

8 Precipitation - dissolution reactions

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8.1 Introduction

Many elements that occur naturally in the soil, as well as compounds that are of importance with respect to pollution, can occur in the soil system as a three dimensional precipitate. Other possibilities are the occurrence as an adsorbed species at the interface between soil particles and the soil solution or they may be present 'dissolved' in the soil solution phase. In Table 8.1 some examples are given for a few elements with respect to the solid phases in which these elements may occur in the soil. It will be clear that in this table only a very small fraction of the various possibilities are listed.

Table 8.1. Elements and solid phases in which these element may be incorporated.

Element	Solid phase (mineral)
Na	feldspar
K	feldspar
Cd	$\text{CdCO}_3(\text{s})$, $\text{CdS}(\text{s})$
Fe	$\text{Fe}(\text{OH})_3(\text{s})$, $\text{FeCO}_3(\text{s})$, $\text{FeS}(\text{s})$, $\text{FeS}_2(\text{s})$
Pb	$\text{Pb}_3(\text{PO}_4)_2(\text{s})$, $\text{PbSO}_4(\text{s})$
Ca	$\text{CaCO}_3(\text{s})$, calciumoxalate

Also sparingly soluble organic compounds can be present in solid organic precipitates. As an example may be mentioned the polyaromatic hydrocarbons most of which are very insoluble in an aqueous medium. Often one is interested in the activity (concentration) of an element, or the activity of a certain dissolved complex or species that contains this element in the soil solution. The activity in the solution phase may be determined completely by the occurrence of one or more solid phases. The resulting activity may be the result of equilibrium processes, the result of slow formation of compounds, or the result of very slow dissolution kinetics of compounds present in the system. With respect to the behaviour of some pollutants in the soil system these processes may be of great importance. For instance, the solution concentration of cadmium in calcareous soils may be determined by $\text{CdCO}_3(\text{s})$, whereas the solution concentration of heavy metals under reduced conditions may be governed by equilibrium with metalsulfide precipitates, which have a very low solubility.

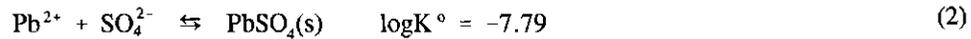
8.2 Equilibrium

An important characteristic of a *pure* solid phase is that the chemical activity of such a solid phase equals one. This implies that the equilibrium composition of the system is independent of the amount of the solid phase present, as long as it is present.

A solid phase can be formed when the change of the Gibbs free energy of the reaction of formation, ΔG_r , is smaller than zero. In case ΔG_r equals zero, there is equilibrium and if its value is positive than dissolution has to take place until equilibrium is reached provided the solid phase is still present in the system. If the solid phase is not present in the system and if the calculated ΔG_r value is positive, then it means that this phase can not be formed from this solution phase. The ΔG_r can be calculated as follows:

$$\Delta G_r = RT \ln Q/K^\circ \quad (1)$$

where R is the gas constant, T the absolute temperature, Q the ion activity product of the reaction and K° the equilibrium constant of the reaction. As an example the formation reaction of lead sulphate is given:



The ion activity product Q of this reaction equals:

$$Q = \frac{(\text{PbSO}_4(\text{s}))}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} = \frac{1}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} \quad (3)$$

The formulation of the ion activity product equals the formulation for the equilibrium constant, in case of equation (2) this is:

$$K^\circ = \frac{1}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} \quad (4)$$

The difference between Q and K° is that Q may have any value which depends on the composition of the system, whereas K° is a constant. In case $Q = K^\circ$ it follows from equation (1) that $\Delta G_r = 0$ meaning equilibrium conditions.

In practice often the saturation index is used to test whether a system is undersaturated, at equilibrium, or supersaturated with respect to a solid phase. The saturation index, SI, can be expressed as:

$$\text{SI} = \log(Q_{\text{SP}}/K_{\text{SP}}) \quad (5)$$

Where K_{SP} is the solubility product of the solid phase and Q_{SP} is the ionactivity product of the solid phase written as a dissolution reaction. For the same example it follows that Q_{SP} equals:

$$Q_{\text{SP}} = (\text{Pb}^{2+})(\text{SO}_4^{2-}) \quad (6)$$

and

$$K_{\text{SP}} = \frac{1}{K^\circ}$$

It follows that Q_{SP} :

$$Q_{SP}/K_{SP} = (Q/K^0)^{-1} \quad (7)$$

This has as result that $SI > 0$ indicates that the system is supersaturated with respect to the solid phase and $SI < 0$ indicates that it is undersaturated.

An important restriction in case of chemical equilibrium calculations is that the system should not be 'overdetermined' (more independent equations than unknowns). An example of an 'overdetermined' system is when two different $Al(OH)_3(s)$ minerals are present at the same time, for example gibbsite and amorphous $Al(OH)_3(s)$. The reaction equations for the formation reaction are identical, the only difference is the value of the equilibrium constant which is different because the structure of the solid phase is different. At complete equilibrium it is impossible that two solid phases with the same formulation of the ion activity product but with different equilibrium constants can coexist. This can very easily be illustrated using the given example:



$$\log K_{am}^0 = -9.66 \quad \log K_{gibb}^0 = -8.04$$

$$\rightarrow (Al^{3+}) = (K^0)^{-1} (H^+)^3 \quad (9)$$

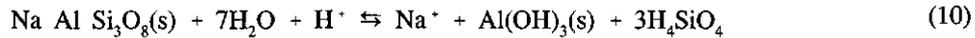
Equation (9) implies that the value of (Al^{3+}) at a certain pH depends on the type of $Al(OH)_3(s)$ being present. If both would be present at the same time then equation (9) predicts that at a certain pH the solution should have two different values of (Al^{3+}) , which is impossible in a homogeneous solution phase. Application of equation (9) with the appropriate $\log K$ values given at equation (8) shows that equilibrium with amorphous $Al(OH)_3$ will give at a certain pH value a higher Al^{3+} concentration than equilibrium with gibbsite. The higher Al^{3+} concentration means super saturation with respect to the gibbsite and amorphous $Al(OH)_3$ will be transformed to a less soluble form (gibbsite). At complete equilibrium all amorphous $Al(OH)_3(s)$ should have been dissolved and only gibbsite can be present. However, the solution phase can be in equilibrium with amorphous $Al(OH)_3(s)$ during a very long time, provided that the rate of dissolution of amorphous $Al(OH)_3(s)$ is much larger than the rate of formation of gibbsite and that the latter in absolute terms is also characterised by a very low rate of formation. Such a transition period can last very long (years), and during this transition period the composition of the soil solution is in equilibrium with the more soluble phase, although also the more stable phase may be present. For equilibrium calculations one can thus use the $\log K^0$ value of amorphous $Al(OH)_3(s)$ in such a case. Such a situation is called partial equilibrium.

Chemical equilibrium calculations of even very complex systems can at present be performed relatively easily from a computational point of view using computer programs to calculate chemical speciation. In practice however, it is much more complicated because one needs to have insight in the chemical kinetics. Especially in relation to equilibria involving solid phases the kinetics are often rather slow and of a complex nature.

The book of Lindsay (1979) is an illustration of many solid phase equilibria that are of relevance for the soil system. This book is based upon the idea that the activity in solution of various species is fully determined by equilibrium between the solution phase and one or more solid phases. In practical situations kinetics may be important and/or adsorption phenomena instead of equilibrium with solid phases.

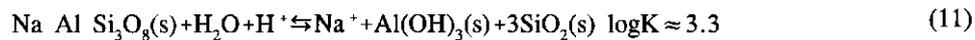
8.3 Some aspects of kinetics of dissolution and precipitation

Several reactions involving formation or dissolution of solid phases that are of environmental concern are characterised by slow kinetics. For a quantitative description it is necessary to deal with the kinetics of the processes next to equilibrium aspects. Primary minerals in the soil or aquifer system like various feldspar minerals (aluminium silicates) are rather soluble at pH values below pH 7. However, of many feldspars the rate of dissolution is very low. These primary minerals play an important role with respect to the buffermechanism of the soil or subsoil with respect to protons. They are also important as a source of cations like K^+ , Ca^{2+} and Mg^{2+} . The following reaction equation describes the solubility relationship for the sodium feldspar, albite:



This equation describes the incongruent dissolution of the sodium feldspar. It is called incongruent dissolution because part of the ions present in the mineral do not dissolve but are retained in the form of a secondary mineral, in this case $Al(OH)_3(s)$. During the process of soil formation, as we will see later, the reaction of equation (10) is often not in equilibrium but goes to the right. The result of the dissolution process is that a proton is replaced by a cation, here the sodium ion. Weathering of other feldspars results in replacement of protons for other cations like K^+ and Ca^{2+} . The aluminium ion is not released into the soil solution during weathering if the pH is above five, because the solubility of $Al(OH)_3(s)$ is very low. Apart from formation of $Al(OH)_3(s)$ also secondary aluminium silicate clay minerals may be formed as a result of the weathering process.

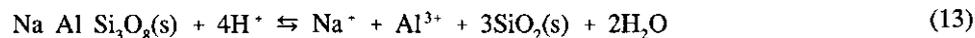
Equation (10) can be written in a slightly different form if we realise that in the soil always quartz or other silicon oxides are present. The concentration of H_4SiO_4 can in principle not become higher than the solubility of $SiO_2(s)$. This leads to the following equation:



Realising that the activity of the pure phases can be set to one, it follows that:

$$(Na^+) = (H^+)10^{3.3} \quad (12)$$

If the pH equals 3.3, which is a realistic value in acid forest soils, the sodium concentration at equilibrium according to equation (12) should be one mole per liter. The actual concentration in an acid forest soil may be around 0.3 mmol/l. Conclusion, there is no equilibrium. The same reasoning can also be done as follows, at 0.3 mmol/l for (Na^+) , according to equation (12) the pH should be 6.8 at equilibrium. In other words if there would be equilibrium the forest soil would probably not be very acid! In practice, there is no equilibrium, the soil solution is undersaturated with respect to feldspar and there is a continuous driving force for dissolution ($\Delta G_r < 0$) of feldspars. The continuous weathering of feldspar has led to a built up of $Al(OH)_3(s)$ in the soil. With a lowering of the pH below five the solubility of $Al(OH)_3(s)$ starts to increase strongly and the dissolution reaction can now be written as:



The main process that is now responsible for the consumption of protons is the release of aluminium ions. The aluminium ions will mainly be the result of dissolution of $Al(OH)_3(s)$

already present in the soil, because the dissolution kinetics of $\text{Al}(\text{OH})_3(\text{s})$ are faster than that of most feldspars. The increase in Al^{3+} leads to a release of Mg^{2+} of the exchange complex that may be leached to the groundwater. The high ratio of ($\text{Al}^{3+}/\text{Mg}^{2+}$) that results and the increased concentrations of heavy metal ions lead to a deterioration of the soil quality which may result in a deterioration of the quality of the forest and even lead to forest die back.

A semi-empirical equation that is sometimes used to describe the dissolution kinetics of minerals is:

$$R = \text{mol-mineral}/(\text{time}\cdot\text{unit-soil}) = k^* \left(1 - \frac{Q}{K^o}\right) \quad (14)$$

The parameter b is an empirical constant, K^o is the chemical equilibrium constant of the dissolution reaction, $10^{3.3}$ in case of equation (11), Q is the reaction quotient of the same reaction and k^* is a rate constant that includes the surface area of the dissolving mineral per unit soil. Equation (14) leads to $R = 0$ when $Q = K^o$, in other words the net weathering rate is zero when there is equilibrium. When there is a strong undersaturation, $Q \ll K^o$, there is a positive dissolution rate which under these conditions simply equals:

$$R = k^* \quad (15)$$

Equation (15) predicts a constant dissolution rate for large undersaturation. However, the rate may still depend on the pH of the solution. For this reason an asterix is used as a superscript for the rate constant.

The dissolution rate for a potassium feldspar may be in the order of $50 \mu\text{mol}$ silica per m^2 feldspar per year. Small particles will therefore contribute much more to the dissolution rate than larger particles. However, feldspars are normally found in the larger size fraction of the soil mineral phase and that is another reason why the effective weathering rate of feldspar in the field is rather low.

A more detailed mechanistic approach may yield insight in the factors that influence the value of k^* . As an example of such an approach reference is made to Hiemstra & van Riemsdijk (1990) and references cited in that paper.

8.4 Diffusion - precipitation kinetics

The formation of a solid phase may be a relatively fast reaction when all the components forming the new solid phase are initially present in the solution phase. The initial precipitate being formed may be a rather disordered, amorphous, mineral phase which may be very slowly converted into a more stable crystalline solid phase.

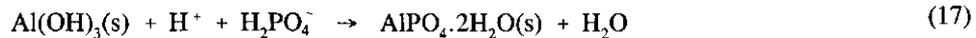
Another situation occurs when one of the constituents of the new solid phase to be formed is initially present in another solid phase. In that case reaction rates are often rather low. An example is a sheet of aluminum metal in the presence of air. The oxygen content of the air is approximately constant and under these conditions the chemically stable situation is that all aluminum metal should be converted into aluminumoxide or aluminumhydroxide:



What happens in practice is that O_2 molecules first adsorb on the surface of the aluminum

metal, the aluminum atoms at the interface between metal and air are converted into aluminum(hydr)oxide and this newly formed phase remains attached to the underlying metal. The reaction can now only proceed when the oxygen diffuses through this thin coating of aluminum(hydr)oxide to reach the underlying aluminum metal. The thicker the coating becomes the slower the conversion rate will become. If the coating has a rather high resistance against diffusion (not very porous) and if the coating sticks to the underlying material it is said that a protective coating is being formed that practically stops further conversion of the underlying material.

A similar situation may occur in soils. Iron and aluminum(hydr)oxides are very insoluble for $\text{pH} > 5.2$. This means that only an extremely low concentration of aluminum and iron ions is present in the soil solution phase under these conditions. When phosphate is added to the soil *e.g.* in the form of liquid manure (pig slurry etc.) or as commercial fertilizer the situation may become such that the system is supersaturated with respect to the formation of aluminum phosphate. The following reaction now should take place:



Reaction (17) states that an aluminum phosphate phase is being formed at the expense of $\text{Al(OH)}_3(\text{s})$. When the pH and the phosphate concentration in solution are kept constant, a constant supersaturation or driving force will exist for the formation of the aluminum phosphate phase. Such an experiment can be performed in the laboratory. The result of such an experiment is that initially phosphate reacts quite rapidly and then the reaction rate becomes lower and lower the further the reaction proceeds. Even after a year reaction time only a small fraction of the original $\text{Al(OH)}_3(\text{s})$ is converted into aluminum phosphate although the equilibrium condition for such an experiment would be a complete conversion.

This is thus typically a process where kinetics are very important. The reaction rate is most probably diffusion controlled. The process is schematically depicted in Figure 8.1. The diffusion rate depends on:

- the thickness of the coating, δ , which is a function of the amount that has been sorbed in the coating, S
- the reactive surface area, A , which may be a function of S
- effective diffusion constant, D , of the chemical species through the coating
- shape of the particle.

The size of the particles also plays a very important role. Small particles have a high surface area per unit mass of solid, the degree of conversion of the particles into the new phase will for certain conditions be strongly dependent on the initial particle size.

Very small particles can be completely converted into the new phase whereas very big particles are hardly converted at all. A very nice example of the effect of particle size on this type of kinetics is the oxidation of iron, in the presence of air. For larger particles the process of conversion of iron metal into iron(hydr)oxide is rather slow, but very tiny particles known as pyrophoric iron (pyros = fire) will react very vigorously, it will 'burn' when it comes into contact with air (remember the experiment at the end of the lecture).

In the engineering literature the diffusion precipitation model is also known as the unreacted shrinking core model. In the model it is assumed that a relatively sharp (moving) boundary will develop between the coating that is formed at the expense of the original particle and the not yet converted original particle. In Figure 8.2 the movement of phosphate into ferrihydrite particles is shown. The white dots represent phosphate and the

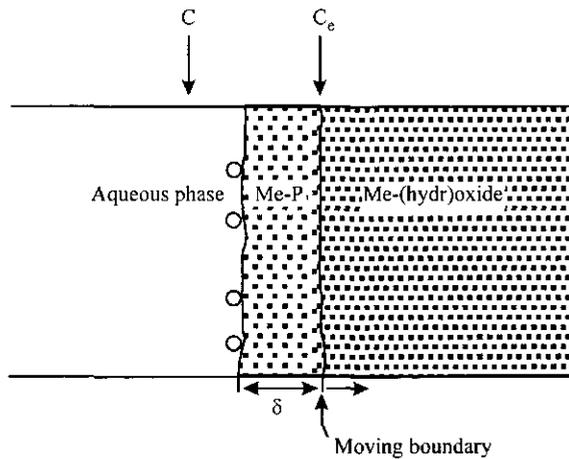


Figure 8.1. Schematic representation of the diffusion precipitation process. C represents the phosphate concentration in solution, and c_e the concentration at the interface between the two solid phases; c_e may represent the concentration when there is equilibrium between the two phases. The open circles represent adsorbed phosphate.

Migration of PO_4 in ferrihydrite

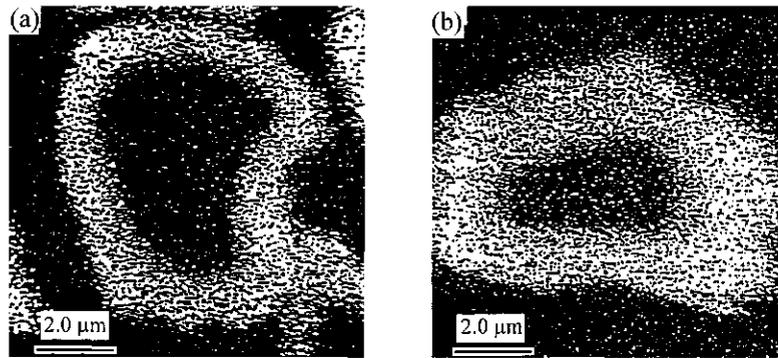


Figure 8.2. The distribution of phosphate in ferrihydrite particles. (a) Ferrihydrite particle reacted with phosphate for 1h. (b) Ferrihydrite particle reacted with phosphate for 1d.

black innercore is the part of the particle which the phosphate has not yet reached. By comparing the result for one hour (Figure 8.2a) and one day (Figure 8.2b) it can be seen that the phosphate front moves into the particle and that the boundary is indeed rather sharp. In this case the particles are highly porous and it is questionable whether a real coating is being formed or that it is more a diffusion process plus adsorption on the walls of the pores.

The reaction rate for unreacted shrinking core (USC) model can be described as:

$$\frac{\partial S}{\partial t} = f(S,L)(c-c_e) \quad (18)$$

The term $f(S,L)$ means that it is a function of the amount sorbed in the coating, S , and the shape and size of the particle, L . Only for a very well defined particle the expression for $f(S,L)$ can be substituted in equation (18) and it can be solved. For a soil a whole collection of different reactive particles may exist. For each reactive particle that reacts according to a USC process equation (18) applies.

We can integrate equation (18) according to:

$$\int f(S,L)^{-1} dS = \int (c-c_e) dt = \text{Int.} \quad (19)$$

The term $f(c-c_e)dt$ can be calculated if the solution concentration is measured as a function of time and if a value for c_e is assumed. The value of this integral should be equal to $f(S,L)^{-1}dS$. For a particle with a given shape and size there is a unique relationship between the measurable value of Int. and the amount reacted in the coating formation process S . The relationship itself can only be predicted in case the particle size and shape and the effective diffusion constant are known.

The integral defined in equation (19) is an 'exposure integral', which is also known in the field of toxicology. What equation (19) tells us is that a given value of the exposure integral for a certain particle corresponds with one value of S . One and the same value of the exposure integral can be obtained for quite different circumstances. A low concentration during a long reaction time may yield the same integral value as a higher concentration during a short reaction time, the model says that in both cases the 'exposure' is the same and that also the amount reacted should be the same. The same arguments also apply for any mixture of particles with different particle sizes and shapes. It is thus expected that the model might be applicable to a soil.

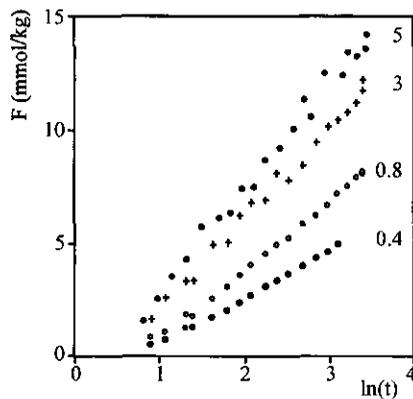


Figure 8.3. Phosphate sorption to a sandy soil (F , in mmol/kg) as a function of the natural logarithm of reaction time (t in hours) where the phosphate concentration is kept constant during the reaction. In the figure four different experiments are represented, the difference being the phosphate concentration in solution (0.4, 0.8, 3 and 5 mmol/L phosphate).

In Figure 8.3 the total phosphate sorption, denoted by F , as a function of time on a logarithmic scale is plotted as measured for four different phosphate concentrations in solution ranging from 0.4 mmol/L - 5 mmol/L. During an experiment the solution concentration is kept constant. On a logarithmic scale almost straight lines result, meaning that the rate decreases exponentially with the progression of the reaction.

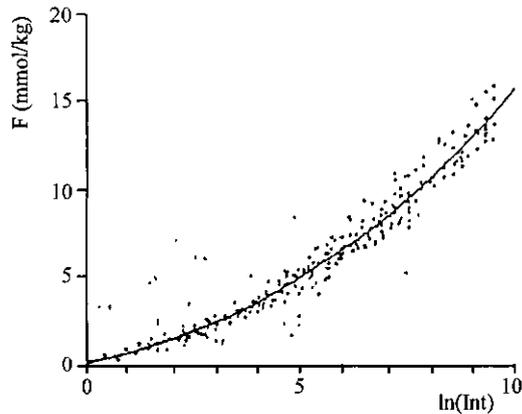


Figure 8.4. Phosphate sorption measured at a whole series of constant phosphate concentrations (see Figure 8.3) represented as a function of the natural logarithm of the calculated 'exposure' integral. The line represents a polynomial that was fitted through the data prints.

In Figure 8.4 data originating from a whole series of experiments similar to those of Figure 8.3 are now plotted as a function of the natural logarithm of the exposure integral. The theory states that all points with the same exposure should coalesce into one point. Since the total sorption of course increases with the exposure a line should result. The course of this line is not predicted from theory, apart from the fact that the slope of the line should be ≥ 0 .

The drawn line is a polynomial that is fitted through the points. It is clear that the points do not correspond exactly to the theory since deviation from the line in vertical direction do exist. These deviations may be partly due to experimental error in the measurement and partly due to the fact that the suggested model is not perfect. Once the relationship between F and the exposure integral is established for a soil this relationship (the polynomials) can be used to make independent predictions.

In Figure 8.5 an experiment is performed where at $t = 0$ phosphate is added to a soil/water mixture with a certain solid solution ratio. The concentration is measured as a function of time (open circles). The solid line is predicted based on the polynomial of Figure 8.4. The agreement between the prediction and the measurements is very good. In Figures 8.3-8.5 a logarithmic scale is used not because of principal reasons but because in this way rather small values and relatively large values can be represented more clearly in one figure.

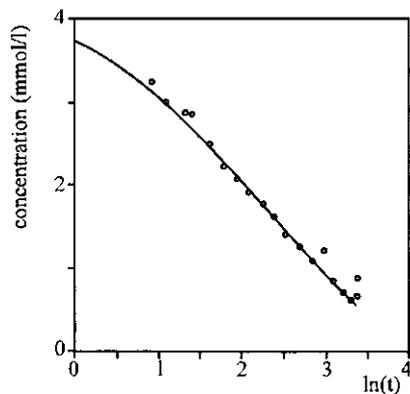


Figure 8.5. The concentration in the solution phase during reaction of phosphate with a sandy soil as a function of (the natural logarithm of) the reaction time ($t = \text{hr}$). The concentration decreases as a consequence of the proceeding sorption process. The circles represent measurements, the line is an independent prediction based on the application of the diffusion/precipitation model (or USC model) using the earlier obtained relationship between sorption and the exposure integral (see Figure 8.4).

8.5 References

- Hiemstra, T. & van Riemsdijk, W.H., 1990. Multiple activated complex dissolution of metal (hydr)oxides; a thermodynamic approach applied to quartz. *Journal of Colloid and Interface Science* 136: 132-150.
- Lindsay, W. 1979. *Chemical equilibria in Soil*. Wiley and Sons, New York. 449 pp.
- van der Zee, S.E.A.T.M., Fokkink, L.G.J. & van Riemsdijk, W.H., 1987. A new technique for assessment of reversibly adsorbed phosphate. *Soil Science Society of America Journal* 51: 599-604.
- van Riemsdijk, W.H., Bouma, L.J.M. & de Haan, F.A.M., 1984. Phosphate sorption by soils I. A diffusion-precipitation model for the reaction of phosphate with metaloxides in soil. *Soil Science Society America Journal* 48: 537-540.