Bioavailability of organic chemicals in soil related to their concentration in the liquid phase

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ABSTRACT

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Available data in the literature were tested against the hypothesis that bioavailability of organic chemicals is a function of the concentration of the dissolved chemical in the liquid phase in soil. In the order of ten studies on uptake or on effects of organic chemicals supported the hypothesis qualitatively; in these tests the concentration was estimated. Quantitative tests in which the concentration was measured directly, were not available. A theoretical analysis showed that the amount of chemical sorbed to dissolved organic matter is negligibly small as compared to the amount sorbed to organic matter present in the solid phase.

Keywords: review, bioavailability, organic chemicals, herbicides, soil, dissolved organic matter, sorption, uptake, effects

CONTENTS

PREFACE

SUMMARY

Bioavailability of organic chemicals in soil is important for assessment of the significance of soil contamination with these chemicals. This study is based on the hypothesis that bioavailability of organic chemicals is a function of the concentration of the dissolved chemical in the liquid phase in soil.

Available methods for estimating the concentration of the dissolved chemical in the liquid phase in soil are reviewed. This concentration is mainly controlled by the coefficient for sorption to the solid phase in soil (for chemicals that are not highly volatile). If the sorption coefficient for a given chemical/soil combination is estimated from literature data on adsorption of the chemical by other soils, the uncertainty in the estimated concentration in the liquid phase of fresh soil residues of the chemical can be a factor 10. Moreover, desorption coefficients measured with aged soil residues may be one to two orders of magnitude higher than expected from short-term adsorption experiments. Because of these uncertainties in estimating the concentration in the liquid phase, it is recommended to measure it directly in studies aimed at testing the bioavailability hypothesis.

On the basis of literature data and a theoretical analysis it is shown that the contribution of the sorption to dissolved organic matter is always negligible as compared to the contribution of bulk organic matter, the main reason being that the amount of bulk organic matter in soil is about 10 000 times as large as the amount of dissolved organic matter.

In the order of ten studies on uptake or on effects of organic chemicals (most with herbicide/plant systems, a few with chlorophenol/earthworm systems) supported the hypothesis qualitatively. Three quantitative tests for herbicide plant/systems showed variable results (effects at too high and too low concentration levels in the first and second test, respectively and good correspondence in the third test). However, in these three tests the concentration in the liquid phase was not measured directly but estimated. This may have been the cause of the discrepancies.

Although existing experimental evidence seems to support our hypothesis, it is not yet conclusive: accurate quantitative tests are not available and almost all experiments have been carried out with herbicide/plant systems. However, it is clear that bioavailability may be reduced strongly as a result of sorption to the solid phase. Further tests of the hypothesis are needed in which the concentration of the dissolved chemical in the liquid phase should be measured directly to eliminate the errors in estimating this concentration.

1 INTRODUCTION

The aim of this study is to relate data in the literature on bioavailability of organic chemicals in soil to the concentration of organic chemical in the liquid phase. We start from the hypothesis that bioavailability of organic chemicals is a function of the concentration of the dissolved chemical in the liquid phase in soil (Graham-Bryce, 1968; Van Gestel & Ma, 1990). In this context "dissolved" indicates that individual molecules are present in the liquid phase and not bound to dissolved organic matter. The rationale of this hypothesis is that only dissolved molecules can easily pass biological membranes.

Contamination of soils with toxic organic chemicals is a major environmental problem. Bioavailability of organic chemicals in soil is important for assessment of the significance of soil contamination with these chemicals for various reasons. For instance, bioavailability influences effects of organic chemicals on plants and soil organisms and it influences residue levels of organic chemicals in edible crops (via its influence on the uptake of these chemicals). Moreover, bioavailability influences the rate of transformation of the organic chemicals by soil microorganisms which may be important for the decontamination of the soil. It is therefore relevant to consider which factors determine bioavailability.

Firstly, available methods for estimating the concentration of the dissolved chemical in the liquid phase are briefly reviewed (in Section 2) because this is the essential quantity in our hypothesis which has to be assessed in any study considered. Thereafter (in Section 3) a review is given of data sets in which availability to plants and soil organisms is related to this concentration. The review is restricted to data sets which can be used to test our hypothesis.

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2 ESTIMATING THE CONCENTRATION IN THE LIQUID PHASE

2.1 Equilibrium concepts

Let us consider a system that consists of moist soil which contains a given organic chemical. In soil contamination studies usually the extent of contamination is described in terms of the content of organic chemical in the soil. This content (to be denoted as m_t) is defined as the mass of organic chemical in the system divided by the mass of dry soil in the system (M M^{-1}). After the introduction of a quantity we give its dimension expressed in M and/or L and/or T (M is mass, L is length and T is time). The mass of organic chemical is usually assessed by organic solvent extraction followed by chemical analysis of the extract. We assume that m_t is known. So our aim is now to estimate the concentration of the dissolved chemical in the liquid phase from a known m_t value.

We assume that the organic chemical is present in four forms in the system: dissolved in the liquid phase, sorbed to dissolved organic matter (DOM) in the liquid phase, sorbed to the solid phase in soil and present in the gas phase. The mass balance equation for the system is then given by:

$$m_t = W\,c_1 + W\,O\,X_{DOM} + X_s + G\,c_g \tag{1}$$

where W is the volume of liquid phase divided by the mass of solid phase ($L^3\,M^{-1}$) to be denoted as massic volume of liquid (using the nomenclature for derived quantities proposed by Rigg et al., 1985), c_1 is the concentration of dissolved organic chemical in the liquid phase (M L^{-3}), O is the concentration of DOM in the liquid phase (M L^{-3}), X_{DOM} is the content of organic chemical sorbed to DOM (defined as the mass of organic chemical sorbed to DOM divided by the mass of DOM and with dimension M M^{-1}), X_s is the content of organic chemical sorbed to the solid phase (M M^{-1}), G is the volume of gas divided by the mass of solid phase ($L^3\,M^{-1}$) to be denoted as massic volume of gas and c_g is the concentration of organic chemical in the gas phase (M L^{-3}).

We assume (as a first approximation) that sorption to the solid phase and to the DOM can be described with linear sorption isotherms:

$$X_{DOM} = K_{DOM}\,c_1 \tag{2}$$

$$X_s = K_s\,c_1 \tag{3}$$

where K_{DOM} and K_s are the sorption coefficients ($L^3\,M^{-1}$) for the DOM and the solid phase. For nonionic organic chemicals it may be assumed as a first approximation that K_s is proportional to organic matter (see, for instance, review by Gerstl, 1990). Eqn 3 may then be rewritten as

$$X_s = f\,K_{OM}\,c_1 \tag{4}$$

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where f is the mass fraction of organic matter in the soil (M M^{-1}) and K_{OM} is the organic-matter/water distribution ratio (L^3 M^{-1}), describing the sorption to soil organic matter in the solid phase (referred to as bulk organic matter; abbreviated BOM).

We assume that the partitioning of the chemical between the gas and liquid phases can be described by Henry's law:

$$c_g = K_H c_l \tag{5}$$

where K_H is the dimensionless Henry's law constant (Suntio et al.,1988).

Eqn 1 may then be rewritten as:

$$m_r = Q c_l \tag{6}$$

where Q is defined by

$$Q = W + W O K_{DOM} + K_s + G K_H \tag{7}$$

According to our hypothesis, only the concentration of the dissolved chemical in the liquid phase determines the effect on soil organisms. Therefore it is relevant to define the fraction (F) of m_r that is dissolved in the liquid phase:

$$F = W c_l / m_r \tag{8}$$

Using Eqns 6 and 7 then gives:

$$F = 1 / [1 + O K_{DOM} + K_s/W + (G/W) K_H] \tag{9}$$

2.2 Estimation of partition coefficients

Following the approach in the preceding paragraph we need to estimate the partition coefficients K_{DOM}, K_s and K_H in order to estimate c_l from m_r (see Eqns 6 and 7).

First we consider K_{DOM}. Because only little information is available on K_{DOM} we will try to relate it to K_{OM}. So we define the ratio, r, as

$$r = K_{DOM} / K_{OM} \tag{10}$$

Chiou et al. (1986) reported r values for DDT and 2,4,4'-PCB and fulvic acid extract from soil to range between 0.1 and 0.2.; for a humic acid extract from soil they found an r value of about 0.5. Lee & Farmer (1989) found for the herbicide napropamide and fulvic acid extracts from two soil types an r value of about 0.1; for soil humic acid extracts they found r values of 1.1 and 2. In conclusion, r values in the literature were found to range from 0.1 to 2.

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The coefficient describing partitioning over the gas and liquid phases, K_H, may be estimated from the ratio between saturated vapour pressure and water solubility (Suntio et al., 1988).

As described before, the sorption coefficient, K_s, may be estimated from the organic-matter/water distribution ratio, K_{OM}. If for a given compound no K_{OM} is available, K_{OM} may be estimated with methods based on water solubility, octanol/water partition coefficient or molecular connectivity indices (see, for instance, review by Gerstl, 1990). These methods are based on regression models that use measured K_{OM} values of different organic chemicals as input. However, the accuracy of these methods is generally low. As may be derived from data collected by Gerstl (1989) the uncertainty in any estimated K_{OM} can easily be a factor 10.

A further complication in estimating K_s is that the K_{OM} of a given compound is not constant for different soils. Gerstl (1990) showed for a number of compounds that K_{OM} values were log-normally distributed and that their variability was comparatively large. For example, he collected 216 K_{OM} values of atrazine and it may be derived from his data that the 95%-confidence interval of the K_{OM} of atrazine covers a range of a factor 10.

2.3 Kinetics of partitioning between the phases

In the previous section equilibrium was assumed for the partitioning of the chemical over the four phases in the system (liquid, gas, solid and DOM). We will now consider experimental information on the kinetics of the partitioning processes.

Partitioning over the liquid and gas phases proceeds rapidly: in the literature the time constant of the liquid/gas exchange process is reported to be in the order of 1 h or less (Brusseau et al., 1990; Cho & Jaffe, 1990). Consequently, instantaneous equilibration can be assumed in most estimates on the exposure of organisms in the soil to the chemical.

Little information is available on the kinetics of sorption of organic chemicals to DOM. Khan (1973) studied the kinetics of adsorption of 2,4-D and picloram to humic acids and found a rapid increase in the amount sorbed during the first 1.5 h followed by a slower increase up to 48 h. No information about sorption kinetics on a larger time scale is available so far.

Various studies are available on sorption kinetics of organic chemicals to the solid phase. From pesticide adsorption experiments with soil or sediment suspensions using equilibration periods between a few minutes and a few days, it may be derived that c_l decreases very rapidly during the first half hour or even the first few minutes. Thereafter the decrease in c_l levels off and a further decrease is difficult to measure (Hance, 1967; Kay & Elrick, 1967; Wauchope & Myers, 1985; Miller & Weber, 1986; White et al., 1986; Dao & Lavy, 1987; Boesten & Van der Pas, 1988). Based on this information, the sorption coefficient, K_s, is usually derived from experiments

in a soil suspension using equilibration periods between a few hours and a few days.

However, sorption experiments with moist soil that were continued for weeks, months or years, have shown that sorption does not reach equilibrium on a time scale of a few days but continues at a larger time scale (Boesten & Van der Pas, 1983; McCall & Agin, 1985; Steinberg et al., 1987; Walker, 1987; Pignatello, 1989; Lehmann et al., 1990; Pignatello & Huang, 1991). Boesten & Van der Pas (1983) found that desorption coefficients of 121-days-old field residues of cyanazine and metribuzin were 6 to 8 times as high as expected from short-term adsorption experiments. Steinberg et al. (1987) found that desorption coefficients of field residues of 1,2-dibromoethane that were 0.9 to 13 years old, were about 100 times as high as expected from short-term adsorption experiments. Walker (1987) found that desorption coefficients of 47-days-old residues of four herbicides were about two times as high as expected from short-term adsorption experiments. Pignatello (1989) found that the desorption coefficient of a 22-days-old residue of tetrachloroethene was about 30 times as high as expected from a short-term adsorption experiment. Lehmann et al. (1990) found that desorption coefficients of 203-days-old residues of fluroxypyr were 7 to 8 times as high as expected from short-term adsorption experiments. Pignatello & Huang (1991) found that desorption coefficients of 2- to 15-months-old residues of metolachlor and atrazine were 2 to 42 times as high as expected from short-term adsorption experiments.

Other evidence for slow sorption equilibration is given by the decrease in extractability of residues with organic solvents in time. Chiba & Morley (1968) found that the content of dieldrin extracted from a field soil varied about by a factor of three depending on extraction method and organic solvent employed. They also showed that all methods gave recoveries of 90-100% when applied 2 days after mixing dieldrin into the soils. Mattson et al. (1970) found that the content of atrazine extracted from a soil 284 days after application varied by about a factor of two, depending on the extraction method and organic solvent employed. If used at 1 day after application, probably all extraction methods would have resulted in recoveries of 90-100%. Smith (1981) found the same result for 1-year-old atrazine residues in three field soils.

Because sorption is not at equilibrium, there is much uncertainty in the estimation of c_1. It would be useful if sorption kinetics of organic chemicals in soil could be predicted by mathematical models. Karickhoff & Morris (1985) proposed a two-site model to describe sorption kinetics of nonionic organic chemicals in sediment suspensions. Their model can be rewritten as

$$X_1 = K_{s,1} \, c_1 \tag{11}$$

$$dX_2 / dt = k_2 \, (K_{s,2} \, c_1 - X_2) \tag{12}$$

where the subscripts 1 and 2 refer to class-1 and class-2 sites, respectively, where t is time (T) and where k_2 is the desorption rate constant for class-2 sites (T^{-1}). Boesten et al. (1989) showed that a three-site model was necessary to explain leaching behaviour of herbicides at a time scale of months. Assuming a linear

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sorption isotherm, the three-site model consists of Eqns 11 and 12 and a third equation for describing sorption at class-3 sites:

$$dX_3 \,/\, dt = k_3 \, (K_{s,3} \, c_1 - X_3) \tag{13}$$

where the subscript 3 refers to class-3 sites.

For moderately sorbing organic chemicals, class-1 sites equilibrate on a time scale of minutes; class-2 and class-3 sites equilibrate on time scales of hours/days and weeks/months, respectively. There is evidence that sorption at class-1 sites is completely reversible (Boesten & Van der Pas, 1988). Studies by Brusseau et al. (1991) indicate that the mechanism for sorption at class-2 sites is probably intraorganic-matter diffusion.

Wu & Gschwend (1986) proposed a diffusion model for sorption kinetics of organic chemicals in soil or sediments. They assumed that the soil or sediment consists of porous spherical particles in which Fickian diffusion takes place and in which sorption is at equilibrium according to a linear isotherm. Inputs to the kinetic part of the model are the measured particle size distribution and the effective intraparticle diffusion coefficient (D_{eff}).

We will now consider the ability of the available models to predict sorption kinetics for aged residues of organic chemicals in soil. We first consider the two-site model (Eqns 11 and 12). If we assume that the total sorption coefficient, K_s, is known, the model has two parameters, namely the ratio $K_{s,1}/K_s$ (or $K_{s,2}/K_s$) and the rate constant k_2. Karickhoff & Morris (1985) found that k_2 was inversely proportional to K_s. Brusseau & Rao (1989) analyzed existing data on sorption kinetics of hydrophobic organic chemicals in the literature and found that the relationship between k_2 and K_s could be described with the empirical equation

$$k_2 = a \, K_s^{-b} \tag{14}$$

with $b = 0.67$ and $a = 48$ d^{-1}(dm^3 kg^{-1})^b. However the data set used by Brusseau & Rao did not include results of desorption experiments with aged residues such as those carried out with 1,2-dibromoethane and tetrachloroethene by Steinberg et al. (1987) and Pignatello (1989). Using Eqn 14 k_2 values in the order of 10 d^{-1} are found for these two chemicals. Such k_2 values cannot explain the desorption coefficients of aged-residues observed by Steinberg et al. (1987) and Pignatello (1989) which were one or two orders of magnitude as high as expected from short-term adsorption experiments. These discrepancies indicate that a model with at least three sites is necessary to predict sorption kinetics of aged residues of organic chemicals in soil. Boesten (1987) showed that the ratio between the rate of desorption of class-3 sites and the rate of decrease of c_1 is a critical parameter for the prediction of sorption of aged residues. However, no methods are available so far to estimate parameter values for sorption kinetics at class-3 sites independently.

Wu & Gschwend (1986) applied their diffusion model to sorption kinetics of chlorobenzenes onto sediments and soils. The duration of their experiments was

between a few seconds and 7 days. They found that the effective intraparticle diffusion coefficient, D_{eff}, derived from fitting the model to the measurements, decreased from 10^{-9}-10^{-10} cm^2 s^{-1} for $K_s = 100$ dm^3 kg^{-1} to about 10^{-11} cm^2 s^{-1} for K_s = 10000 dm^3 kg^{-1}. In theory it would be possible to predict sorption kinetics for other systems using the relationship between D_{eff} and K_s found by Wu & Gschwend (1986). However, Steinberg et al. (1987) used the model developed by Wu & Gschwend to describe the results of their desorption experiments with aged residues of 1,2-dibromoethane and found D_{eff} values that were about 10^{10} times as low as expected from the D_{eff} values found by Wu & Gschwend (1986). These results indicate that D_{eff} values derived from the short-term experiments by Wu & Gschwend are not useful for predicting sorption kinetics of aged residues of organic chemicals in soils.

2.4 Discussion and conclusions

The information in the literature on the K_{DOM} / K_{OM} ratio (i.e. r) may be used for a first assessment of the significance of the contribution of sorption to DOM. Using $K_s = f K_{OM}$ and Eqn 10, Eqn 7 may be rewritten as:

$$Q = W + K_{OM} [r W O + f] + G K_H \tag{15}$$

Values of the concentration of DOM, O, are commonly in the order of 10 g m^{-3} (Lee & Farmer, 1989). The value of the massic volume of liquid, W, will usually be in the range 0.1-0.3 dm^3 kg^{-1}. As described in Section 2.2, r values found in the literature are in the range 0.1-2. So the product $r W O$ will be in the order of 10^{-7} or 10^{-6} which is orders of magnitude smaller than values to be expected for the mass fraction of organic matter, f, (a few per cent, so in the order of 10^{-2}). So in general we may expect that sorption to DOM is negligibly small as compared to sorption to BOM in soils.

It may be derived from Eqn 7 that the contribution of the gas phase to the content of organic chemical in the soil, m_r, will often be negligible: because G and W are in the same order of magnitude, K_H has to be larger than 0.1 in order to have a significant fraction of m_r in the gas phase. This is only the case for very volatile chemicals.

The assessment of the significance of the amount of organic chemical sorbed to DOM is only valid for the concentration in the liquid phase in an isolated soil layer. If we would have been interested in, for instance, leaching to ground water, transport of organic chemical molecules sorbed to DOM may significantly increase the amount moving downward because retardation of the molecules sorbed to DOM may be less than that of the molecules dissolved in the liquid phase (see, for instance, Magee et al., 1991).

It may be concluded that partitioning between the solid and liquid phases will often be the most important partitioning process influencing the bioavailability of an organic chemical in soil. If we ignore the presence of organic chemicals in the gas

phase and the sorption to DOM, c_l may be estimated (using Eqns 1 and 3) from

$$c_l = m_r / (W + K_s) \tag{16}$$

It may be derived from Eqn 16 that estimated c_l values are very sensitive to the value of K_s. Only for weakly sorbing chemicals W values are comparable to K_s values. For moderately to strongly sorbing chemicals c_l is next to inversely proportional to K_s. As discussed in Section 2.2, available methods for estimating K_s from literature data are inaccurate: estimating K_{OM} from other molecular properties may lead to uncertainties of a factor 10 and estimating K_s from a given K_{OM} value results a similar uncertainty. Moreover sorption kinetics on a time scale of weeks, months or years may lead to a systematic underestimation of effective K_s values (by a factor of 2 to 100) of aged residues of organic chemicals. The actual magnitude of this underestimation in a specific situation is difficult to predict from available mathematical models for sorption kinetics (see Section 2.3).

Whether an estimation method for K_s is accurate enough depends on the aim of the study. In view of all uncertainties in estimating effective K_s values for a specific experimental situation, we recommend to measure c_l independently in studies aimed at testing the bioavailability hypothesis described in the introduction.

3 BIOAVAILABILITY RELATED TO THE CONCENTRATION IN THE LIQUID PHASE

When interpreting results from bioavailability studies, it is useful to define (in analogy with Eqn 8) the fraction, F_{bio}, of the content of organic chemical in soil, m_r, that is actually bioavailable to the organism:

$$F_{bio} = W \, c_{l,50} \, / \, m_{r,50} \tag{17}$$

where $c_{l,50}$ is the concentration of the dissolved organic chemical in the liquid phase at 50% effect on the organism (e.g. growth reduction in case of plants, killing in case of animals) and $m_{r,50}$ is the content of the organic chemical in soil at 50% effect. Values of F_{bio} give an indication of the significance of the reduction in bioavailability as a result of sorption: $F_{bio}=1$ implies complete bioavailability and $F_{bio}=0$ implies zero bioavailability.

3.1 Availability to plants

3.1.1 Uptake by plants

Saha et al. (1971) studied the uptake of dieldrin by wheat from seven soils. They also measured sorption of dieldrin to the soils in suspension experiments. From their sorption data we calculated the concentration in the liquid phase in the soils. Assuming that wheat growth is independent of soil properties, we would expect on the basis of our hypothesis that the content of dieldrin in the wheat plants is directly proportional to the dieldrin concentration in the liquid phase in soil. We replotted the data of Saha et al. (1971) in Figure 1 which shows that their results support our hypothesis.

Walker (1972) studied the uptake of atrazine by wheat from 12 soils. He also measured sorption of atrazine to the soils in suspension experiments and from the results the c_l value in each soil type was estimated. He found that the content of atrazine in the shoots was proportional to the estimated c_l values in soil. This is support for our hypothesis. Walker (1973) carried out a similar study on uptake of linuron by wheat from 19 soils and found that the content of linuron in the shoot was roughly proportional to the c_l values in soil estimated from suspension experiments. However, there was considerable scatter in the plot content in plant versus c_l in soil for linuron. He showed that the accuracy of estimating c_l values from the suspension experiments was low by comparing them to c_l values measured in the soil solution obtained by a membrane pressure apparatus. This low accuracy may have been the cause of the scatter in the data.

Content in plant (mg kg⁻¹)

Concentration in liquid phase (mg m⁻³)

• data
— line
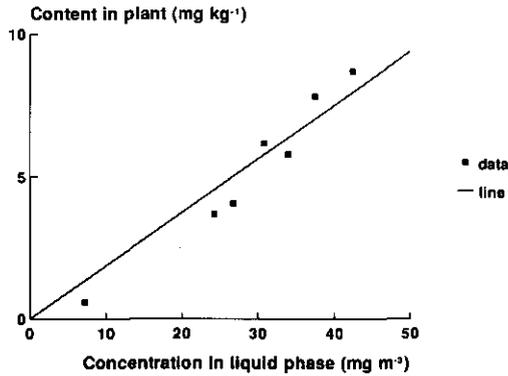
Fig. 1 Relationship between the content of dieldrin in wheat plants and the concentration of dieldrin in the liquid phase as calculated from adsorption measurements for seven soils by Saha et al. (1971). The points are the measurements and the line is a linear regression approximation forced through the origin.

The plant uptake studies by Saha et al. (1971) and Walker (1972) provide qualitative support for our hypothesis. For a quantitative test data are necessary describing plant uptake from a non-sorbing medium under the same experimental conditions. Graham-Bryce & Etheridge (1970) collected such data for disulfoton and dimethoate and wheat plants. They found that the amount taken up from the soil considered, corresponded reasonably well with predictions based on our hypothesis.

3.1.2 Effects on plants

Ignoring the presence of the organic chemical in the gas phase and its sorption to DOM, Eqns 6 and 7 may be rewritten as

$$m_r = c_1 (W + K_s) \tag{18}$$

Effects of organic chemicals on plants are usually described in terms of the content in soil (m_r) required for 50 % growth reduction ($m_{r,50}$). According to our hypothesis the uptake of an organic chemical (and therefore also its effect) is determined by its c_1 value. So if data on different soils are available for one organic chemical and for one plant species, the c_1 at 50% growth reduction ($c_{1,50}$) should be identical for all soils. So we would expect that the $m_{r,50}$ is described by the formula:

$$m_{r,50} = c_{1,50} (W + K_s) \tag{19}$$

If $c_{1,50}$ has been measured independently in experiments with nutrient solution or using a non-sorbing solid phase, the $m_{r,50}$ in the different soils can be predicted from Eqn 19 and the data set could be used for a quantitative test of our hypothesis. If not, the data set can only be used for a qualitative test, by plotting $m_{r,50}$ versus $W + K_s$ which, according to our hypothesis, should give a straight line through the origin (with a slope that is *a priori* unknown).

We searched the literature for data sets that contain both $m_{r,50}$ values and values of W and K_s for various soils (at least four). The experiments we found were all carried out with herbicides and they are compiled in Figure 2. All values of the sorption coefficient (K_s) used to make Figure 2 were derived from soil suspension experiments. Sorption data that were too inaccurate according to Boesten (1990) were not included

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in Figure 2. If the presented $m_{r,50}$ values were very inaccurate, they were also not included. If W values were not given, we estimated them. As may be derived from the values of $W + K_s$ in Figure 2, W (which may be expected to be in the range 0.1-0.5 dm^3 kg^{-1}) was usually very small as compared to K_s. In Figure 2A we combined data for two chemicals (atrazine and cyanazine) because experiments by Anderson et al. (1980) in nutrient cultures showed that the $c_{1,50}$ values of atrazine and cyanazine found for barley were close to each other (0.043 and 0.049 g m^{-3}). Grover et al. (1979) presented their doses of herbicide in terms of kg ha^{-1} and we calculated the corresponding $m_{r,50}$ values assuming a dry bulk density of the soils of 1 kg dm^{-3}.

In general the description of the data in Figure 2 with Eqn 19 is satisfactory. Sometimes there is large scatter in the data (see Figures 2A and 2C). This may have been caused by experimental errors in the $m_{r,50}$ values which can be very large (see the study on reproducibility of such measurements by Nyffeler et al., 1982). Another possibility is that the estimation of $c_{1,50}$ with Eqn 19 was inaccurate. This estimation was based on K_s values measured in soil suspension and it may be inaccurate as a result of the sorption process not being at equilibrium as discussed in Section 2.3.

In most of the studies given in Figure 2 the $c_{1,50}$ values were not directly measured (which is necessary for a quantitative prediction of $m_{r,50}$ values from $W + K_s$ using Eqn 19). Only Anderson et al. (1980) measured $c_{1,50}$ values of atrazine and cyanazine in a bioassay of barley in a quartz sand nutrient culture. The result given in Figure 2A shows that the measured $m_{r,50}$ values were 3 to 6 times as high as predicted with Eqn 19 from the $c_{1,50}$ values measured in nutrient solutions. A possible explanation is that the sorption in the soil during the course of the bioassay (duration 3 weeks) was underestimated by the sorption experiment (shaking for 4 h). This is not unlikely because in the bioassay the chemicals were added in 0.1 cm^3 water to air-dry soil: Graham-Bryce (1967) and Hance & Embling (1979) found that desorption after equilibration in dry soil may be lower than expected from adsorption experiments in soil suspensions. Especially in the case of cyanazine transformation in soil during the bioassay may have contributed to the difference: Anderson et al. (1980) showed that less than 40% of the cyanazine was left after 3 weeks (in the same soil more than 90% of the atrazine was left).

The experiments by Anderson et al. (1980) enable calculation of the bioavailable fraction using Eqn 17 because their data set contains both measured $c_{1,50}$ values and measured $m_{r,50}$ values. The bioavailable fraction was calculated to be in the range 0.003 to 0.006 which is very small.

Stalder & Pestemer (1980) carried out phytotoxicity studies with eight herbicides growing *Brassica rapa L.* as the indicator plant on a soil and on a non-sorbing substrate (vermiculite). They also carried out sorption studies with all herbicides and the soil. We calculated sorption coefficients from their data and found K_s to vary from 1 to 30 dm^3 kg^{-1}. Stalder & Pestemer (1980) expressed the results of their measurements in terms of the fraction, Z, of the herbicide said to be available to the plant. They defined Z as

$$Z = H_{50,n} / H_{50,s} \tag{20}$$
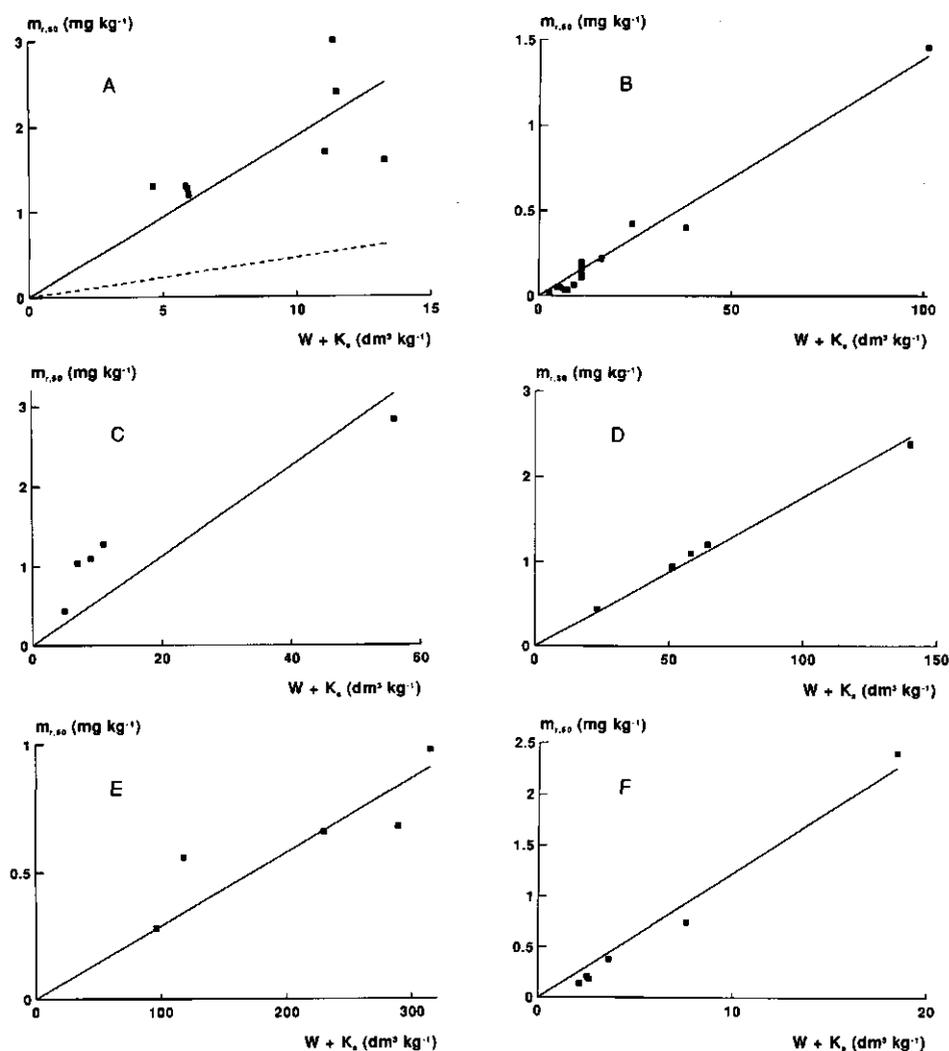
Fig. 2 *Relationships between content of organic chemical in soil at 50% growth reduction of plants in bioassays ($m_{r,50}$) and the sum of massic volume of liquid and the sorption coefficient ($W + K_s$) for different soils as found in the literature. The points are the measurements and the solid lines are linear regression approximations according to Eqn 19. The dashed line in 2A is based on measured $c_{l,50}$ values using Eqn 19.*

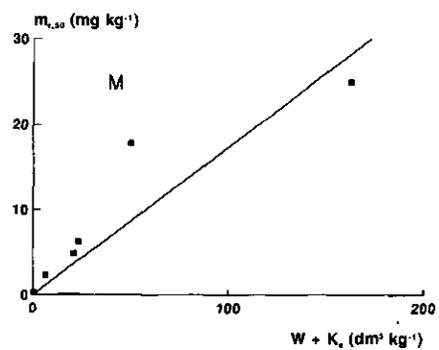*A: atrazine or cyanazine and barley (Anderson et al., 1980)*
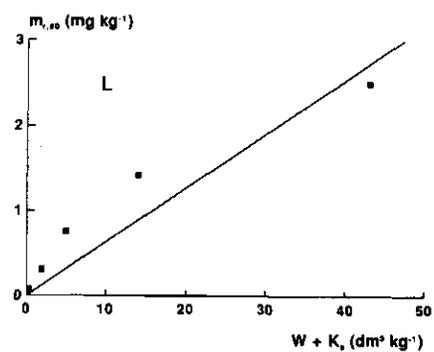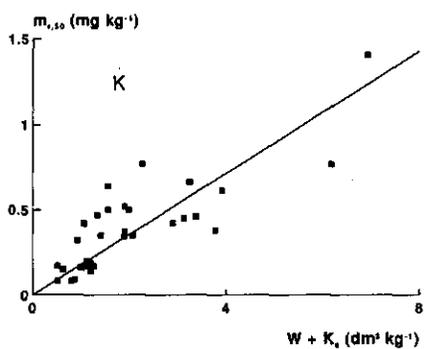*B: fluridone and sorghum (Loh et al., 1979)*
C: diallate and oats (Grover et al., 1979)
D: triallate and oats (Grover et al., 1979)
E: trifluralin and oats (Grover et al., 1979)
F: atrazine and oats (Streibig, 1979)
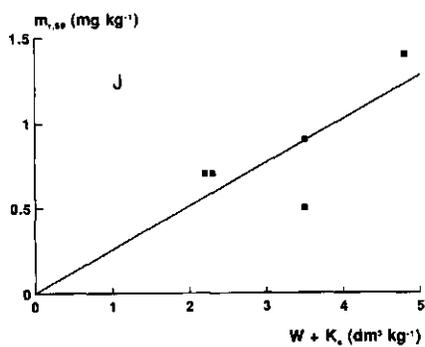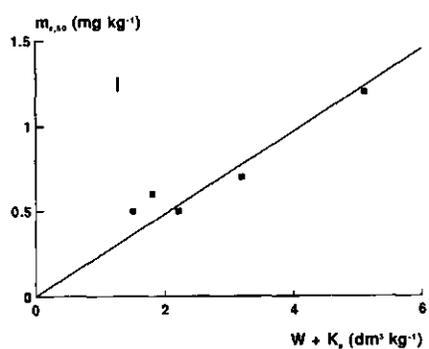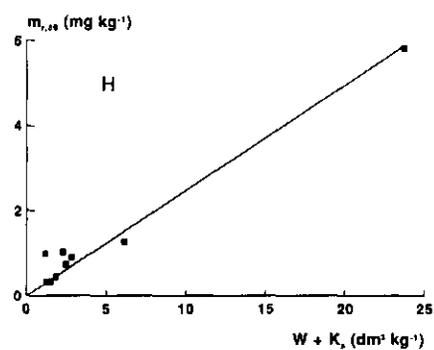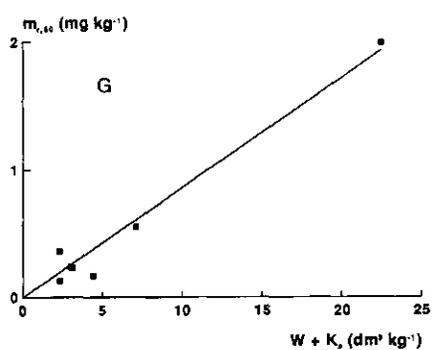
G: simazine and oats (Streibig, 1979)
H: chloridazon and oats (Streibig, 1980)
I: atrazine and soybean (Winkle, 1980)
J: alachlor and sorghum (Winkle, 1980)
K: simazine and oats (Harris & Sheets, 1965)
L: monolinuron and garden-cress (Pestemer, 1977)
M: methabenzthiazuron and garden-cress (Pestemer, 1977)

where $H_{50,n}$ and $H_{50,s}$ are the masses (M) of herbicide necessary for 50% growth reduction in the non-sorbing system and in the soil system, respectively. To test their results against our hypothesis, we have to derive an expression for Z in the context of our hypothesis. Assuming sorption equilibrium and a linear isotherm, the mass balance of their system may be written as:

$$H = c_1 \, (V + M \, K_s) \tag{21}$$

where H is the mass of organic chemical (herbicide) in the system, V is the volume of liquid in the system (L^3), and M is the mass of solid phase in the system (M). So the mass balance equations for the two systems in the case of 50% growth reduction may be written as:

$$H_{50,n} = c_{1,50,n} \, V_n \tag{22a}$$
$$H_{50,s} = c_{1,50,s} \, (V_s + M_s \, K_s) \tag{22b}$$

where the subscripts n and s refer to the non-sorbing and soil systems, respectively. According to our hypothesis $c_{1,50,n}$ and $c_{1,50,s}$ should be equal. So from Eqns 20, 22a and 22b we predict that Z is given by:

$$Z = V_n \, / \, (V_s + M_s \, K_s) \tag{23}$$

Figure 3 shows that the measured Z values decrease with increasing K_s as predicted from by Eqn 23. However, the measured Z values are systematically higher than those predicted by Eqn 23. This systematic difference may be expressed quantitatively by calculating the ratio R defined by

$$R = c_{1,50,s} \, / \, c_{1,50,n} \tag{24}$$

Note that, according to our hypothesis, R should equal unity. We calculated R from the data presented by Stalder & Pestemer (1980) to be on average 0.36 (standard deviation 0.08) for the eight herbicides. So in the soil the effects occurred at estimated c_1 values that were approximately one-third times those in the non-sorbing system. A possible explanation is that the c_1 values in the bioassays were not accurately predicted by their sorption experiments which were conducted using demineralized water at a solid/liquid ratio of 0.7-0.9 kg dm^{-3}. It cannot be excluded that this measuring procedure resulted in sorption coefficients that were higher than those corresponding with the actual c_1 values in the soil during the bioassays (where the solid/liquid ratio was 3 kg dm^{-3}). Grover & Hance (1970) found that the sorption coefficient of linuron at a solid/liquid ratio of 1 kg dm^{-3} was 1.6 times that found at a ratio of 4 kg dm^{-3}. They attributed this difference to greater dispersion of soil aggregates at the lower solid/liquid ratio. The use of demineralized water by Stalder & Pestemer (1980) is likely to have induced dispersion of soil aggregates in the suspension experiments and may therefore be the cause of the discrepancy.

In the experiments by Stalder & Pestemer (1980) V_n was equal to V_s. It may then be derived from Eqns 17, 20, 22a and 22b that Z is equal to the bioavailable fraction, F_{bio}. As shown by Figure 3 the bioavailable fraction ranged from 0.04 to 0.56 in their experiments.

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Fraction available

0.6

0.4

— Eqn
■ data

0.2

0

| 0 | 10 | 20 | 30 | 40 |

K_s (dm³ kg⁻¹)
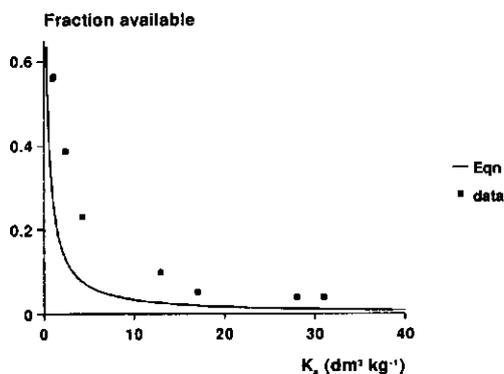
Fig. 3 Relationship between the fraction available, Z (defined by Eqn 20), and the sorption coefficient K_s as calculated from the data of Stalder & Pestemer (1980) for eight herbicides and one soil. The points are the measurements and the line is calculated using Eqn 23.

Extreme examples of reduction of organic chemical bioavailability due to sorption to the solid phase, are the bipyridilium herbicides paraquat and diquat. This may be illustrated by results obtained in phytotoxicity studies with paraquat. Riley et al. (1976) found that the $c_{l,50}$ value for reduction of shoot growth of wheat seedlings grown on nutrient solution was approximately 0.05 g m⁻³. In a bioassay with three mineral soils and the same plant species, they found $m_{r,50}$ values of 500-1300 mg kg⁻¹. This corresponds with a bioavailable fraction (F_{bio} value as estimated with Eqn 17) as low as 10⁻⁵. Riley et al. (1976) carried out sorption studies and from their data we estimated K_s values (at an equilibrium concentration in liquid phase of 0.05 g m⁻³) ranging from 8300 to 22000 dm³ kg⁻¹. Using these values and Eqn 19 we calculated the expected $m_{r,50}$ values and found that these were 0.8, 0.9 and 1.7 times the measured ones. This is a very good correspondence in view of all uncertainties involved in the sorption and bioassay experiments. So these data confirm our hypothesis in a case of extreme reduction of bioavailability as a result of very strong sorption.

3.2 Availability to soil microorganisms

It follows from our hypothesis that the transformation rate of organic chemicals by soil microorganisms is determined by the concentration of dissolved organic chemical in the liquid phase in soil. However, it is very difficult to test this consequence of our hypothesis with soils. When we compare transformation rates of an organic chemical in different soils with different sorption coefficients (in analogy to the studies with plants in Section 3.1), this does not result in a test of our hypothesis because the microbial populations in the different soils are different. Moreover, transformation of an organic chemical in soils is usually not a purely microbial process. As a result there is, in general, no clear relationship between the transformation rate and the extent of sorption in soils (see, for instance, the review on herbicides by Hurle & Walker, 1980). A test for one specific soil is also difficult because we then have to compare the transformation rate in the soil to that in the liquid phase and it is almost impossible to measure the latter independently. Indirect support for our hypothesis may be obtained from studies with soil suspensions ("slurries"). However, extrapolation of the results of such studies to the actual soil system in the field is questionable so we limit our review to a few examples. Ogram et al. (1985) studied 2,4-D mineralization in suspensions of three soils. The soils had

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been sterilized and pure cultures of 2,4-D transforming bacteria were added to the suspensions. They found that sorbed 2,4-D was completely protected from biological transformation which supports our hypothesis. Rijnaarts et al. (1990) studied biomineralization rates and desorption kinetics of α-HCH in soil suspensions and found that the biomineralization rate was controlled by the desorption rate. This indicates that the transformation rate was determined by the α-HCH concentration in the liquid phase which supports our hypothesis.

3.3 Availability to other soil organisms

A literature search yielded only very limited information on the relationship between the concentration in the liquid phase and the bioavailability to other soil organisms than plants and microorganisms. Van Gestel & Ma (1988, 1990) studied the toxicity of five chlorophenols, 2,4-dichloroaniline and 1,2,3-trichlorobenzene to two earthworm species (*Eisenia fetida andrei* and *Lumbricus rubellus*) in four soil types. For nearly all chemical/earthworm combinations they found considerable differences between the $m_{r,50}$ values of the four soils (highest $m_{r,50}$ up to six times as high as the lowest $m_{r,50}$). They also measured sorption isotherms and calculated the corresponding $c_{l,50}$ values. Their results support our hypothesis qualitatively: the differences in the $c_{l,50}$ values calculated for the four soil types were much smaller than the differences in the $m_{r,50}$ values for nearly all chemical/earthworm combinations.

3.4 Discussion and conclusions

In the order of ten studies on uptake or on effects of organic chemicals (nearly all with herbicide/plant systems) support our hypothesis qualitatively. Only three quantitative tests are available (all for herbicide/plant systems). In the first one (Anderson et al., 1980) the content of organic chemical in soil at 50% effect ($m_{r,50}$) was three to six times as high as expected. In the second (Stalder & Pestemer, 1980) it was on average one-third of the $m_{r,50}$ value expected and in the third (Riley et al., 1976) the $m_{r,50}$ corresponded well with the expected values. In none of the three quantitative tests the concentration of the dissolved chemical in the liquid phase (c_l) was measured directly during the bioassays: the concentration was always calculated from adsorption data obtained in soil-suspension experiments. This may have been the cause of the discrepancies observed.

Although existing experimental evidence seems to support our hypothesis, it is not yet conclusive: accurate quantitative tests are not available and almost all experiments have been carried out with herbicide/plant systems. However, it is clear that bioavailability may be reduced strongly as a result of sorption to the solid phase. Further tests of the hypothesis are needed in which the concentration of the dissolved chemical in the liquid phase should be measured directly to eliminate the errors in estimating this concentration.

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