plants rooting that soil has been found difficult to predict. Many experiments have led to the conclusion that there is no straightforward relationship between the total content of a contaminant in soils and its biological action. This is often attributed to differences in availability of the contaminant in different soils or under different conditions.

The term availability, as commonly used in soil science, has its origin in the field of soil fertility. It is related to the supply of nutrients from soil to plants (Barber, 1984). For contaminants, being of no use to organisms, the term availability would seem less appropriate. When considering the types of biological action which are of concern with respect to contaminants, terms like transferability and (phyto-)toxicity appear more suitable, the former in relation to the extent to which a contaminant passes from the soil to the plant, the latter in relation to deleterious effects on growth. Nevertheless, transferability and toxicity of contaminants are governed by the same factors that affect nutrient availability, albeit the relative importance of the individual factors involved may vary.

The most important soil-related factors are amount, intensity and mobility of the contaminant. Amount is an *extensive* variable, defining a mass or amount of substance of contaminant and designated in units of mole or kg. Only the dissolved free (hydrated) ion and labile forms both in the soil solution and associated with the solid phase are assumed to contribute to the amount factor. Labile forms are by defi-

nition those forms that may dissociate rapidly when the free ion is being removed.

Intensity as an *intensive* variable. It is given by the (electro-)chemical potential, the amount of free energy per unit amount of matter, expressed in joules per mole. It measures the 'pressure' a contaminant exerts on plant roots. For practical purposes differences in the intensity factor may be estimated from differences in the concentration or activity of the free ion in a solution with a fixed background electrolyte level (e.g. 0.01 mol/l $CaCl_2$) in equilibrium with soil. Free ion concentration may be measured electrochemically (ion-specific electrodes) or from analytically determined concentrations using speciation models. For a given soil under given conditions amount (Q) and intensity (I) of a contaminant are related via the Q-I curve. Its slope ($b = dQ/dI$) is the buffer intensity of the soil for that contaminant. Buffer intensity may vary greatly between different soils and for a given soil with conditions such as pH and redox status. It also may vary with the position on the Q-I curve, e.g. in case of non-linear adsorption isotherms.

Mobility is related to the rate at which a contaminant can move through soil to sorbing roots by convection and/or by diffusion (Nye & Tinker, 1977). Free ions and labile forms of the contaminant in solution all contribute to its mobility. Consequently, the nature and concentration of dissolved ligands may be important factors affecting mobility.

The relative importance of amount, intensity and mobility may vary with the contaminant and the type of biological action considered. In the case of phytotoxicity induced by heavy metal cations like Cu^{2+} and Zn^{2+} the intensity factor is considered to play a predominant role and evaluation of soil quality in this respect may benefit from methods of soil analysis aimed at measuring the intensity factor (Lexmond, 1981). In the case of transferability of lead, however, mobility might be the key factor, as is indicated by the increase in lead uptake in the presence of EDTA (Marten & Hammond, 1966).

Plants affect contaminant behaviour in soil surrounding their roots in several ways. Sorption of a contaminant by roots lowers its potential and gives rise to concentration gradients. Roots may bring about changes in pH and redox status of surrounding soil, changing thereby the Q-I curve of the contaminant. In addition, soluble organic compounds excreted by roots (exudates) may increase contaminant mobility. Such organism-related effects may be strongly amplified in case of ingestion of contaminated soil. In spite of these complications detailed knowledge of the Q-I relationship of contaminants and its relation to soil composition under relevant conditions of pH and redox status will prove to be essential for an understanding of the biological action of contaminants.

Heterogeneity

A fundamental feature of soil at all scales is the inherent heterogeneity of the system. When studying the fate of contaminants of soil, these heterogeneities have to be taken into account. Recently some progress has been made to include small-scale and large-scale heterogeneity explicitly in the description of the behaviour of chemicals in soil. Because in this area Dutch research has made a significant contri-

bution this subject is given some specific attention here.

On microscale the interaction of chemicals with soil is, broadly speaking, influenced by two different types of heterogeneity. First, there is the effect of particle size, and of the aggregation status of these particles on the reactivity of the soil. Secondly, there is the effect of a range of chemical interaction energies for a specific chemical with a specific reactive surface (van Riemsdijk et al., 1984a, 1984b, 1986), or more obviously a distribution of interaction energies due to the presence of different reactive surfaces in a given soil. Microscale heterogeneity influences both physical (diffusion, water transport; cf. Van Genuchten & Cleary, 1982) and chemical processes (oxidation/reduction; precipitation/dissolution; adsorption/desorption). Insight in these different interaction processes and in their dependency on heterogeneity is essential for modelling contaminant behaviour in soil.

The effect of particle size on the kinetics can be illustrated with the dissolution rate of feldspar in acid soil. Under acid conditions feldspars are in principle relatively soluble. However, the maximum dissolution rate which occurs at large undersaturations is extremely low, and controlled by the surface area of the particles. For K-feldspar this rate amounts to 50 μmol silica released per year per square metre of mineral surface area (Lasaga, 1983). When the solution is approaching saturation this rate will be even much lower. In order to demonstrate what this means in terms of proton buffering in an average sandy soil, some calculations are presented in Fig. 2. The proportion of K-feldspar used in these calculations corresponds with 50 g/kg for a soil layer of 20 cm thickness over a hectare of soil. It is assumed that this proportion is present in spherical particles, all of the same size. The maximum proton buffering rate can now be calculated as a function of time, for different particle sizes. In this case the life-time of the different particles is proportional to and the
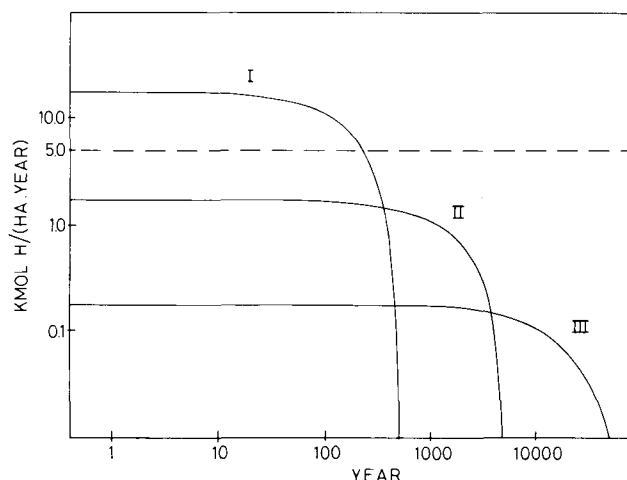

Fig. 2. The maximum acid neutralization rate as a function of time (proceeding dissolution) due to K-feldspar weathering in soil, assuming a uniform feldspar particle size of: 1 μm (I); 10 μm (II) or 100 μm (III). For further details see text.

initial buffering rate is inversely proportional to the (initial) radius of the particles. When it is considered that the acid input for the Netherlands may be as high as 5 kmol/(ha.yr) it follows that the feldspars can only buffer this input (in the top 20 cm of soil) when all particles have a diameter smaller than 7 μm. This seems very unlikely. More likely is that a small weight fraction of the feldspars present in soil has a very small particle size, thus contributing considerably to the overall buffering rate of the soil. The life-time of these particles is also rather limited. High inputs of acid over a long period of time may thus strongly reduce the buffering rate of the topsoil, resulting in deteriorated quality of soil for plant growth. For a more detailed description of the effects of acid input on the composition of the soil solution much more factors have to be taken into account.

On a larger scale soil heterogeneity is also evident. Differences of variables visible in the field are used to distinguish soil horizons and to classify soils on the basis of differences between soil profiles. The dependency of heterogeneity on the scale of observation is illustrated well by differences of maps of the same region but of different scales.

Properties that are not readily visible will also exhibit a spatial variability. Thus for phosphate (P), which is present in animal slurries derived from intensive animal husbandry, and which is disposed off on agricultural soil, the reactivity depends predominantly on the contents of oxalate-extractable iron and aluminum (Fe + Al)$_{ox}$; see e.g. Beek, 1979). The sorption capacity of soil for P, denoted by F_m, is approximately proportional to (Fe + Al)$_{ox}$. The proportionality constant, α_m, found by van der Zee & van Riemsdijk (1985) for samples of a single field (see Table 1), is slightly smaller than values reported by Lexmond et al. (1982). This is due to the lower concentrations of P used in the measurements: 3 mmol P instead of 5 mmol P per litre (see also de Haan & van Riemsdijk, 1986).

Both P$_{ox}$, which is a measure of the cumulative amount (A_T) of P applied locally to the soil surface, and F_m are approximately normally distributed, with frequency distributions denoted by $f(A_T)$ and $f(F_m)$. Assuming local sorption equilibrium and disregarding the pore scale dispersion, van der Zee & van Riemsdijk (1985) express the field averaged dimensionless concentration of P in the solid phase, $<\Gamma>$, as a function of $f(A_T)$ and $f(F_m)$, using stochastic theory. The general idea this model is based on is shown in Fig. 3. The lengths of the arrows and of the tubes in Fig. 3a represent the magnitude of A_T and F_m, respectively, for ten particular soil columns. If both A_T and F_m are normalized with respect to F_m (i.e. divided by F_m) the fraction of

Table 1. Statistics for a field situation based upon 67 sampling spots ($N = 67$). Average value (m), standard deviation (s), coefficient of variation (CV) and correlation coefficient with (Fe + Al)$_{ox}$ (ϱ) for depth-averaged properties.

	m	s	CV	ϱ
P$_{ox}$ (mmol/kg)	11.9	3.37	0.28	0.59
P$_m$ (mmol/kg)	33.2	7.99	0.24	0.82
(Fe + Al)$_{ox}$ (mmol/kg)	67.2	12.95	0.19	1
α_m	0.5	0.07	0.14	–0.18

1 2 3 4 5 6 7 8 9 10

a

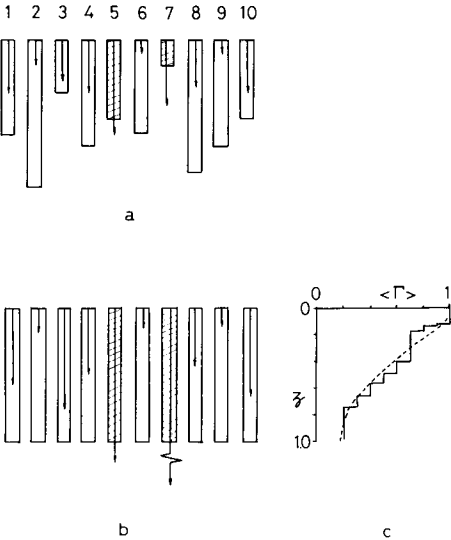b   c

Fig. 3. Schematization of the calculation of the P profile. 3a: magnitude of input (arrow) and retention capacity (tube) for ten columns. 3b: input normalized with respect to retention capacity for each column. 3c: average profile of P for the ten columns.

the retention capacity already used for each column results (Fig. 3b). Now $\Gamma(\zeta, t)$ is the relative number of columns (here with repect to ten) for which the front has arrived at relative depth ζ (Fig. 3c). If the statistics (m, s) for an individual application A, and for F_m, are known or estimated, the value of $<\Gamma>$ may be calculated for times of interest ($\sim$ number of applications of P) and depth ζ. This is done in Fig. 4 for the case where A_T and F_m are assumed to be correlated positively (1), negatively
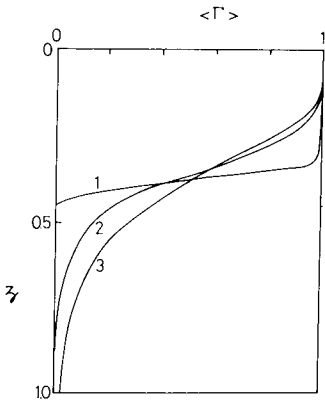

Fig. 4. Profiles of dimensionless concentration in the solid phase averaged for the field, $<\Gamma>$, as a function of dimensionless depth, ζ. Coefficient of correlation ϱ between A_T and F_m is: $\varrho = 1$ (curve 1), $\varrho = 0$ (curve 2) or $\varrho = -1$ (curve 3).

(3) or uncorrelated (2). The statistics of A_T and F_m are given in Table 1. Case 1 corresponds approximately to the result where the mean values of A_T and F_m are used. Since no a priori reasons exist to assume a correlation between A_T and F_m, it may be concluded that calculations where average values are used, are generally incorrect. The results compiled in Fig. 4 show that small values of $<\Gamma>$ will usually reach the groundwater level ($\zeta = 1$) earlier, than the average front ($<\Gamma> = 0.5$). Thus part of the field considered will show a much faster breakthrough of P than the field on average. Since a P concentration of 3 mmol/l is a thousand-fold of the concentration where eutrophication occurs, a breakthrough in 0.1 % of the total area (corresponding to $<\Gamma> = 0.001$) is sufficient to pollute the percolation water of the entire field.

In general the field average displacement of reactive solute will be controlled, amongst others, by the heterogeneity of the sorption parameters and of the input of solute.

Some conclusive remarks

Although the above-mentioned aspects are equally important with respect to contaminant exposure judgement and consequently to soil quality evaluation, it becomes apparent from literature that they did not receive comparable attention so far. Whereas compound speciation and heterogeneity aspects obtain increasing attention, bio-availability of contaminants stays behind with respect to a systematic quantitative elaboration of the problem area.

Soil science from its very beginning has been an interdisciplinary science, reclining on and combining basic sciences such as chemistry, physics and mathematics. Organism-related disciplines such as biology and physiology became of growing importance when the adjustment of compound presence in soil came into the picture. Concepts derived in the field of nutrient availability should find wider application with respect to the biological action of contaminants in soil. Where the sciences mentioned earlier all have greatly contributed to the nutrition of mankind in a quantitative way, it may be hoped that they will equally adapt their experience and knowledge to the area of guarding human nutrition which, although very essential, is merely one aspect of the significance of soil for life on earth.

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