Quality of Groundwater, **Proceedings of an International Symposium, Noordwijkerhout, The Netherlands, 23–27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.),**
***Studies in Environmental Science*, Volume 17**

© Elsevier Scientific Publishing Company — Printed in The Netherlands

COMPUTER SIMULATION OF LEACHING OF ALDICARB RESIDUES FROM ARABLE SOILS IN WINTER

M. LEISTRA and J.H. SMELT
Institute for Pesticide Research, Marijkeweg 22, 6709 PG Wageningen, the Netherlands

ABSTRACT

A computer model was used to simulate the movement and conversion in soils of two biologically active oxidation products of aldicarb, its sulfoxide and its sulfone. Basic data on these compounds, as measured in the laboratory, were introduced into the computations. Starting points were the moisture profiles and concentration patterns in soil measured in a field experiment with columns of grassed soils 0.8 or 1.0 m long in the autumn, 165 d after application of aldicarb in spring. Weather data and soil characteristics were introduced as measured or estimated in the same experiment.

The amounts of percolation water simulated to flow from the soil systems during the winter period with 470 mm of precipitation were mostly somewhat lower than measured. The shape of the effluent curves for the sulfoxide and sulfone were fairly well described by the computations, as were the concentration patterns remaining in the lower part of loam soil columns. Cumulative leaching of sulfoxide plus sulfone from the two loam soil systems 1.0 m long was simulated to be 1.9 and 1.5% of the dosage, respectively, which was in the range of values measured in the experiment. Leaching from the humic sand soil 0.8 m long was simulated to be 17% of the dosage, whereas measured leaching ranged from 10 to 16% of the dosage.

INTRODUCTION

When the insecticide and nematicide aldicarb [2-methyl-2-(methylthio)propionaldehyde O-methylcarbamoyl oxime] is applied to arable soil in spring, residues of its biologically active oxidation products sulfoxide and sulfone may still be present in the soil in autumn (ref. 1). At the end of October (165 days after application), the amount of sulfoxide plus sulfone corresponded to 6, 7, and 19% of the dosage for grassed columns of two loam soils and a humic sand soil, respectively (ref. 2). The residues were largely retained in the upper 30 cm of the soils. The behavior of aldicarb and its oxidation products in grassed soils in the summer period was simulated with a computation model and the computed concentration patterns were similar to the measured patterns (ref. 3).

The two oxidation products of aldicarb are only weakly adsorbed onto soils (ref. 4) and may thus move to deeper soil layers with precipitation surplus in winter. Aldicarb sulfoxide and sulfone were recently measured in the winter leachate from grassed soil columns (0.8 or 1.0 m long) under field conditions (ref. 2). It would be useful if leaching under field conditions could be simulated with a computer model, which could then be used for quick evaluation of the extent to which pesticidal compounds may be leached under diverse conditions in winter.

A computer model described by Leistra and Smelt (ref. 3) was used to simulate movement and conversion of the oxidation products of aldicarb in three soils in winter. Basic parameters and relationships for the compounds, as measured in the laboratory, were introduced into the computations. Data on weather conditions were collected and soil characteristics were measured or estimated. The results of the computations were compared with the effluent curves and concentration patterns in soil measured in the experiment by Smelt et al. (ref. 2).

PROCEDURES

Soil and weather

Three soil systems were considered, corresponding to Westmaas loam soil, Wierum loam soil and Vortum-Mullem humic sand soil, respectively. The composition and various chemical characteristics of these soils have been given before (ref. 2). The soil systems were divided into two layers for hydraulic characteristics. The moisture retention curves and the relationships between hydraulic conductivity and volume fraction of liquid have been given by Leistra and Smelt (ref. 3).

The volume fraction of moisture ε_1 at the beginning of the computations was introduced as measured in grassed soil columns dug out on 26 October 1979 (ref. 2). In the Westmaas and Wierum loam soil systems it ranged from about 0.17 m^3/m^3 at the top to about 0.30 m^3/m^3 at the bottom. Initially, in the Vortum-Mullem soil system, it decreased from 0.05 m^3/m^3 in the top layer to 0.02 m^3/m^3 around 0.5 m depth and below that increased to 0.07 m^3/m^3 at the bottom. The volumic masses (bulk densities) of the soils, as described (ref. 3), were introduced as a function of depth.

Precipitation was measured daily at the meteorological station near the site where the columns were dug into the soil. The rim of the rain gage (diam. 23 cm) was 40 cm above the soil surface. Besides, precipitation over periods of about a week was measured with tubes of inner diameter 12 cm dug into the soil with their rims 1 cm above the surface. One of the tubes was covered with gravel and the other was left open. The amounts of rainfall measured with the tubes were divided into daily amounts in proportion to the daily amounts measured with the rain gage. Daily precipitation derived for the open tube (one of the patterns introduced into the computations) is shown in Fig. 1, together with cumulative amounts for open tube, gravel-covered tube and rain gage. The differences in measured precipitation were substantial and were presumably caused by differences in aerodynamic conditions on a micro-scale. The greatest deviations were found for periods with snow and stormy wind.

Evaporation from a water surface calculated by Penman's method for the De Bilt weather station has been reported by KNMI (ref. 5) and cumulative evaporation is represented in Fig. 1. Transpiration by the grass was assumed to equal this evaporation, so the cumulative amount of transpiration was 87 mm. Interception and evaporation from the soil were neglected. Relative root activity was introduced as a function of depth, as described for the end of the growing season (ref. 3). Maximum rooting depth was 1.0 m in the loam soil systems and 0.6 m in the humic sand soil system.

Movement and conversion of the substances

The concentration patterns of aldicarb sulfoxide and aldicarb sulfone measured in the grassed soil columns at the end of October 1979 (ref. 2) were introduced as initial distributions in the computations. Aldicarb itself was completely

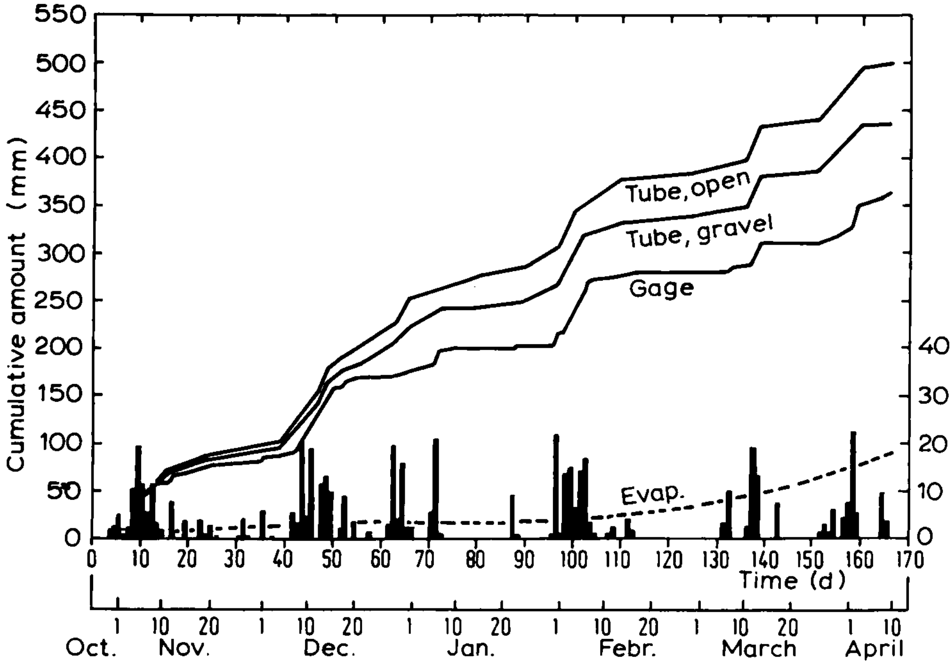

Fig. 1. Cumulative amounts of rainfall measured with a rain gage, a gravel-covered tube and an open tube. Daily amounts of rainfall derived for the open tube. Cumulative evaporation from a water surface.

converted in autumn, so it could be ignored. For a few layers, only total residues were available and these were partitioned between sulfoxide and sulfone according to their ratio in the other layers. The vast majority of the residue was in the layer 10 - 20 cm for loam. In the humic sand, most residue was in the upper 30 cm, though comparatively low concentrations had penetrated to depths around 60 cm.

The differential equations, parameters and relationships used for describing adsorption and movement of the substances in the soil systems have been given by Leistra and Smelt (ref. 3).

Temperature measurements were available for depth 15 and 40 cm (ref. 2). A representative temperature-time relationship was introduced into the computations by specifying 35 points (taking the movement of the concentration patterns into account) and by interpolating linearly between these points. The rate coefficients for conversion of sulfoxide and sulfone used in the computations and their dependence on soil temperature, moisture pressure and depth in the soil have been described (ref. 3). The submodel and parameters for uptake of the substances by the crop are given in the same paper.

Design of the computer program

The lengths of the soil systems were 1.0 m for the loam soils and 0.8 m for the humic sand soil. The systems were divided into computation compartments almost 4 cm thick, which gave 26 compartments for the loam soil systems and 21 compartments for the humic sand soil system, including a sand filter at the base. The set of differential equations, the parameters and the relationships were programmed in the computer language CSMP III (ref. 6). The rate equations were integrated numerically by Euler's method for time intervals $\Delta \underline{t}$ of 0.01 d. Further details of the computations have been given before (ref. 3) and a copy of the computer program is available on request.

RESULTS AND DISCUSSION

Measured and computed water percolation

The percolation of water measured for the three columns of each of the three soils is given in Fig. 2. The percolation started in December when the soils were sufficiently wetted by rainfall. The cumulative amounts of percolation in the beginning of April varied from 180 to 347 mm. Water percolation from the columns in poly(methylacrylate) tubes was distinctly greater than that from the columns in steel tubes. This difference was possibly caused by the position of the columns at the site. The poly(methylacrylate) tubes were dug into the soil about 0.5 m from a trench covered with a fibre-glass roof at the level of the soil surface.

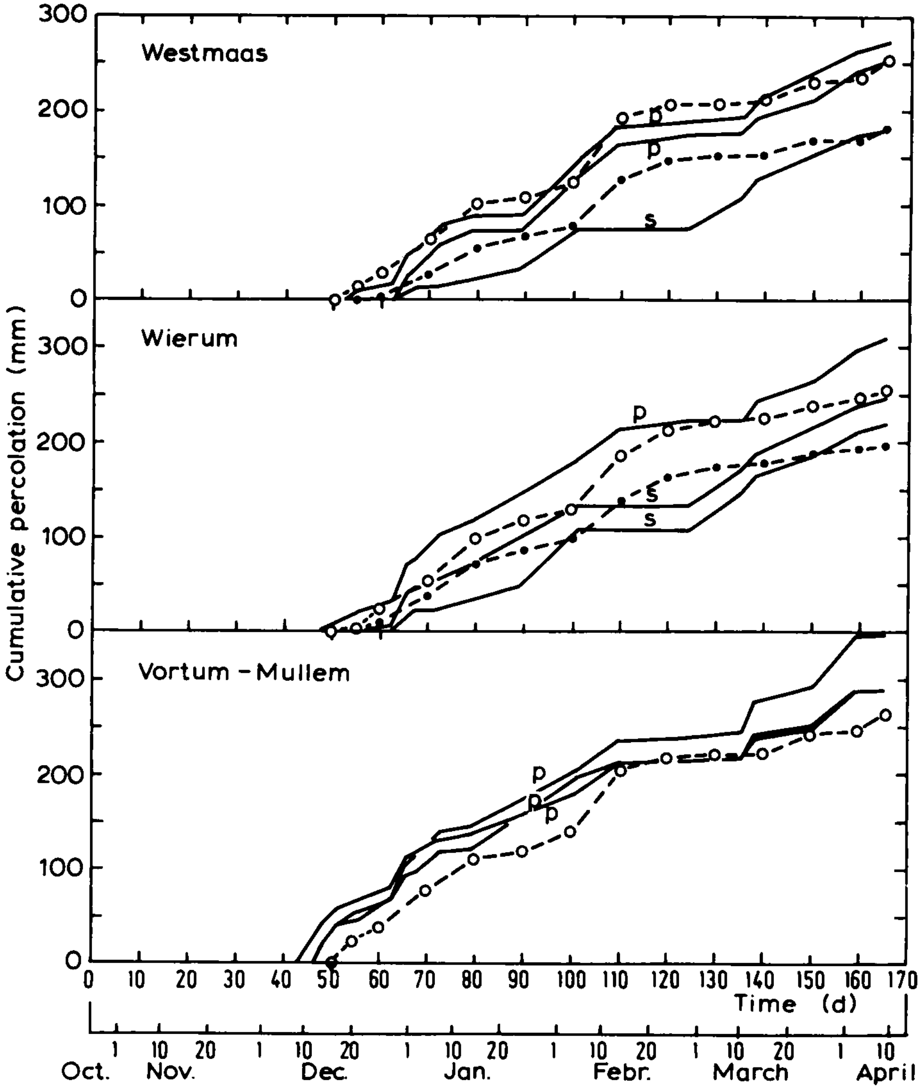

Fig. 2. Percolation of water measured for the soil columns in poly(methylacrylate) (p) and in steel (s) tubes. Water percolation computed with the precipitation patterns measured with open (o) and with gravel-covered (●) tubes.

The grassed surface beside this roof may have caught more precipitation (especially snow) than the grassed surface several meters from the roof where the steel columns were placed.

Water percolation computed for the soil systems is also shown in Fig. 2. Percolation computed with the precipitation pattern derived from open-tube measurements roughly corresponded with that measured for poly(methylacrylate) tubes. Introduction of the pattern derived from the gravel-covered tube gave computed amounts of percolating water that roughly correspond to those measured for the steel tubes. The percolation computed for February was greater than measured, especially for the loam soil systems, whereas in the month March/April computed percolation was comparatively low. The percolation computed for the Vortum-Mullem soil was lower than measured, though the position of the open tube and the soil columns in relation to the trench was the same. Precipitation patterns for the open tube and gravel-covered tube were used in the computations on the movement of the oxidation products in the soil systems. The volume fractions of liquid in the soil systems computed for the end of the period were slightly higher than those measured in the corresponding soil columns in the beginning of April 1980.

Behavior of the substances

The concentrations of aldicarb sulfoxide and sulfone in fractions of the effluent and in layers of the soil columns, as measured (ref. 2) are represented in Fig. 3 to 7 as block diagrams. For many fractions and layers, the oxidation products were measured separately, whereas for the others they were measured as total residue.

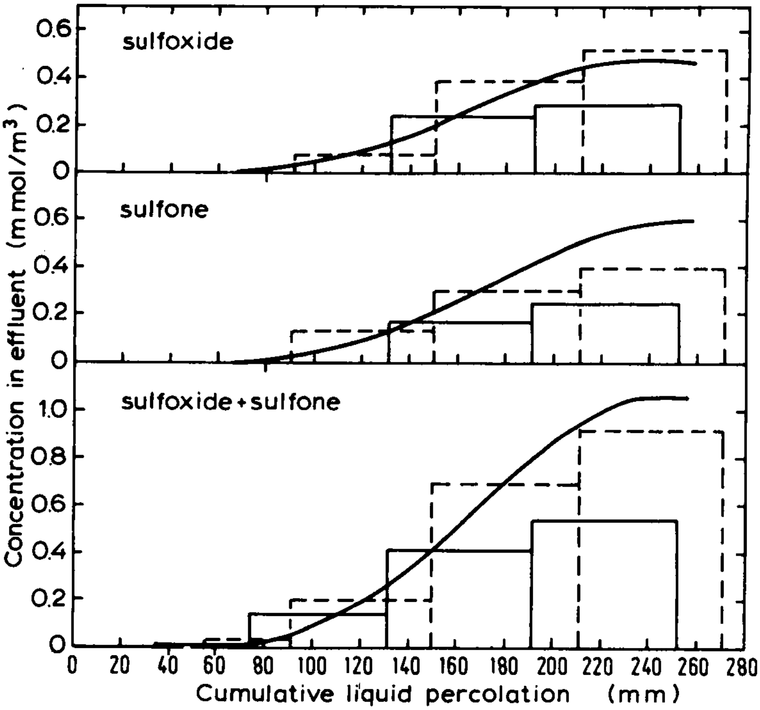

Fig. 3. Concentrations of aldicarb sulfoxide and sulfone in effluent from columns 1 m long of Westmaas loam soil during the winter of 1979/1980. Blocks in solid and broken lines represent duplicate columns in poly(methylacrylate) tubes; smooth line, computer simulated with the precipitation data from open tube.

Test runs with the computer model, using a dispersion length parameter $\underline{L}_d$ = 0.01 m, resulted in a small spread in the concentrations and in the effluent curves with respect to measured spread. The $\underline{L}_d$ used was increased to 0.02 m for the loam soil systems and to 0.03 m for the humic sand soil system. These values are within the range reported for leaching studies in columns in the laboratory (ref. 7).

The concentrations of aldicarb sulfoxide and sulfone computed for the effluent of the Westmaas loam soil system are represented in Fig. 3. Both the measured and simulated percolation of the substances starts low fairly soon after the start of percolation. The shape of the breakthrough curves is fairly well described by computer simulation. However the concentration of aldicarb sulfone in the last effluent fractions is distinctly overestimated by the model.

The concentrations computed to remain in the Westmaas loam soil at the beginning of April 1980 are given in Fig. 4. Computed movement seemed to be greater than measured. The concentration of sulfoxide in liquid phase, $\underline{c}_1$, as calculated from the measurements for the bottom layer was 0.47 mmol/m^3 on the average. Comparison with $\underline{c}_1$ measured in the effluent (Fig. 3) shows that the peak of the measured sulfoxide distribution was around the filter part, so the difference between computed and measured position of the peak was small. The concentration of sulfone measured in the bottom layer corresponds to a $\underline{c}_1$ of 0.58 mmol/m^3, which implies that the peak of the measured sulfone distribution was still in the layer

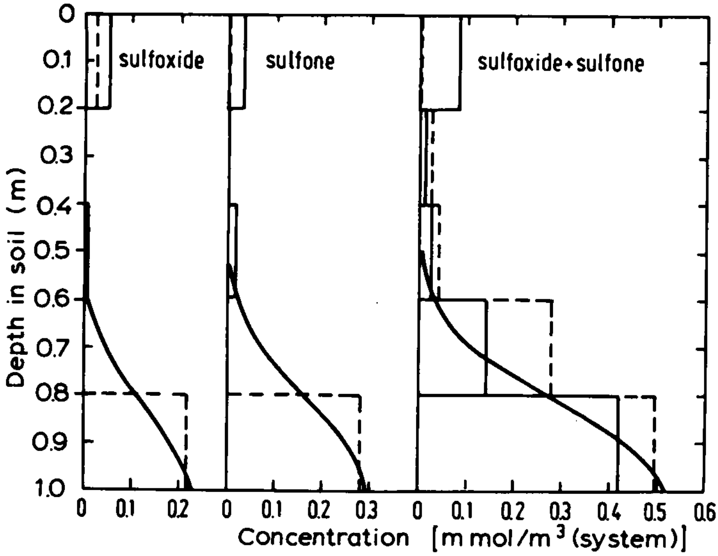

Fig. 4. Concentrations of aldicarb sulfoxide and sulfone in Westmaas loam soil in poly(methylacrylate) tubes in April 1980, about 11 months after application of aldicarb in May 1979. Blocks in solid and broken lines represent duplicate soil columns; smooth line, computer simulated with the precipitation data from open tube.

0.8 to 1.0 m. The movement of sulfone was thus somewhat overestimated by the model. Low concentrations of the oxidation products were measured to be retained in the top layers of the columns. This retention was not simulated with the present model.

The concentrations in the effluent computed for the Wierum soil system are represented in Fig. 5. Leaching of the substances was computed to start after about 50 mm of water had percolated. In the corresponding experiment, very low residues were already found in the first effluent fraction from one of the columns. After an initial period, the computed concentrations of both sulfoxide and sulfone were higher than measured. The difference between the computed and measured effluent curves was presumably exaggerated by underestimation of the conversion rates of sulfoxide and sulfone in this soil.

The concentrations computed for the Wierum loam soil system at the beginning

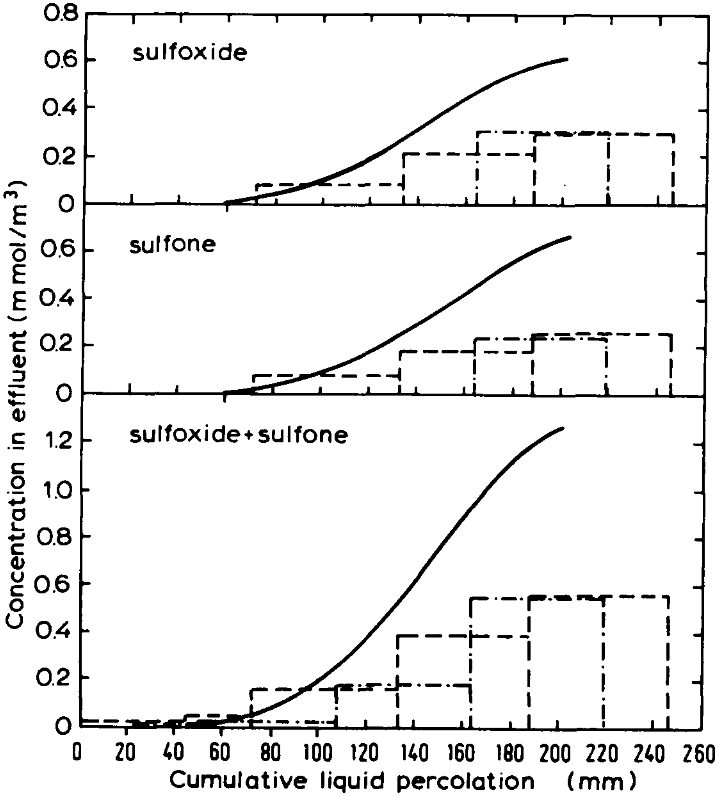

Fig. 5. Concentrations of aldicarb sulfoxide and sulfone in effluent from columns 1 m long of Wierum loam soil in steel tubes during the winter of 1979/1980. Blocks in solid and broken lines represent duplicate soil columns; smooth line, computer simulated with precipitation data from covered tube.

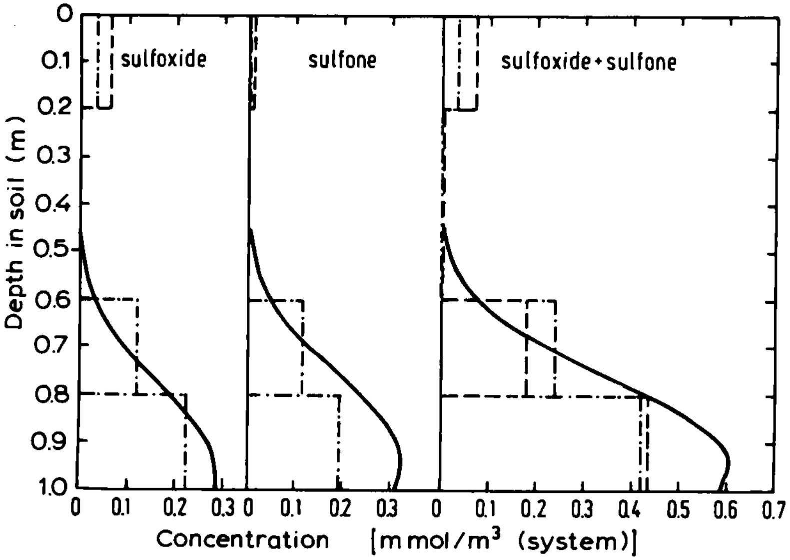

Fig. 6. Concentrations of aldicarb sulfoxide and sulfone in columns of Wierum loam soil in steel tubes in April 1980, about 11 months after application of aldicarb in May 1979. Blocks in solid and broken lines represent duplicate soil columns; smooth line, computer simulated with precipitation data from covered tube.

of April 1980 are shown in Fig. 6. The concentrations of the sulfone were overestimated in the lower layers. The measured concentrations of sulfoxide and sulfone in the liquid phase of the bottom layer corresponded to 0.51 and 0.43 mmol/m^3, respectively. Comparison of these concentrations with the effluent concentrations shows that the peaks of the measured sulfoxide and sulfone were still in the layer 0.8 to 1.0 m. The computed movement was somewhat greater with the peaks near the lower end. Again, retention of comparatively low concentrations of the oxidation products in the upper 0.2 m was measured but not simulated.

The computed concentrations of aldicarb sulfoxide and sulfone in the effluent from the Vortum-Mullem humic sand soil system are shown in Fig. 7. According to computation the substances should already appear at the start of percolation. In the experiment, the substances were indeed found in the first effluent fraction, for one of the columns, even in fairly high concentration. The computed position of the peak of the effluent curves corresponds fairly well with the position of the peaks measured for two of the columns. For the third column, the measured position of the peak was behind the computed one. The strong tailing in the measured effluent curves is only partly described by the computer model.

Computed material balances

The material balance for the Westmaas loam soil system (open-tube precipitation)

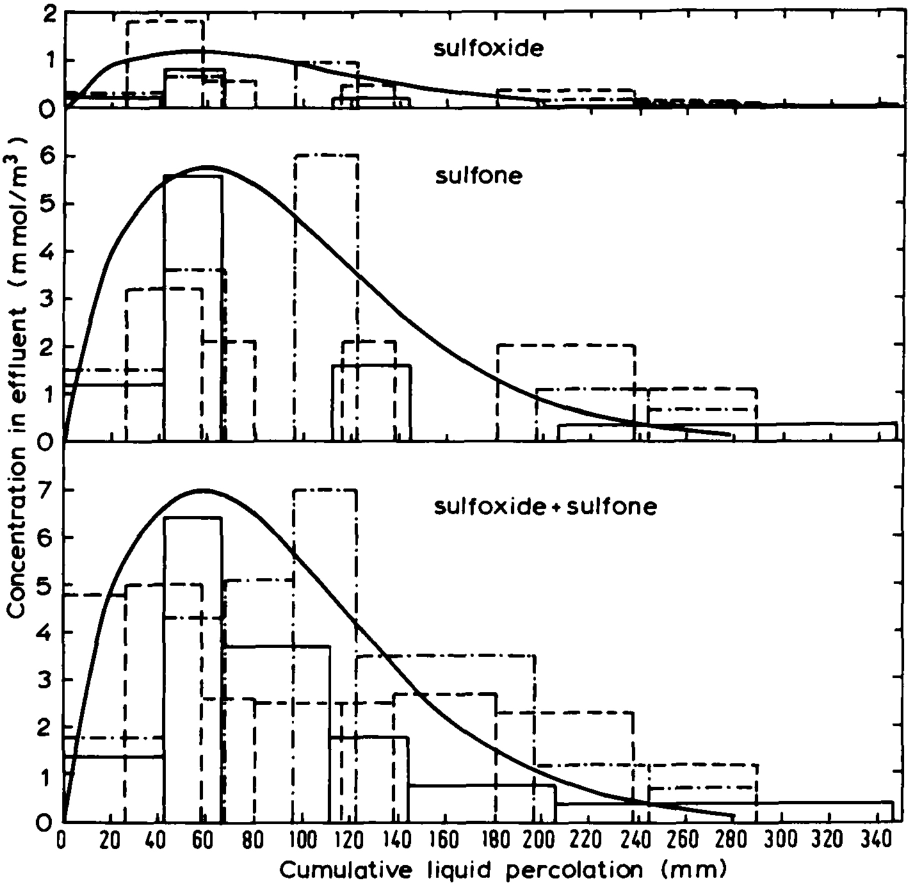

Fig. 7. Concentrations of aldicarb sulfoxide and sulfone in the effluent from columns 0.8 m long of Vortum-Mullem humic sand soil during the winter of 1979/1980. Blocks in solid and broken lines represent triplicate columns; smooth line, computer simulated with precipitation data from open tube.

in the winter 1979/1980 was computed and the items are expressed as percentage of the dosage of aldicarb applied in May 1979, which was 5.24 mmol/m^2 (about 10 kg/ha) At the start of the computation (26 October 1979), 6.0% of the dosage (on average) was present as sulfoxide (3.2%) plus sulfone (2.7%). The items of the material balance for sulfoxide plus sulfone computed for the winter up to 9 April 1980 were: left in soil, 2.4%; converted in soil, 1.5% taken up by plants, 0.1%; and leached from the soil, 1.9% of the dosage. The measured leaching ranged from 0.5 to 2.0% of the dosage (ref. 2).

At the end of October 1979, 6.9% of the dosage (on average) was present in the Wierum loam soil as sulfoxide plus sulfone. The items of the material balance over the winter computed for this system with the covered-tube precipitation pattern was: left in soil, 3.4%; converted in soil, 1.8%; taken up by plants, 0.2%; and leached from soil, 1.5% of the dosage. Smelt et al. (ref. 2) found that leaching from the corresponding soil columns ranged from 0.8 to 2.2% of the dosage.

In October 1979, the Vortum-Mullem humic sand soil contained a comparatively large amount of sulfoxide plus sulfone: 18.4% of the dosage (on average). According to the computations, only 0.2% was left in the soil system in April 1980, while 1.1% was converted in soil in winter and 0.5% was taken up by the plants. Computed leaching from the soil was 16.6% of the dosage, 2.8% as sulfoxide and 13.8% as sulfone. This was somewhat more than the measured leaching that ranged from 10 to 16% of the dosage for three columns (ref. 2).

The basic data on the conversion kinetics of the substances used in the computations were taken from laboratory studies with other soils, albeit related ones, so some deviation between computed and measured amounts would be expected.

GENERAL DISCUSSION

The movement of weakly adsorbed pesticidal substances in soil, resulting from the precipitation surplus in a winter period, could be reasonably well described with a standard computer model. Both measurements and computations indicated that much of the residue still present in autumn was leached down to depths of 1 to 2 m with about 450 mm of precipitation in winter.

The items of the water balance in the field must be measured or estimated as accurately as possible. Unfortunately, under the winter conditions in this study, an unambiguous precipitation pattern could not be obtained from direct measurements. Measuring water percolation in combination with the initial and final soil moisture profiles provided a check on the correctness of the precipitation data introduced into the computations.

The movement of the substances could be fairly well simulated with the standard convection-dispersion type description, using normal values of dispersion length. There seemed to be a fair degree of equilibration between the concentrations in fractions of the liquid phase and in the adsorbing phase, especially in the loam soils. The somewhat stronger tailing measured for the humic sand soil suggested that uneven water flow had some effect.

Residues of leached pesticidal substances often remain for several months at depths of about 1 to 2 m, so it would be useful to know more about conversion rates at those depths. The measured conversion rates of aldicarb sulfoxide and sulfone became lower with increasing depth in the aerobic zone of a loam soil and of a peaty sand soil (refs. 8-9). However further information on the conversion rate in various subsoils, part of them being water-saturated and deficient in oxygen, is urgently needed.

REFERENCES

1 J.H. Smelt, C.J. Schut, A. Dekker and M. Leistra, Neth. J. Plant Pathol. (1981a) (submitted).
2 J.H. Smelt, C.J. Schut and M. Leistra, J. Environ. Qual (1981b) (submitted).
3 M. Leistra and J.H. Smelt, J. Environ. Qual. (1981) (submitted).
4 R.H. Bromilow, R.J. Baker, M.A.H. Freeman and K. Görög, Pestic. Sci. 11(1980)371-378.
5 KNMI, Maandelijks overzicht der weersgesteldheid. Royal Netherlands Meteorological Institute, De Bilt, 1979, 1980.
6 IBM, Continuous system modeling program III (CSMP III). Program Reference Manual, Program No 5734-XS9. Data Processing Division, White Plains, N.Y., 1975.
7 M.J. Frissel, P. Poelstra and P. Reiniger, Plant Soil 33(1970)161-176.
8 J.H. Smelt, M. Leistra, N.W.H. Houx and A. Dekker, Pestic. Sci. 9(1978a)279-285.
9 J.H. Smelt, M. Leistra, N.W.H. Houx and A. Dekker, Pestic. Sci. 9(1978b)286-292.