

A management model to assess the extent of movement of chemicals through soils

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ABSTRACT. A model for the movement of chemicals in soils, STRASS (Simulation of TRansport And Sorption in Soils) based on the numerical solution to the one-dimensional convection-dispersion equation is presented in this study. The general convection/dispersion equation is coupled to adsorption/desorption formulations (linear, Langmuir and Freundlich) which all have in common that the sorption process can be formulated as a combination of zero- and first-order terms for a relatively small change in the system. For each timestep (typically one year) of a model simulation the 'pseudo' rate constants are re-evaluated in each segment of the physical schematization, thus adjusting for the typical behavior of each of the sorption types. Furthermore, uptake by plant roots as a function of soil depth and soil solution concentration is included as a first-order process coupled to plant water uptake. Other zero- and first-order processes (e.g. decay of the substance or fixation) can be added without changing the model structure.

The model performance is illustrated with an example of arsenic movement in a (contaminated) Dutch agricultural soil. In this example, the arsenic sorption is described by Freundlich isotherms. The Freundlich coefficients for arsenic vary with depth in the soil column because of changes in oxalate extractable iron and aluminum, and pH.

INTRODUCTION

This article describes the model STRASS (Simulation of TRansport And Sorption in Soils). STRASS is a numerical, one-dimensional convection/dispersion model with zero- and first-order kinetics. STRASS treats the soil as a (vertical) column of segments. Each segment can contain its own kinetic process and transport parameters. Therefore the vertical differences (e.g. soil horizons) can be included in the model. The model is only capable of including zero- and first-order (chemical, microbiological) kinetic processes, and as such is not capable of dealing with (more complicated) chemical equilibria which involve more than one component (e.g. speciation in solution can only be lumped by introducing a forcing function, there is no way to calculate this dynamically). STRASS can be used to calculate the dynamic changes in the soil system with respect to a substance, as long as chemical equilibria involving other substances do not interfere strongly. The model is especially useful to study long term changes. Results of STRASS are quantitative.

STRASS consists of a soil column of variable length, which is divided into 100 layers. The model calculates the movement of a chemical through the soil column, and the fluxes from the soil column, including plant uptake. Typical model runs simulate 100-1000 years.

MODEL FORMULATION

General mathematical structure

For the mathematical model formulation, units have to be consistent. In this article the following units have been chosen: amount of the chemical = milligram (mg), unit of length = meters (m), surface area = m², volume = m³, unit of solid mass = kilograms (kg). The unit of time in the model is one year.

For a substance in a one-dimensional column, for a segment i , equation (1) applies (law of mass conservation):

$$(C_i * V_i)_{t+\Delta t} = (C_i * V_i)_t + \Delta t * T + \Delta t * R_i \quad (1)$$

where

- C_i = concentration of substance in segment i ($\text{mg} \cdot \text{m}^{-3}$)
- V_i = volume of segment i , to which C_i applies (e.g. water volume) (m^3)
- Δt = time step (year)
- T = change through transport ($\text{mg} \cdot \text{year}^{-1}$)
- R_i = change through reactions occurring in i ($\text{mg} \cdot \text{year}^{-1}$)

Focussing on transport through diffusion/dispersion, we can define a mixing volume for the cell interface $i-1,i$ (based on Fick's first law):

$$M_{i-1,i} = \frac{D_{i-1,i} * A_{i-1,i}}{0.5 * (\Delta x_{i-1} + \Delta x_i)} \quad (2)$$

where

- $M_{i-1,i}$ = mixing volume ($\text{m}^3 \cdot \text{year}^{-1}$) for the interface $i-1,i$
- $D_{i-1,i}$ = diffusion/dispersion coefficient for interface $i-1,i$, with dimension $\text{m}^2 \cdot \text{year}^{-1}$ (which in itself can be a function of tortuosity and/or water fraction, temperature etc.)
- $A_{i-1,i}$ = surface area of the interface $i-1,i$ (m^2)
- Δx_i = diameter of layer i (m)

The transport through mixing for cell i can be written:

$$T_{\text{mix},i} = M_{i-1,i} * (C_{i-1} - C_i) + M_{i,i+1} * (C_{i+1} - C_i) \quad (3)$$

Convection from $i-1$ to i to $i+1$ (downward flow) can be brought in (Frissel and Reiniger, 1974): if it is assumed that the concentration which flows from $i-1$ to i , is the concentration at the interface, this concentration is $(C_{i-1} + C_i)/2$. Similarly, the outflowing concentration is $(C_i + C_{i+1})/2$. The flow rate through the interface is $v_{i-1,i}$ resp. $v_{i,i+1}$:

$$T_{\text{adv},i} = [v_{i-1,i} * (C_{i-1} + C_i) - v_{i,i+1} * (C_i + C_{i+1})] / 2 \quad (4)$$

where v = flow in $\text{m}^3 \cdot \text{year}^{-1}$.

This discretization of the flow is known in the literature as the central-difference scheme, and is the natural outcome of a Taylor-series formulation (Patankar, 1980). It is, however, only stable as long as

$$P = (v_{\text{adv}} * \Delta x / D) \leq 2 \quad (5)$$

for each cell interface. P is the Peclet number. The Peclet number is a measure of the ratio of convective transport to diffusive/dispersive transport.

Flow upward through the column will only change the indexes of equation (4): $i-1$ becomes $i+1$ and $i+1$ becomes $i-1$.

Combining equation (1), (3) and (4) gives the mass conservation equation:

$$\begin{aligned}
C_{i,t+\Delta t} = & (C_i * V_i)_t / V_{i,t+\Delta t} \\
& + \Delta t * [(M_{i-1,j} + v_{i-1,j}/2) / V_{i,t+\Delta t}] * C_{i-1} \\
& - \Delta t * [(M_{i-1,j} + M_{i,j+1} + v_{i,j+1}/2 - v_{i-1,j}/2) / V_{i,t+\Delta t}] * C_i \\
& + \Delta t * [(M_{i,j+1} - v_{i,j+1}/2) / V_{i,t+\Delta t}] * C_{i+1} \\
& + \Delta t * R_i / V_{i,t+\Delta t}
\end{aligned} \tag{6}$$

When the volume of the segment does not change by transport, then $V_{i,t} = V_{i,t+\Delta t} = V_i$. The terms between the square brackets in equation (6) form a tridiagonal matrix, A. In vector notation equation (6) can be rewritten as:

$$C_{t+\Delta t} = C_t + A * C * \Delta t + (R/V) * \Delta t \tag{7}$$

where C, R and V are vectors, and A is the transport matrix

We define

$$(R/V) = R_0 + R_1 * C \tag{8}$$

where R_0 is a vector of zero-order rate coefficients ($\text{mg.m}^{-3}.\text{year}^{-1}$) and $R_0 \geq 0$ (for stability), and R_1 is a vector containing first-order rate coefficients (year^{-1}).

Also,

$$C = (1-\sigma) * C_t + \sigma * C_{t+\Delta t} \tag{9}$$

where ($0 \leq \sigma \leq 1$). σ is the degree of implicitness. The general solution of the set of equations (7), (8) and (9) is:

$$[E - \sigma * \Delta t * (A + E * R_1)] * C_{t+\Delta t} = [E + (1-\sigma) * \Delta t * (A + E * R_1)] * C_t + \Delta t * R_0 \tag{10}$$

where E represents the unity-matrix.

By putting the value of σ to 0 we get the so-called explicit solution scheme:

$$C_{t+\Delta t} = [E + \Delta t * (A + E * R_1)] * C_t + \Delta t * R_0 \tag{11}$$

Examples of explicit models are the soil models of Frissel and Reiniger (1974), and Van Genuchten and Wierenga (1975). Explicit models have one severe drawback: they are not unconditionally stable. A discussion of stability is given by Press et al. (1986). Generally, explicit models require a time step which assures that the volumes transported are smaller than the segment volumes to remain stable, which make them unpractical to calculate situations with small segment sizes and large transport volumes.

Increasing σ increases model stability, with only the value $\sigma = 1$ assuring unconditional stability. The solution scheme is then called implicit and can be found by a matrix-inversion:

$$C_{t+\Delta t} = [E - \Delta t * (A + E * R_1)]^{-1} * (C_t + \Delta t * R_0) \tag{12}$$

This solution scheme is much more powerful than the explicit scheme because irrespective of the size of the transport terms the solution is stable, and no oscillations can occur. Only when the matrix, that has to be inverted is singular then no solution can be found. In practice, this never occurs.

The method described is based on the work of Crank (1975). A good discussion of the merits of implicit methods compared to explicit methods is given by Patankar (1980). The solution algorithm is also discussed by Press et al. (1986).

Equation (12) is the basic equation of the model presented here.

Transformation of equilibrium sorption models into the kinetic transport equation

The term sorption, as used in this article, refers to the selective uptake, storage and release by soil solids of solute substances. To enable the quantification of the sorption process, a relation has to be established between the (change in) concentration in solution and the (change in) concentration sorbed to the solids of the soil. This relation can either be a kinetical or an equilibrium equation. Travis and Etnier (1981) provide a survey of models which are used to describe sorptive behavior in soils.

In the case of a kinetical model, the inclusion of the sorption model into equation (12) can be established by changing the values of R_0 and R_1 , as long as the sorption model can be rewritten towards zero- and first-order terms.

Equilibrium sorption can also be introduced in the convection/dispersion equation (12) by changing the values of R_0 and R_1 . If sorption is in equilibrium with the soil solution, the amount sorbed will be governed by the dissolved concentration at $t+\Delta t$. Since the implicit scheme uses this concentration to calculate the extent of all processes in Δt , sorption can be introduced as a first order extraction from the soil solution (and thus also acting on $C_{t-\Delta t}$). The amount sorbed has to be introduced as zero order input to each segment, and is thus available for all processes to act upon in Δt . The advantages of this scheme are: 1) each segment can carry its own sorption coefficients, 2) the process parameters of sorption can be evaluated independent from the transport parameters and 3) no iteration over the interaction between sorption and transport is necessary, since both are solved simultaneously.

Three sorption models are standard in STRASS: linear sorption, Freundlich sorption and Langmuir sorption.

Linear sorption

In the simplest case a linear sorption model applies:

$$Q_{s,i} = \pi_{L,i} * C_i \quad (13)$$

where

$Q_{s,i}$ = amount sorbed in the solid fraction (mg.kg solid⁻¹)

$\pi_{L,i}$ = partition coefficient (m³.kg solid⁻¹)

C_i = concentration of the substance (mg.m⁻³)

If we consider the amount sorbed in each segment each time step as a zero-order input for that segment, and the sorption as a first-order extraction, then for $X_{s,i}$, the total amount of solid in segment i ,

$$R_{0,i} = Q_{s,i} * X_{s,i} / (V_i * \Delta t) \quad (14)$$

and

$$R_{1,i} = -\pi_{L,i} * X_{s,i} / (V_i * \Delta t) \quad (15)$$

Substituting (14) and (15) into eq. (12) each time step gives the required solution.

Non-linear sorption models

The method of transforming sorption curves from non-linear to linear uses the first derivative of the sorption curve towards the dissolved concentration as the estimator of sorption within a time step Δt .

This derivative is functionally equivalent with the partition coefficient of the linear sorption model described in section 2.2.1. The situation described here is graphically presented in figure 1.

Since the product of the partition coefficient and the concentration in solution (C_t in figure 1) will not yield the total solid concentration ($Q_{s,t}$), the part of the sorbed substance which is not represented in this way, is considered inactive during the timestep (inactive part = $Q_{s,t,inactive}$, active part = $Q_{s,t,active}$).

After each timestep the inactive part is added to the (new calculated) active sorbed part. The linearization always produces an overestimation of the sorbed amount ($Q_{s,t1}'$), since all cords along a Langmuir or Freundlich isotherm are above the curve. The equilibrium sorbed amount ($Q_{s,t1}$), which corresponds to the calculated dissolved concentration (C_{t1}), can be calculated with the original Freundlich or Langmuir equation. The difference between the calculated solid amount of chemical and the equilibrium amount is added to the zero-order input (to the R_0 term) for the next time step (ΔQ).

After each time step new partition coefficients are calculated, the equilibrium solid amount is re-partitioned into 'active' and 'inert' etc. The method can be called a local linear sorption model, with iterative adjustment.

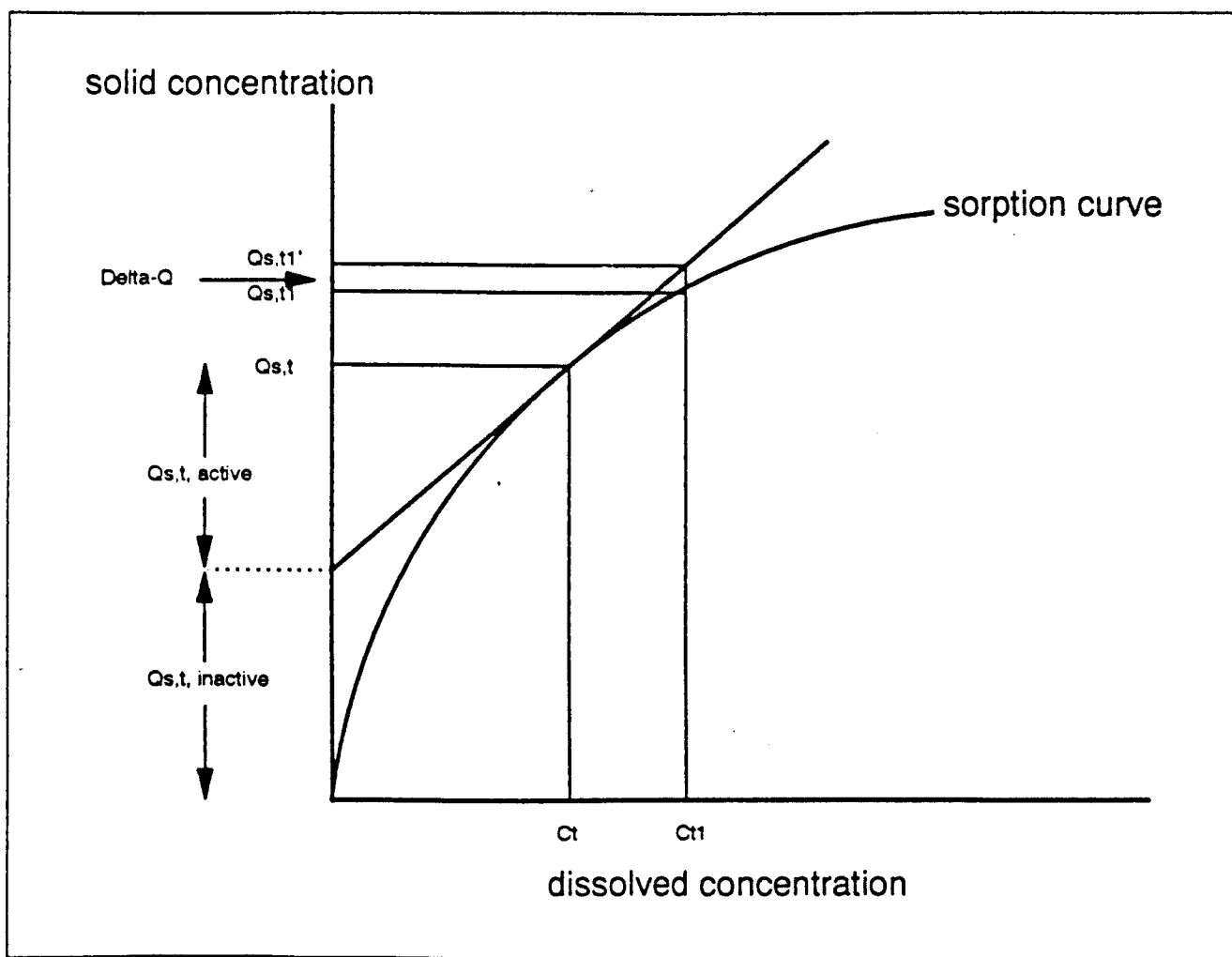


Figure 1. Handling of non-linear sorption by STRASS.

Freundlich sorption

The general formulation of a Freundlich isotherm is:

$$Q_{s,j} = K_{F,j} * C_i^n \quad (16)$$

and ($0 < n \leq 1$) ($n = 1$ yields a linear sorption model)

The first derivative of this function to C_i , and hence the partition coefficient needed in the model formulation is:

$$\pi_{F,j,\Delta t} = (dQ_{s,j}/dC_i)_t = (K_{F,j} * n * C_i^{(n-1)})_t = n * Q_{s,j} / C_i \quad (17)$$

$$\text{The 'inert' fraction is: } Q_{in,j,t} = (1-n) * Q_{s,j} \quad (18)$$

$$\text{The 'active' fraction is: } Q_{ac,j,t} = n * Q_{s,j} \quad (19)$$

If the 'overshoot' from the previous time step is called ΔQ_i , then the kinetic parameters can be defined as:

$$R_{0,j} = (Q_{ac,j,t} + \Delta Q_i) * X_{s,j} / (V_i * \Delta t) \quad (20)$$

$$\text{and } R_{1,j} = -\pi_{F,j,\Delta t} * X_{s,j} / (V_i * \Delta t) \quad (21)$$

Langmuir sorption

The general formulation of a Langmuir isotherm is:

$$Q_{s,j} = K_{1,j} * C_i * (1 + K_{2,j} * C_i)^{-1} \quad (22)$$

The first derivative of this function towards C_i and thus the partition coefficient is:

$$\pi_{L,j,\Delta t} = (dQ_{s,j}/dC_i)_t = (K_{1,j} * (1 + K_{2,j} * C_i)^{-1} - K_{1,j} * K_{2,j} * C_i * (1 + K_{2,j} * C_i)^{-2})_t \quad (23)$$

$$\text{The 'inert' fraction is: } Q_{in,j,t} = Q_{s,j} - \pi_{L,j,\Delta t} * C_{i,t} \quad (24)$$

$$\text{The 'active' fraction is: } Q_{ac,j,t} = Q_{s,j} - Q_{in,j,t} \quad (25)$$

And so the kinetic parameters for timestep Δt are:

$$R_{0,j} = (Q_{ac,j,t} + \Delta Q_i) * X_{s,j} / (V_i * \Delta t) \quad (26)$$

$$\text{and } R_{1,j} = -\pi_{L,j,\Delta t} * X_{s,j} / (V_i * \Delta t) \quad (27)$$

Plant uptake of the substance

Plant uptake of the substance is modelled as a first-order process where the first-order rate coefficient (Δt^{-1}) is:

$$R_{1,j,upt} = -K_{upt} * V_{upt,j} / V_i \quad (28)$$

$V_{\text{upt},i}$ is the volume of water taken up by the plant in segment i in time Δt . K_{upt} is a coefficient which describes the efficiency of the substance uptake. If this coefficient is 1, the concentration in the water which is taken up is the pore water concentration. Lower values give preferential exclusion, higher values preferential uptake.

Since the model assumes that all substance which is taken up, is removed from the soil column, the value of K_{upt} is usually lower than 1, except when strong preferential uptake occurs.

Since rate coefficients are additive, the value of $R_{1,i,\text{upt}}$ is added to the value of $R_{1,i}$.

Other zero- and first-order processes

Other zero- and first-order processes (e.g. decay, microbial production) can be included into R_0 and R_1 . A column for R_0 (dim. $\text{mg}\cdot\text{year}^{-1}\cdot\text{m}^{-1}$) and R_1 (dim. year^{-1}) is available in the standard input file to the program. The values can be zero (which is the default choice).

Model assumptions about water flow and dispersion

The model assumes a water-filled porosity (Θ_w , the part of the pores filled with water) for each segment of $0.7 \cdot$ the porosity of the segment.

The model assumes plant water uptake to appear only between 0 and the specified maximal rooting depth in the profile. The amount taken up in each segment linearly decreases with depth to zero at the maximal rooting depth. The amount taken up in a segment i is $V_{\text{upt},i}$.

The water flow through each segment is given by:

$$v_{i,i+1} = v_{i-1,i} - V_{\text{upt},i} \quad (29)$$

where $v_{i-1,i}$ is the flow of water into segment i ($\text{m}^3\cdot\text{m}^{-2}\cdot\text{year}^{-1}$), $v_{i,i-1}$ is the flow out of segment i . The water flux into segment 1 is defined as the sum of total plant water uptake and groundwater recharge.

Dispersion is set at 0 over the upper boundary of the modelled column. For the lower boundary it is assumed that the concentration of the chemical in the boundary always equals the concentration in the last segment of the model column at the previous time.

In soils, an often used formulation for dispersion is (e.g. Frissel and Reiniger, 1974):

$$D = \alpha_L \cdot v_{\text{adv}} + D_{\text{mol}} \cdot \Theta_w \cdot \Gamma \quad (30)$$

where α_L is the so-called dispersion length (m), D_{mol} is the molecular diffusion coefficient and Γ is the tortuosity factor. The value of α_L is input to the model. The model assumes D_{mol} to be $0.04 \text{ m}^2\cdot\text{year}^{-1}$, and Γ to be 0.3. The model requires α_L to be larger than Δx (the size of the cells of the soil column), e.g. if $\Delta x = 0.01 \text{ m}$ (1 cm), then $\alpha_L \geq 0.01 \text{ m}$. This is generally no problem, since normal values of α_L in soils range from 2 to 20 cm. If α_L is larger than or equal to Δx , equation (5) will always give a Peclet number smaller than 1 (because of the contribution of molecular diffusion to D), which assures that the central difference scheme used for the convective flow of water is a valid model.

Model input

The input to the model is split into two parts. Input specific to each of the segments of the soil column is read from an input file, which has to be created for each run. This input contains the initial amount of chemical (mg.kg solid^{-1}), the density of the solids (kg.m^{-3}), the total porosity, additional zero-order coefficients ($\text{mg.year}^{-1}.\text{m}^{-1}$), additional first-order coefficients (year^{-1}), and sorption parameters: for a linear model one parameter ($\Pi_{L,i}$ $\text{m}^3.\text{kg}^{-1}$), for a Freundlich model two parameters ($K_{F,i}$ and n_i respectively) and for a Langmuir model two parameters ($K_{1,i}$ ($\text{m}^3.\text{kg}^{-1}$) and $K_{2,i}$ ($\text{m}^3.\text{mg}^{-1}$) respectively).

Information which has to be added interactively after the start of the program is: length of the soil column (L_o) in cm, maximal rooting depth of plants ($L_p \leq L_o$), plant water uptake (m.year^{-1}), groundwater recharge (m.year^{-1}), input of chemical to the soil ($\text{mg.m}^{-2}.\text{year}^{-1}$), factor to be used for plant uptake of chemical ($K_{\text{upt}} \geq 0$), dispersion length α_L (equation 30), number of years to simulate and type of sorption model used.

APPLICATION OF THE MODEL TO THE MOVEMENT OF ARSENIC IN A CONTAMINATED DUTCH AGRICULTURAL SOIL

This section illustrates the model presented in the previous part for the case of the movement of arsenic in a contaminated agricultural soil. More complete details of the arsenic study will be published elsewhere (Bril, 1993, in prep).

In April 1990 four agricultural soils, of which three had received arsenic in the years 1953-1985 (about ten times during this period), were sampled. All soils are from the northern part of the Netherlands, and are characterized as sandy loams ('jonge zeeklei'). All soils contain calcium carbonate. The arsenic was used as a defoliant in potato cultivation (Dolman, 1981; Loch, 1982). Since 1985 the use of arsenic has been banned. Some characteristics of one of the sites sampled are given in table 1.

Table 1. Some characteristics of a soil column contaminated with arsenic.

Depth (cm)	% <2 μm	% OM ⁰	pH ¹	Fe-ox ²	Al-ox ²	As-tot ³	As-dis ⁴
from to	(clay)		[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.m ⁻³]	
0 20	9.0	1.19	7.49	780	268	18.76	87.8
20 35	9.0	1.34	7.66	785	283	18.45	130.3
35 50	8.9	0.86	7.90	920	274	19.04	56.5
50 65	10.2	0.43	8.04	1220	280	9.68	11.0
65 80	13.3	0.44	8.14	1010	309	8.07	3.8
80 100	10.8	0.31	8.20	810	283	6.74	1.6

⁰ % OM = organic matter content

¹ pH = pH of the soil solution

² ox = ammoniumoxalate/oxalic acid extractable

³ tot = total solid concentration

⁴ dis = dissolved concentration

The model presented here involves the top meter of the soil. The soil is drained artificially at a depth of 1 meter, so it is assumed that when the arsenic reaches this depth, it will be flushed from the soil into the drains.

Data interpretation and model definition

The data on arsenic presented in table 1 show that generally, the soil solids do not have a high arsenic content. According to the formula for the reference value for arsenic in soil (Slooff et al., 1990), the 0-20 cm soil layer would have a reference (A) value of 19 mg.kg⁻¹ soil. So all the soil down to 1 meter is below, or just at, the A standard. However, if the concentrations in the soil pore water are compared to the set of reference values given for groundwater (Slooff et al., 1990), then the soil column down to 65 cm is above the A-level (10 mg.m⁻³), down to 50 cm above the B-level (30 mg.m⁻³), and between 20-35 cm even above the C-level (100 mg.m⁻³). Furthermore, it can be noted that the solid arsenic content of the upper 50 cm is more than twice the content of the 50-100 cm layer. From these observations a number of questions arise: 1) what is the time before the arsenic reaches the drains (at 1 meter depth), 2) what will be the concentration in the drain water, 3) how important is removal through plant uptake of arsenic and 4) what will be the future development of crop quality with respect to arsenic.

Using the model STRASS we can produce estimates as answers to these four questions, provided data about the sorptive behavior of arsenic in these soils is available, and plant uptake is known.

Adsorption parameters for arsenic

The measured arsenic data (total solid and dissolved), together with the data of the three other similar soils, fit to a Freundlich isotherm with pH- dependent exponent n, and with K_F dependent on oxalate-extractable Fe and Al. Oxalate-extractable Fe and Al is assumed (Schwertmann 1964, Huang et al., 1977) to be a good indication of the amount of reactive (hydr)oxides of these metals. Livesey and Huang (1981) found high correlations between ammonium-oxalate/oxalic acid-extractable Al and Fe and adsorption capacity for arsenate in four soils from Saskatchewan, Canada. Jacobs et al. (1970) and Woolson et al. (1971) found that much of the arsenic in soils is being sorbed on to Fe and Al oxides. We derived the following relation for arsenic sorption in the studied soils:

$$Q_s = 0.175 * [Fe+Al] * C^{1.2-0.115*pH} \quad (31)$$

Number of samples = 24. R² = 0.813

where

$$Q_s = \text{mg As.kg solid}^{-1}$$

$$[Fe+Al] = \text{mmol.kg solid}^{-1}$$

$$C = \text{mg As.m}^{-3} \text{ water}$$

Depth (cm)	K _F	n
0 - 20	4.18	0.339
20 - 35	4.29	0.319
35 - 50	4.66	0.292
50 - 65	5.64	0.275
65 - 80	5.17	0.264
80 -100	4.37	0.257

Table 2 gives the calculated K_F and n values for different layers of the soil.

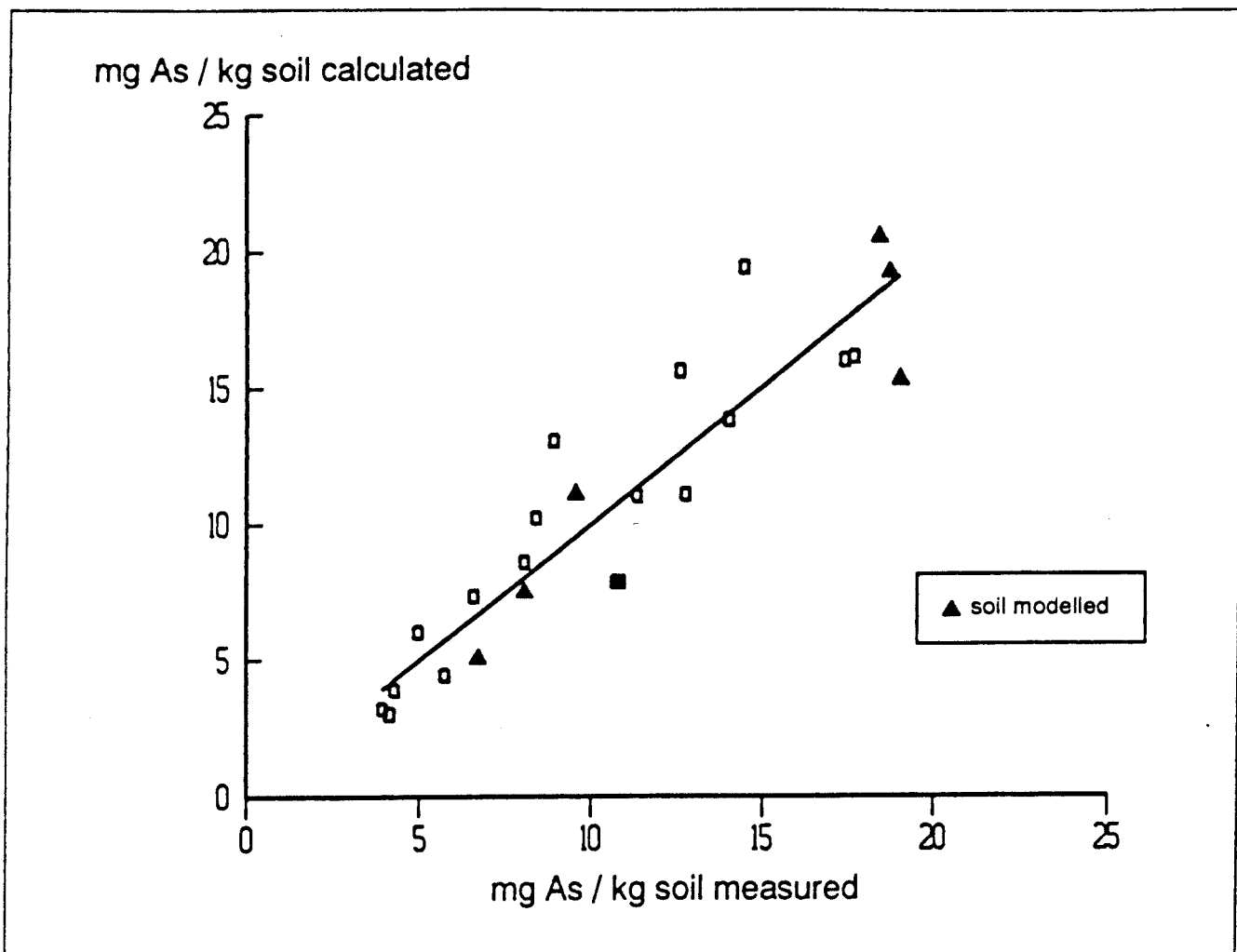


Figure 2. Fit of Freundlich model to soil data.

Figure 2 shows the fit of the Freundlich adsorption model to the measured data. It also includes the data of the three other soil profiles (two where As was applied, one 'clean') from the same region and soil type, used to construct the sorption model.

Other model input

1. Plant uptake coefficient K_{upt}

The plant uptake coefficient is necessary for two reasons: First the mass balance has to take into account the amount removed by harvesting and secondly the concentration in the consumable part of the plant is important from a human health point of view.

Arsenic uptake by barley seedlings is investigated by Asher and Reay (1979). From their work an average coefficient of uptake of arsenic according to equation (28) can be deduced of 0.25 (combining the information from fig. 4b and 4c of Asher and Reay (1979), a steady state As uptake of $.008 \text{ mol As.mol P}^{-1}$ at 1 g As.m^{-3} solution concentration, when P concentration $> 3 \text{ g P.m}^{-3}$ can be calculated). However, this is only valid for the whole plant. Since the harvest takes away only the grains from the field, and very little arsenic is transferred to the grains from the roots (Henkens and Smilde, 1989), this number is not relevant for the objectives of this study.

Therefore, the value of K_{upt} used in this study was derived in another way:

According to Wiersma et al. (1986) the mean arsenic content of potato tubers in the Netherlands is 0.013 mg.kg^{-1} fresh weight. A normal harvest is $41200 \text{ kg.ha}^{-1}.\text{year}^{-1}$ (CBS, 1992, average 1989-1991). The average As concentration in soil pore water in the rooting zone for the entire Netherlands is estimated to be 8

$\text{mg}\cdot\text{m}^{-3}$ (concentration found in the uncontaminated field), and normal water uptake of potatoes = $0.33 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{year}^{-1}$. The combination of these data leads to a 'guestimated' K_{upt} for potatoes of 0.02.

The soils are used in a three years crop rotation scheme: potatoes, sugar beet, cereals. Since no information on arsenic concentration in sugar beet is available, it is assumed that they behave in the same way as potatoes.

For the cereals, the average value of the data of wheat and barley given by Wiersma et al. (1986) is used (content = $0.056 \text{ mg As}\cdot\text{kg fresh weight}^{-1}$). Normal harvest can be estimated at $7500 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ (CBS, 1992, average for wheat 1989-1991). This would imply a K_{upt} of 0.016 for cereals. This is close enough to 0.02 (given all the uncertainties of the presented numbers) to use an overall coefficient of 0.02.

2. Soil column length is 1 m.

3. Plant rooting depth is 0.75 m (average of cereals 1 m, sugar beets 0.75 m, potatoes 0.5 m).

4. Annual water uptake of plants is $0.33 \text{ m}^3\cdot\text{m}^{-2}$.

5. Annual groundwater recharge is $0.33 \text{ m}^3\cdot\text{m}^{-2}$.

6. Annual arsenic deposition (dry and wet) $0.4 \text{ mg As}\cdot\text{m}^{-2}$ (Slooff et al., 1990, p. 63, data for the northern part of the Netherlands).

7. Dispersion length α_L is .1 m

8. For all the segments of the soil column: porosity is 0.45 and solid density is $2500 \text{ kg}\cdot\text{m}^{-3}$.

Results

Figures 3 and 4 show the measured and calculated dissolved and solid concentration profiles for As after 0, 40, 120, 200, 280 and 360 years.

Figure 5 shows the calculated dissolved concentration of As at five depths in the soil column. Figure 6 shows the calculated flux of arsenic from the soil column at 100 cm depth, and the calculated plant uptake. Figure 7 shows the calculated concentration of arsenic in the crops (potatoes and cereals) using the data for production given in 3.1.2.

Discussion of calculation results, and conclusion

The model predicts that the removal of As by the plants is substantially lower than the outflow at 1 meter depth (figure 6). The uptake will rapidly decrease, because the As is moving downward, out of the rooting zone, and the concentration of As in the rooting zone decreases in time (figures 3 and 5). However, in the first 20-40 years after 1990 (the starting year of the simulation) the calculated concentration of arsenic in potatoes is higher than or at the level of the maximum allowable concentration according to the Dutch Pesticides Act ($0.1 \text{ mg}\cdot\text{kg}^{-1}$, Slooff et al., 1990). For cereals no Dutch criterion value could be found. The German 'Bundesgesundheitsamt' gives indicative values of $0.5 \text{ mg}\cdot\text{kg}^{-1}$ (Bundesgesundheitsamt, 1977). For the first 20-40 years the calculated values are above this value.

The outflow of As in the water from the drains remains low for 100 years after 1990, then the concentration in the drain water rises to a maximum of about $50 \text{ mg}\cdot\text{m}^{-3}$ after 200-250 years, after which the concentration slowly decreases. At the maximal flux, the amount of As leached from the field will be about $160 \text{ g As}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. The maximal calculated concentration in the outflow is the same as the drinking water standard for arsenic in the Netherlands ($50 \text{ mg}\cdot\text{m}^{-3}$, Waterleidingbesluit (1985)).

This example shows that STRASS is capable of giving quantitative estimates of the movement of reacting chemicals through soils. The model can be used to determine time scales and intensities of processes. As such the model seems to be a useful management tool to estimate the ~~log~~ long term seriousness of soil pollution, and the effect of different management strategies.

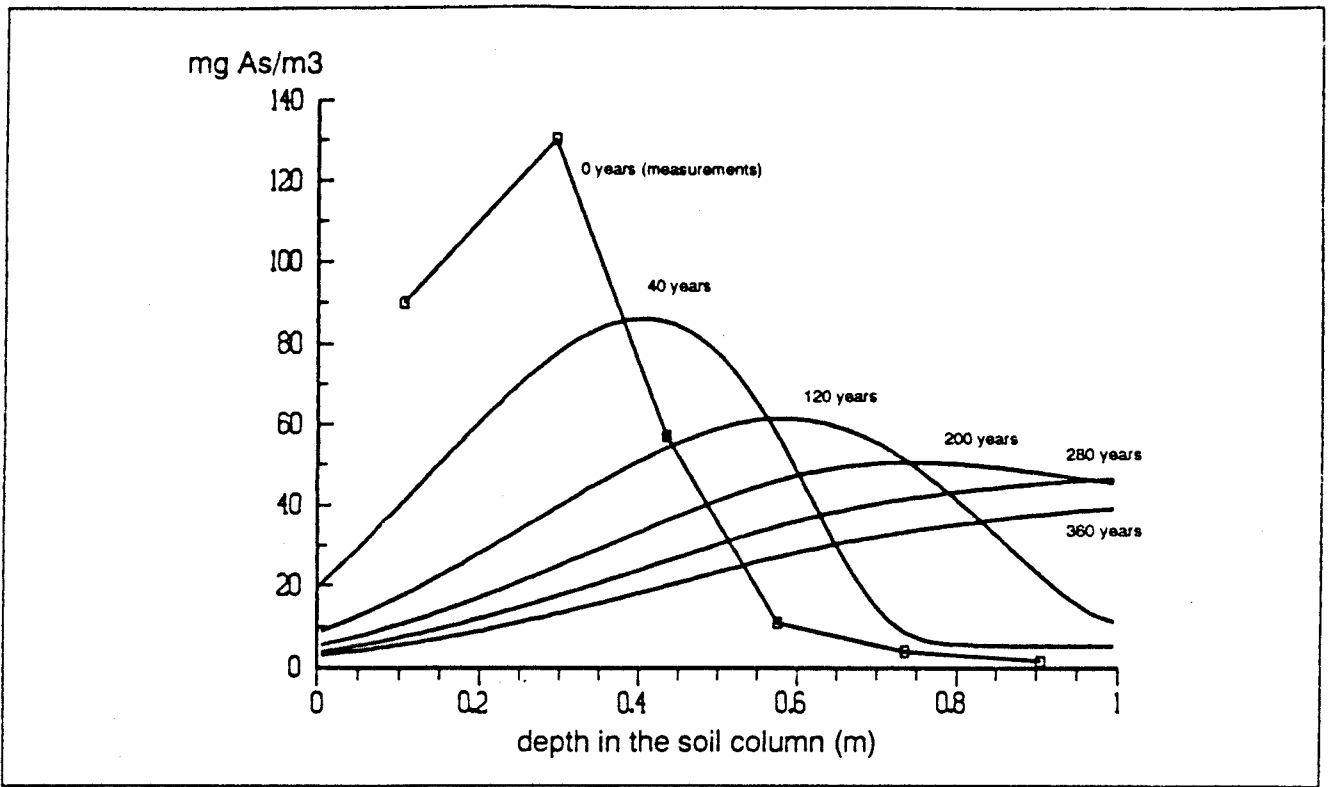
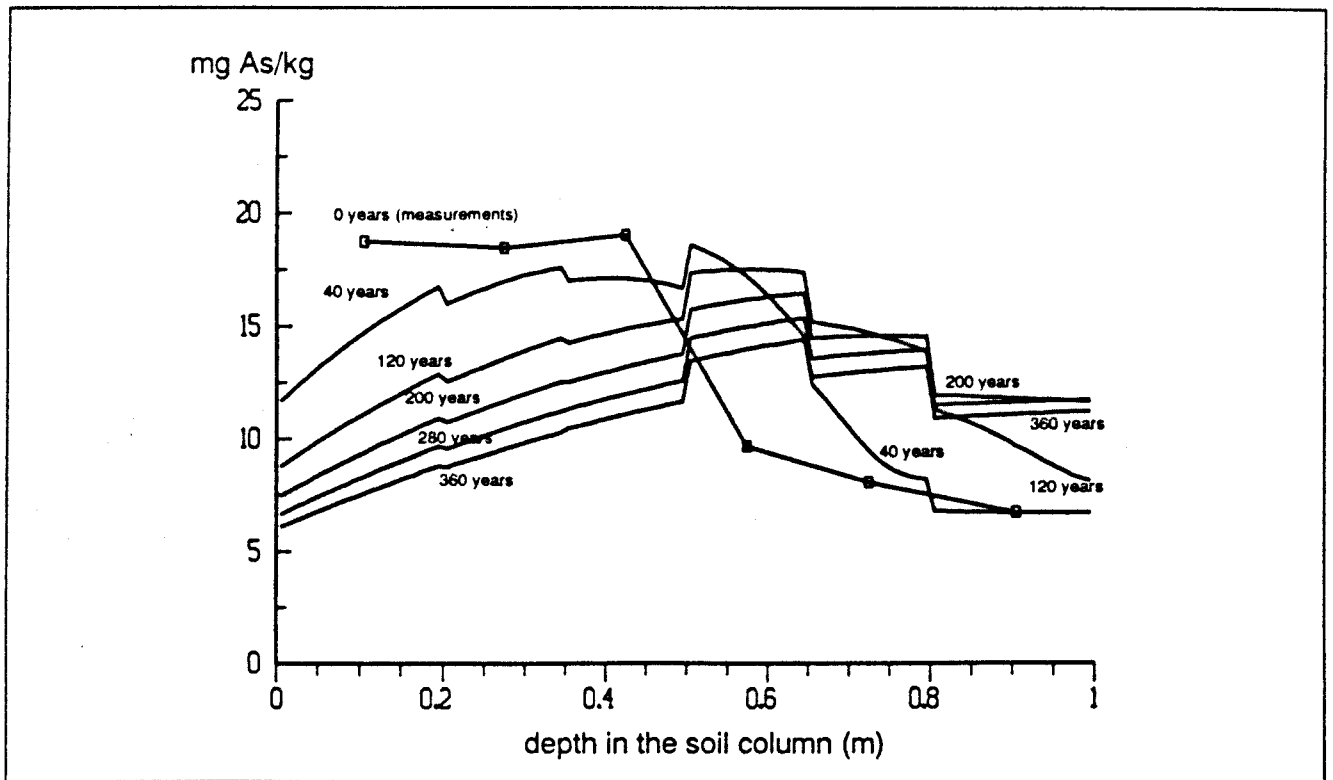


Figure 3. Measured (0 years) and calculated dissolved arsenic profiles.

Figure 4. Measured (0 years) and calculated solid arsenic profiles.



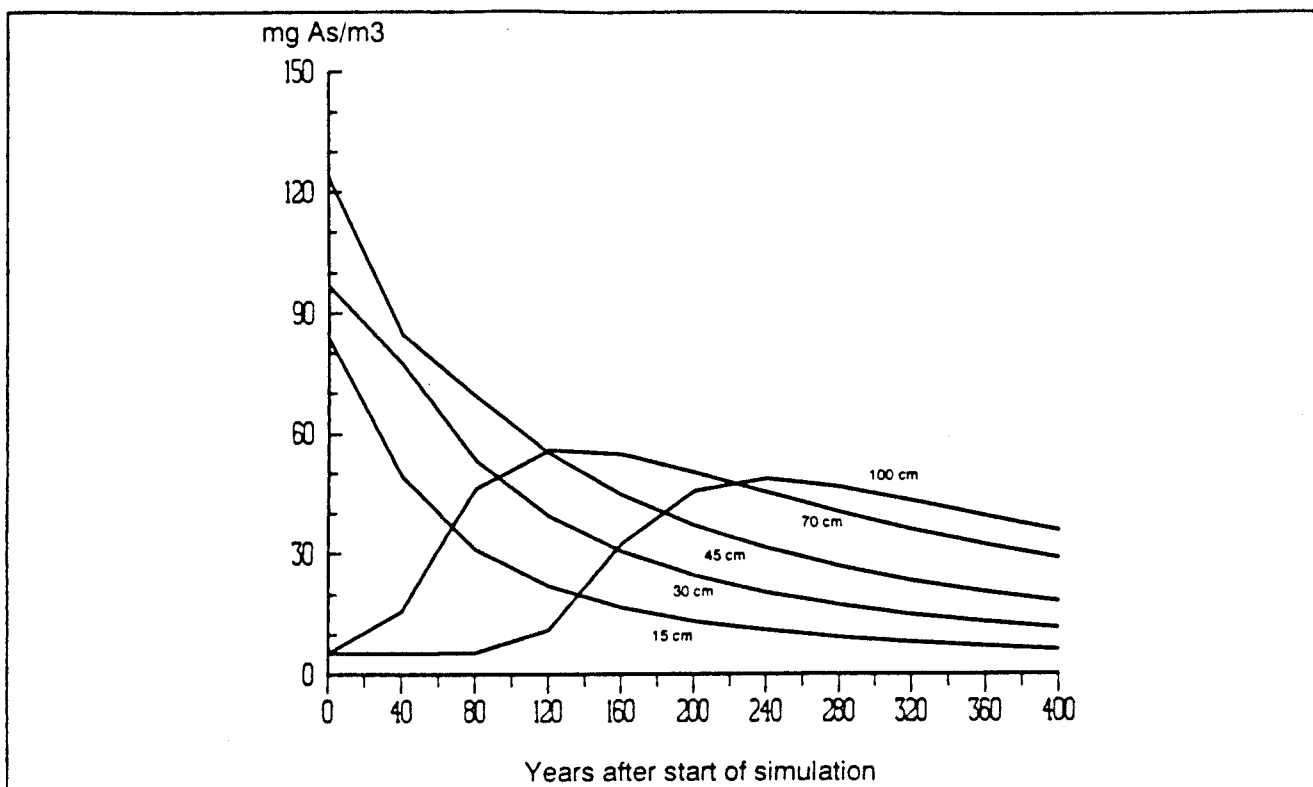
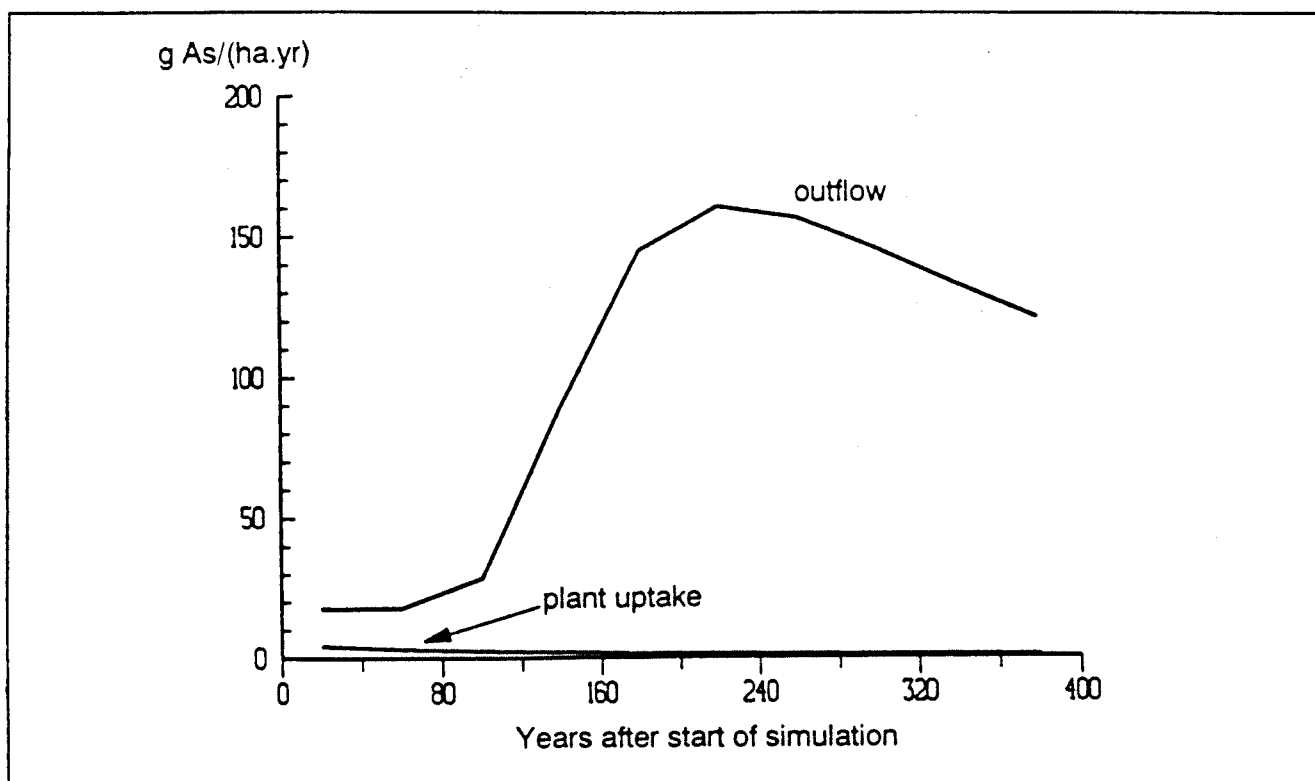


Figure 5. Calculated dissolved arsenic concentration at different depths.

Figure 6. Calculated flux of arsenic from the top metre of the soil.



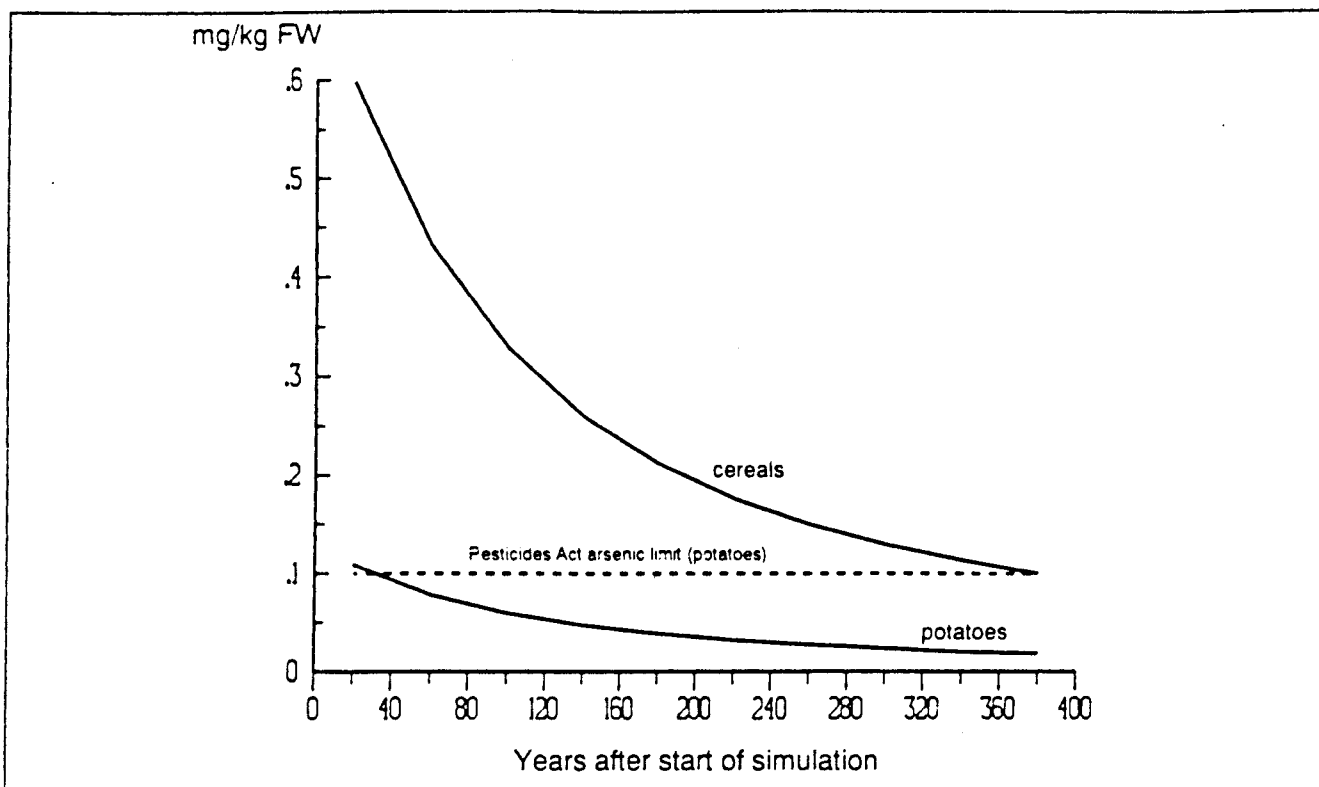


Figure 7. Calculated development of arsenic concentration in crops.

REFERENCES

- Asher C.J. and P.F. Reay (1979). Arsenic uptake by barley seedlings. *Aust. J. Plant Physiol.* 6: 459-466.
- Brii, J. (1993). The behavior of arsenic in contaminated agricultural soils, in prep.
- Bundesgesundheitsamt (1977). Richtwerte 1976 über Arsen-, Blei-, Cadmium- und Quecksilbergehalte in Lebensmitteln. *Bundesgesundheitsblatt* 20, p. 76. (in German).
- CBS (Centraal Bureau voor de Statistiek) (1992). *Statistisch jaarboek 1992*. CBS-publikaties, SDU uitgeverij, 's-Gravenhage, the Netherlands (in Dutch).
- Crank, J. (1975). *The mathematics of diffusion*, 2nd edition. Oxford Science Publications, Clarendon Press, Oxford (UK)
- Dolman, H. (1981). Milieukundige evaluatie van het arseniet-gebruik in de landbouw. Rapport van de biologiewinkel Groningen, No. 2 (In Dutch).
- Frissel, M.J. and P. Reiniger (1974). Simulation of accumulation and leaching in soils. Centre Agric. Publ. and Documentation (PUDOC), Wageningen (the Netherlands)
- Henkens, C.H., and K.W. Smilde (1989). Opnemng en accumulatie van zware metalen door planten. In: *Handboek voor milieubeheer: Deel 4: Bodembescherming*. Uitg. Vermande, IJmuiden, GG5200, pp. 1-22 (in Dutch)
- Huang, P.M., M.K. Wang, M.H. Wu, C.L. Liu and T.S.C. Wang (1977). Sesquioxidic components of selected Taiwan soils. *Geoderma*, 18: 251-263.
- Jacobs, L.W., J.K. Syers and D.R. Keeney (1970). Arsenic sorption by soils. *Soil Sci. Soc. Am. Proc.* 34: 750-754.
- Livesey, N.T. and P.M. Huang (1981). Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *Soil Science* 131: 88-94.
- Loch, J.P.G. (1982). Uitspoelbaarheid van arseen uit de bodem na toepassing van de aardappelloofdoder natriumarseniet. Rijksinst. voor drinkwatervoorziening (RID), rapport CBH 82-260 (In Dutch).
- Patankar, S.V. (1980). *Numerical Heat Transfer and Fluid Flow*. Hemisphere Publishing Corp., New York.
- Press, W.H., B.P. Flannery, S.A. Teukolsky and W.T. Vetterling (1986). *Numerical Recipes, The Art of Scientific Computing*. Cambridge University Press, Cambridge.
- Schwertmann, U. (1964). The differentiation of iron oxide in soil by a photochemical extraction with acid ammoniumoxalate. *Z. Pflanzenernaehr. Bodenk.* 105: 194-201.
- Slooff, W., B.J.A. Haring, J.M. Hesse, J.A. Janus and R. Thomas (ed.) (1990). *Integrated criteria document arsenic*. National Inst. for Public Health and Environ. Protection (RIVM), Bilthoven, the Netherlands, Report No. 710401004.
- Travis, C.C. and E.L. Etnier (1981). A survey of sorption relationships for reactive solutes in soil. *J. Environ. Qual.* 10: 8-17.
- Van Genuchten, M. Th., and P.J. Wierenga (1975). *Simulation of One-Dimensional Solute Transfer in Porous Media*. New Mexico State University, Bulletin Office, Las Cruces (NM 88003, USA)
- Waterleidingbesluit (1985). *Staatsblad* 345, 7 juni 1960, inclusief wijzigingen in werking getreden op 28 februari 1983, *Staatsblad* 41. (in Dutch)
- Wiersma, D., B.J. van Goor and N.G. van der Veen (1986). Cadmium, lead, mercury and arsenic concentrations in crops and corresponding soils in the Netherlands. *J. Agric. Food Chem.* 34: 1067-1074
- Woolson, E.A., J.H. Axley and P.C. Keamey (1971). The chemistry and phytotoxicity of arsenic in soils: I: Contaminated field soils. *Soil Sci. Soc. Am. Proc.* 35: 938-943.