

Environmental Risk Assessment of pesticide use based on the modelling of the environmental fate of pesticides in soil

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Abstract: Based on laboratory and field experiments the environmental fate of four selected pesticides (Dimethoate, Fenvalerate, Malathion, and Metalaxyl) in the Jhikhu-Khola watershed, Nepal was investigated, both on soils representative for irrigated (khet) and rainfed (bari) conditions. The degradation, sorption, and transport behaviour were described with deterministic mathematical models. Based on these models a risk assessment of the accumulation of the pesticides in soil and groundwater was conducted. In order to achieve this standard, worst and best case scenarios were developed. The framework and conditions for the scenarios were set by the physical and socio-economic environment in the watershed, which was investigated by a socio-economic survey. With this method it was possible to assess the risk of groundwater contamination and residue formation in soil on a quantitative basis for parts of the watershed. According to this the risks of severe, actual residue formation are very low, but chances for long term residue accumulation are present. The likelihood of groundwater contamination is also low, but more uncertainties remain as compared to residue formation, because the transport mechanisms are not completely understood and because of insufficient data.

Keywords: Risk assessment; Environmental fate modelling; Pesticides; Preferential flow; Nepal

1. INTRODUCTION

The fate of pesticides in the environment knows many possible ways of degradation, transport and accumulation, as shown in Figure 1.

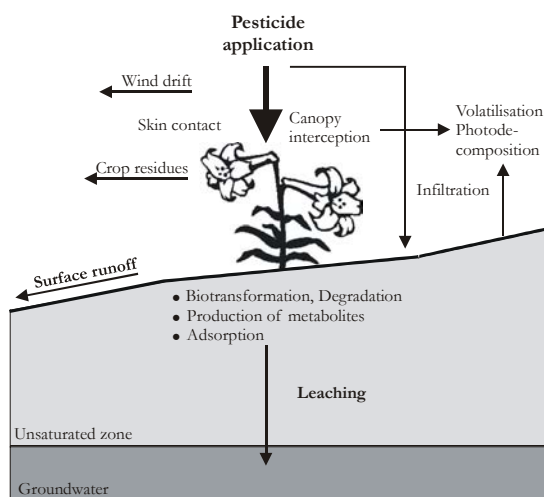


Figure 1. Dissemination pathways of pesticides in the environment

These numerous possibilities challenge every attempt of an environmental risk assessment of pesticide use in general, because it is virtually impossible to describe or even quantify every single dissemination pathway shown in Figure 1,

even for a single pesticide. Nonetheless this is exactly the aim of this paper. Taking an agriculturally intensively used watershed in the Mid-Hills of Nepal, the Jhikhu-Khola watershed, as an example, a viable approach using deterministic mathematical models and statistics is presented in the following chapters.

2. METHODOLOGY

Step 1: Selection of target compounds

If pesticide use in general has to be assessed, a selection of the pesticides used in the investigation area has to be taken, which is representative for the whole range in use. The criteria for the representativeness are:

- frequency and amount used
- pesticide classes
- physicochemical properties

In our case four pesticides were selected according to this criteria:

- | | |
|---------------|---|
| - Dimethoate | organo-phosphorous insecticide, systemic action |
| - Fenvalerate | insecticide, synthetic pyrethroid, contact action |
| - Malathion | organo-phosphorous insecticide, |

- Metalaxyl contact action
 fungicide, systemic action

These four compounds cover the range of pesticide classes used in the watershed, as well as a wide range of physicochemical properties and consequently different assumed environmental fates (cf. Table 1). Only the vapour pressures are in a comparable low range indicating a very low tendency for volatilisation.

	Dimet.	Fenval.	Malat.	Metal.
solubility [mg/l] [†]	238000	0.002 - 1	145	8400
vapour pressure [mPa] [†]	1.1	0.0192	5.3	0.75
K _{ow} [] [†]	506	2.6*10 ⁶	560	56.2
DT ₅₀ [d] [‡]	7 ^{a,e} , 4-20 ^c	35 ^a , 75-80 ^b , 88-287 ^d	1 ^a , 9 ^d , 1-25 ^c	70 ^a , 7-170 ^c

Table 1. Basic physicochemical properties and DT₅₀-values of the selected pesticides. [†] source [Tomlin 1994], [‡] different sources: a) [Di and Aylmore 1997], b) [Tomlin 1994], c) [EXTOXNET 1999], d) [ARS-USDA 1999], e) [Hornsby, Wauchope et al. 1996]

Step 2: Problem definition

After the compound selection the actual environmental problem caused by the pesticides has to be defined in order to design the appropriate experimental setup. The problem definition is ruled by the environmental and agronomic setting. In our case the dominant land use types are small scale terraces with and without irrigation. The irrigated terraces termed “khet land” are level, bounded by earthen walls and irrigated by ponding water in the field with usually three crops per year. On the contrary the rainfed terraces (“bari land”) are sloping without any bounds with only two crops per year due to water shortage in the pre-monsoon season.

The climate is of monsoon type with rainfall concentrated on the months June – September, limiting the number of crops grown on bari land. On both khet and bari land the seasons of high pesticide input are before and after the monsoon, when vegetables are grown as cash crops. Taking these facts into consideration, the most probable dissemination pathways were identified leading to the following problem definition:

1. Probability of residue formation in soil on both khet and bari land.

2. Leaching to groundwater on khet land

Step 3: Laboratory experiments

The next step in the risk assessment comprises laboratory batch experiments for the detection of the degradation and sorption behaviour of the selected compounds in soil taken from the investigation area. In our case the experiments were conducted under varying temperatures during and at three different soil humidity levels ranging from almost dry soil to saturation. This experimental setup produced sufficient data for the detection of not only the degradation and sorption process and parameters, but also for a temperature and humidity dependent formulation of the degradation.

The mathematical model used for the description of the degradation and sorption was the one-site kinetic sorption model [Richter 1996] as shown in equ. (1) – (2)

$$\frac{d}{dt}(\theta c) = -\alpha \rho (K_D c - S) - \theta k(T, \theta) c \quad (1)$$

$$\frac{d}{dt}(\rho S) = \alpha \rho (K_D c - S) \quad (2)$$

with c = solute concentration, S = sorbed conc., α = sorption rate constant, ρ = soil bulk density, θ = volumetric soil water content, K_D = sorption equilibrium constant and $k(T, \theta)$ = temperature and water content dependent degradation rate. For the description of the temperature and humidity response of the degradation different functions were used depending on the data. The response functions are compiled in Richter [1996].

Step 3: Field experiments

Field experiments are necessary to verify the degradation and sorption rates identified in the laboratory experiments and to investigate the transport mechanism in soil. For this purpose Potassium Bromide KBr was used as a conservative tracer for the estimation of the transport parameters additionally to the selected pesticides.

The mathematical model for our problem with ponding irrigation on khet land are stationary convection-dispersion equations (CDEs) coupled with the degradation and sorption terms in two domains (fast and slow), i.e. a preferential flow system was identified. The exchange between the domains are formulated as 1st order processes, analogously to the sorption. Detailed descriptions

of the model can be found in van Genuchten and Wagenet [1989], Gerke and van Genuchten [1993] and Apel [2002].

Step 3: Scenario definition

The overall aim of the scenario calculation is the quantification of uncertainty associated with the transfer of the laboratory and local field experiments to a complete watershed. The quantification of the variance of the parameters involved is prerequisite for a realistic and comprehensible risk assessment. The number of parameters involved depends on the problem definition. In our case the risk of residue formation was assessed by the variation of application doses. The basis for the application variance was a representative survey of 200 households in the watershed [CEAPRED 2000]. Additionally the annual variance of soil temperatures was considered by using temperature dependent degradation rates and a representative soil temperature variation for a complete year.

However, for the variance of the transport velocities necessary for the groundwater contamination assessment no qualified data source was available. This was mainly caused by the preferential flow regime identified in the field experiments, which cannot be estimated by available data like soil type or grain size distribution. This means in consequence that all the following scenarios and risk assessments apply for soils similar to the soils in the field trials only.

The scenarios for the residue formation are defined as mean, worst and best case scenarios under the following conditions and variations:

conditions:

- identified transport mechanism
- saturated water content, stationary flow
- representative soil temperature variation
- temperature/humidity response from batch experiments

variation:

- source: field survey [CEAPRED 2000]
- **mean scenario:** mean of all recorded doses & frequency, 25% applied to soil surface
- **worst case:** highest mean dose + 1.96 standard deviations, highest frequency, all to soil surface
- **best case:** lowest mean dose - 1.96 standard deviations, lowest frequency, 10% to soil surface

The application statistics are taken from the survey, whereas the part applied directly to the soil surface are empirically assumed. The final risk assessment is consequently based on the results of the scenario calculations and the underlying statistics.

3. RESULTS

In this chapter the results for only one selected pesticide, Dimethoate, are presented exemplarily for the complete assessment.

3.1 Laboratory batch experiments

Figure 2 shows the experimental laboratory data set and the model fit. The temperature as well as the humidity response are clearly visible and could be well explained by optimum functions [Apel 2002].

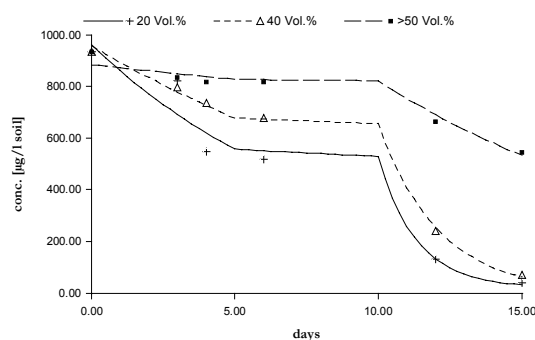


Figure 2. Laboratory data and model fit of Dimethoate with varying temperatures and different soil water contents; temperature change: 20°C/10°C/30°C; total $R^2 = 0.97812$

3.2 Field experiments

In a first step the parameters for the water transport model were estimated with two Bromide profiles five and seven days after application of the substance. Figure 3 shows the resulting fit. The preferential flow regime is clearly visible in the two peaks, one remaining close to the soil surface and the second, faster moving deeper in the profile.

The identified parameter values for the water transport were consequently used for the transport model of the pesticides along with the degradation and sorption parameters estimated in the laboratory experiments. In all cases this resulted in poor fits to the field profiles. Hence further estimations of field degradation rates were necessary, which were typically faster than the laboratory rates. Figure 4 shows the resulting

model fit of this procedure to the Dimethoate profiles. This fit shows that the assumed models for the transport, degradation and sorption are able to sufficiently explain the fate of the substances in soil. This is the prerequisite for the next step, the scenario calculation and the following interpretation, the risk assessment.

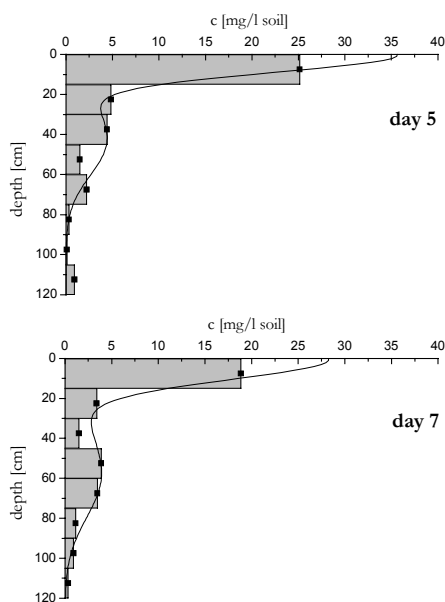


Figure 3. Model fit to Bromide profiles of field trial, overall $R^2 = 0.9671$

3.2 Scenario calculations

The conditions and case variations for the scenarios are listed under Step 3 in chapter 2. The use of the slower laboratory degradation rates are justified by the consideration of the annual soil temperature variation and the conservative approach underlying the scenarios. The results of the mean and worst case scenarios for Dimethoate are shown in Figure 5 and 6 respectively.

The results of the standard scenario show several remarkable facts. The seasonal temperature variation is clearly visible in the degradation, respectively the residue formation within the different cropping periods. The graph in Figure 5 containing the total substance in the calculated profile of 1.2 m depth under 1 m² shows a slow degradation of Dimethoate during the winter (potato) season and consequently a comparatively large residue formation, while the degradation during the summer and monsoon season increases to such an extent that residues are reduced. Although there is a residue reduction during summer and monsoon, an apparently substantial amount of substance is left in the soil column after one year.

At a first glance this appears to be alarming, but a look at the concentration profile of the last day mitigates this impression. The concentration are comparatively low throughout the profile and hardly analytically quantifiable, depending on the quantification limit established. The dotted lines in the graphic indicate two different quantification limits. The higher limit is obtained by recovery experiments through the complete analytical process with all partners involved, the lower one taken from literature is derived by peak heights in the chromatograms. This means that with the experimental quantification limit it would be hard to detect the substance in quantifiable amounts after the three seasons and even with the lower limit the concentration in the deeper profile are unlikely to detect. The consequence is that the residue formation is probable, but in hardly detectable quantities.

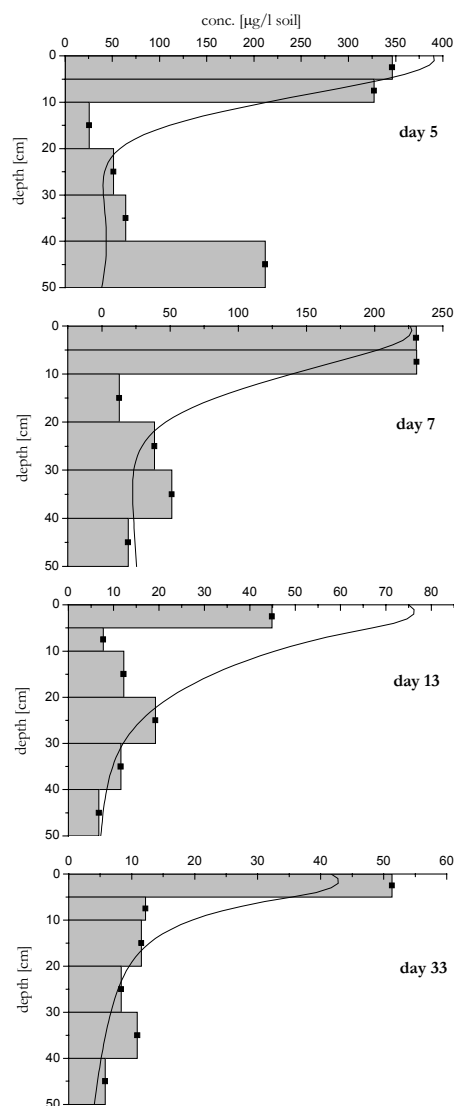


Figure 4. Dimethoate profiles and model fit in

field trial, total $R^2 = 0.793$

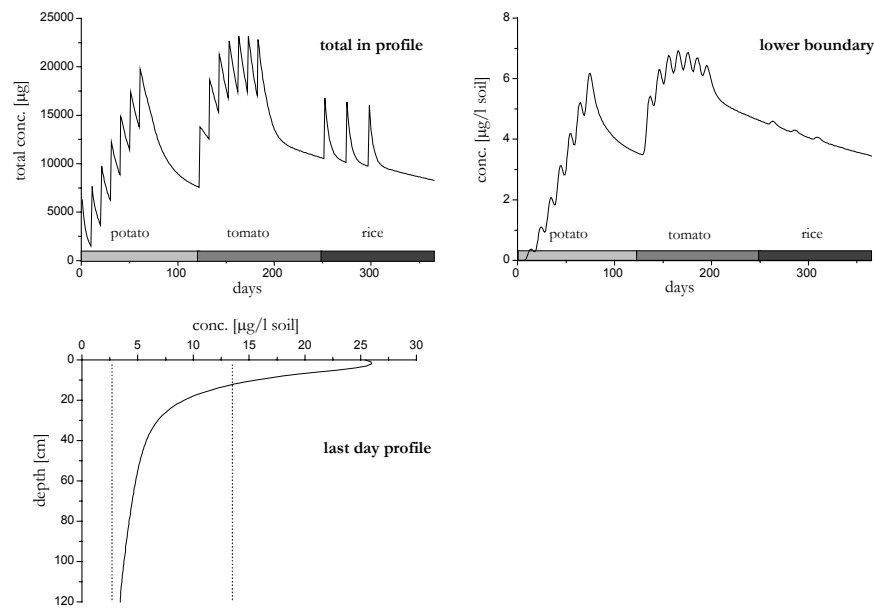


Figure 5. Results of the mean scenario calculation for Dimethoate; reference area: 1 m^2 , dotted lines in last day profile indicate quantification limits

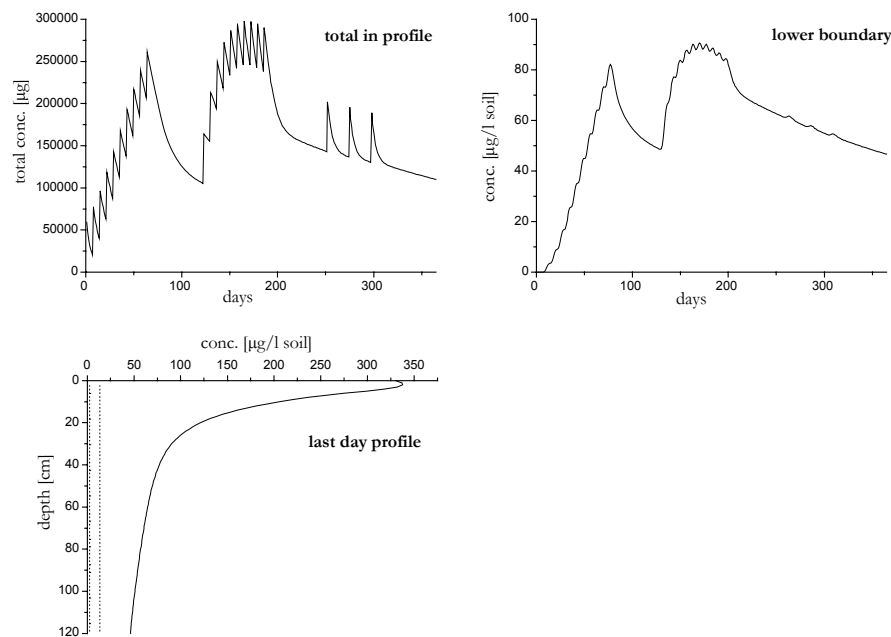


Figure 6. Results of the worst case scenario calculation for Dimethoate; reference area: 1 m^2 , dotted lines in last day profile indicate quantification limits

There is also an amount of the substance leaving the profile, i.e. leaching to lower depths, as the lower boundary graph shows. But again, the concentrations there are in a range difficult to detect. An approximation of the substance outflow yields that about 5% of a single application assumed in the scenario leave the soil column, posing no risk to groundwater contamination due to dilution.

This situation is quite different in the worst case scenario. Here of course the residue formation reaches a worrying quantity as well as the substance leaving the profile (cf. Figure 6). The last day profile shows clearly detectable and quantifiable concentration up to the bottom of the profile and the amount leaving the profile is in the order of one standard application. This case would pose a serious threat to the environment,

especially the residue formation. Fortunately this scenario is very unlikely as further elaborated in the following chapter.

In contrast to this the best case scenario yields a non quantifiable residue situation, even with the low quantification limit. Also the leached amount is of such a low quantity that it can be neglected. However, the probability of this scenario is as low as the best case, since equivalent assumptions were made.

4. RISK ASSESSMENT AND DISCUSSION

Prior to the evaluation of the risks associated with the single pesticides the probabilities of the worst and best case scenarios have to be calculated. As mentioned before the definition of the application doses is based on statistics derived from a representative survey in the investigation area. For the worst case scenarios the highest mean application dose found on the selected crops plus 1.96 standard deviations are taken. Under the normal distribution assumption this means that the probability of a single application of a dose equal or higher as a worst case dose is 2.5 %. This has to be corrected by the probability of the highest mean dose used in the scenario. Under the assumption that all of the six recorded mean doses are equally likely, this evaluates to 1/6, i.e. 16.6 %, because in the survey report [CEAPRED 2000] six mean doses are given for the three crops in the scenarios in two different areas of the watershed. Consequently the final quantifiable probabilities of the worst and best cases are 0.416 % [Apel 2002].

The only unquantifiable factor remaining is the portion reaching the ground. For this only qualitative statements can be given. While the assumption for the mean and best case may be realistic for the mean and the cautious farmer, the "all to ground" assumption of the worst case is quite unlikely to be found at every application date. This means that the probability of the worst case is surely lower than the calculated 0.416 %, but to what extent cannot be quantified with the information present. Taking these probabilities into account the interpretation of all the scenarios for all four substances leads to the final risk assessment for the watershed, which can be summarised with the following two points:

1. There is no acute risk of residue formation or groundwater or open water contamination under the present situation.
2. There are chances of long term residue

formation, especially with synthetic pyrethroids, albeit of low probability (< 1%).

But again it has to be kept in mind this assessment refers to soils similar to the soil in the field experiments only. This means that although this soil type is the most common, a complete risk assessment for the whole watershed was not possible.

Based on this risk assessment and the underlying assumption four general recommendations can be formulated in order to reduce the already low risks or to minimise the uncertainties still present:

1. Improvement of the application techniques.
2. Increased control of the application doses.
3. Cautious use of synthetic pyrethroids.
4. Further research on different soils.

5. REFERENCES

- Apel, H., Risk Assessment of Pesticides in the Mid-Hills of Nepal - Environmental Fate and Population Dynamics Modelling, *Institute of Geoecology, Braunschweig, TU Braunschweig*, PhD Thesis, 127 p., 2002.
- Richter, O., Diekkrüger, B. and Nörtershäuser, P., Environmental Fate of Pesticides - From the Laboratory to the Field Scale, *VCH Verlagsgesellschaft*, 281 p., 1996.
- van Genuchten, M.T. and Wagenet, R.J., Two-site/two-region models for pesticide transport and degradation, *Soil Science Society of America Journal*, 53,1303-1310, 1989.
- Gerke, H.H. and van Genuchten, M.T., A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media, *Water Resources Research*, 29(2), 305-319, 1993.
- CEAPRED, Socioeconomic survey of the Jhikhu-Khola watershed, *unpublished project report*, 47, 2000.
- Tomlin, C., The Pesticide Manual incorporating The Agrochemicals Handbook, *British Crop Protection Council*, Surrey, UK, 1340, 1994
- Di, H.J. and Aylmore, L.A.G., Modelling the probabilities of groundwater contamination by pesticides, *Soil Science Society of America Journal*, 61,17-23, 1997.
- EXTOXNET, The Extension Toxicology Network, <http://ace.orst.edu/info/extoxnet/>, 1999.
- ARS-USDA, Pesticide Properties Database, <http://www.arsusda.gov/ppdb.html>, 1999.
- Hornsby, A.G., Wauchope, R.D. and Herner, A.E., Pesticide Properties in the Environment, *Springer*, 227 p., 1996.