

Modeling pesticide losses from diffuse sources in Germany

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Abstract A GIS-based model estimates the losses from diffuse sources in surface waters in Germany for 42 active ingredients applied to 11 field crops, vineyards and orchards. For the following pathways of entry: tile drainage, runoff and spray drift, the calculated mean pesticide input amounts to 1490 kg/year, 9060 kg/year and 3350 kg/year, respectively, in 1994. The model results are highly sensitive to the model parameters, primarily the chemical properties of the active ingredients. The modeled water inputs were compared with measured pesticide loads in smaller catchments and large river basins to validate model results. Both datasets agree as to the order of magnitude, nevertheless due to the scale of the study the results should be addressed mainly to comparative interpretations with the focus on the proportions between different active ingredients, soil regions, climates and application periods.

Keywords Diffuse sources; Germany; pesticides; runoff; spray drift; tile drainage

Introduction

Pesticide pollution of surface waters represents a considerable hazard for the aquatic environment. However, the mean amount of pesticides reaching the water resources varies considerably between regions and is highly dependent upon application rates, chemical characteristics of pesticides and soil and climate conditions. Any conceptual approach to reduce water pollution with agricultural chemicals is likely to remain ineffective, if the sources of pesticide inputs or the transport processes are not known on a regional scale. Spatially distributed modeling of pesticide losses may help to identify the most relevant pesticides, pathways of entry, site conditions and application techniques for water contamination.

Modeling assessments

The diffuse input of pesticides into surface waters was modeled separately for the three pathways of entry: tile drainage, surface runoff and spray drift. Other non-point sources such as atmospheric deposition or wind erosion are not considered to be relevant on a national scale. In addition, sediment-bound pesticide loss was also not considered because, for the most common pesticides in German agriculture, the bulk of the active ingredients will be transported in the water phase. For detailed information on the modeling approaches and results, refer to Huber *et al.* (1998a, 2000) and Bach *et al.* (2000).

Database

The model is based on a set of digital maps of Germany, e.g. administrative units, agroecological zones, soils, annual precipitation, frequency of storm events, drainage density, CORINE land cover, etc. The GIS-based spatially differentiated model covers the entire area of Germany with a resolution of $1 \times 1 \text{ km}^2$. Calculations were carried out for the 42 active ingredients with the largest volume of sales in 1994 (IVA, 1995). The physical and chemical properties of the active ingredients (Koc, DT50) were taken from databases of the

German Federal Environmental Agency. Based on a representative market survey among 3500 farmers (Produkt und Markt, 1997), the quantities and the dates of application of the 42 active ingredients in pesticides were estimated for each region. CORINE land cover data and results of an agricultural census at the community level were taken to enhance the spatial resolution of the application pattern. In addition to mean doses in each federal state, application probability is an essential parameter to consider both in the relation to the market position of an active ingredient and as an indicator of the intensity of infestation. Hence, application probabilities were calculated for all treatments of 42 active ingredients in 11 field crops, in vineyards and in orchards, and on 11 target-dates of application, based on the relation between the area treated with a pesticide in a given period and the total area cropped with the target culture in each state (Huber *et al.*, 1998b). This information is required as the input data for the individual steps of modeling.

Pesticide leaching and input via tile drainage

The estimation of tile drainage input into surface waters is carried out in two steps (Huber *et al.*, 2000). First, based on the leaching model PELMO (Klein, 1995), for all combinations of site conditions and pesticide applications in Germany, the portion of an active ingredient which is leached to a soil depth up to 0.8 m is simulated. 31,360 PELMO simulation runs using different combinations of the variables (soil, climate, chemical properties of active ingredients, target dates of application and target crops) were calculated. Each model run started with an application of 1 kg/ha on one of the 11 target-dates of application and applying a full year weather record with daily precipitation and temperature data. Chemical leaching was then calculated until the concentration of the original active ingredient fell below an arbitrarily chosen limit of 0.01 µg/l at 0.8 m soil depth. At the end of each run, pesticide loads given as a fraction of the application rate leached below 0.8 m were summarized together with annual percolation volumes.

To regionalize simulation results, regression functions were derived between PELMO results and input parameters of leaching scenarios. The set of input parameters included spatially distributed data such as mean annual percolation rate, soil types and regional application periods. The Koc coefficient and DT50 were assumed to be constant in time and space. Application rates were corrected for treatment probabilities and real doses according to the crop protection database and soil covering. No foliar washoff was considered because pesticides degrade very fast on plant surfaces (Willis and McDowell, 1987) and hence it is presumed that foliar washoff would not contribute to a considerable extent to total leaching loss.

Pesticide mass leached below 0.8 m is then assumed to enter tile drains, and thus to be transported to the surface water system depending upon tile drain density in each grid cell. While a fairly good dataset on tile drain density is available for former Eastern Germany, an extensive survey among local branches of the agricultural extension service was conducted in the western part of the country to compile a map of average tile drain density in agroecological zones. The leaching of pesticides into groundwater and a possible input of active ingredients into surface waters via outflowing groundwater were not taken into account. According to current knowledge, pesticides in groundwater resources in Germany occur only locally. A significant, large-scale load of surface waters with pesticides due to seepage of contaminated groundwater is not observed.

A notable accuracy limitation of predicted leaching loss must be attributed to spatial variability of organic carbon content of arable land which could not be adequately considered on the regional scale. To reduce the number of factor combinations to a manageable amount, PELMO runs were conducted with five different soil type scenarios ranging from a coarse sand to a silt loam, and mean organic carbon contents in the upper soil profile

ranging from 0.7% to 2.4%. Soil scenarios were selected so as to have them represent cultivated soils. Nevertheless, it may be possible that the model predicted erroneous pesticide leaching rates due to a too coarse classification of soils in one of the defined soil scenarios. Another limitation of the PELMO model refers to the preferential flow. This may constitute a considerable drawback when the model is applied to heavier soils. It is evident that highly permeable and thus leaching-susceptible soils are drained to a lower extent than heavier soils. However, it is possible that frequently drained soils in loess areas, which do not exhibit a high leaching potential after PELMO runs, would be classified differently when considering solute transport in macropores.

Pesticide input via runoff

Pesticide loss with surface water is event-specific. The estimate of the pesticide input from surface runoff consists of four components (Huber *et al.*, 2000).

1. At the beginning the mean probability of the occurrence of a runoff-causing rainstorm is determined. Storm frequency is a highly sensitive factor of pesticide runoff losses because the component of pesticide residues which is most susceptible to runoff is rapidly dissipated after application. The time between application and a significant rainfall event is a random variable in contrast to other parameters (like day of application, applied dose, crop cover or pesticide half-life), which are either known or assumed to be constant. That means the time between application and runoff event can only be described in a stochastic way. A frequently used probability distribution for time between significant rainfalls is the Gumbel distribution. The German Meteorological Service (DWD, 1996) provides nationwide datasets with parameters u and w of a Gumbel distribution for various rainstorm durations in a $10 \times 10 \text{ km}^2$ grid. For the input modeling, u and w have been fitted for 24 hour events.
2. The runoff volume is determined using the method for calculating highwater flow developed by Lutz (1984). The approach is based on SCS-curve number method (McCuen, 1981) modified for Central European conditions.
3. The mean time interval between the application and the intense precipitation results from the occurrence probability of the precipitation event and the dates of application. Based on the average length of time between significant rainfalls and the breakdown coefficient, Mills and Leonard (1984) developed a probability density function for the amount of pesticide available for transport at the time when runoff begins.
4. The mean concentration of active ingredients (dissolved phase only) in the runoff is calculated according to the GLEAMS model (Mills and Leonard, 1984; Leonhard *et al.*, 1987). Here, the chemical transfer to surface runoff is a functional relationship between the coefficient K_d , which gives the fraction of the adsorbed and the soluted phase of an active ingredient in the soil, and an empirical extraction coefficient.

The model only calculates the outflow of active ingredients in the dissolved phase. The estimate of the input of pesticides into surface waters by eroded soil material for the entire area of Germany would require the development of an erosion model with a high spatial and temporal resolution. To date the scientific basis for a model-based approach and essential input data for erosion calculation are missing. Furthermore, the approach to calculating runoff pesticide loss differs significantly from erosion modeling as neither terrain information nor precipitation volume are crucial model parameters. Runoff volume depends only upon infiltration capacity of soil, which is a function of porosity, water content, susceptibility to crusting and crop cover. In this way it becomes evident that higher runoff losses are calculated for steep, and therefore, shallow soils in vineyards, while deeper soils in flat areas do not show the same runoff susceptibility, unless a nonpermeable layer in the upper part of the profile exists. Precipitation volume is a crucial parameter in the model only with

regard to its probability of occurrence. The more frequently significant rainstorms occur, the shorter the time for pesticide degradation. Therefore, small rainfall events, which are enough to produce runoff, outweigh extreme rainstorms in relative importance for total pesticide losses because they are far more frequent.

Pesticide input via spray drift

The table values given by the German pesticide registration authority (Ganzelmeier *et al.*, 1995) are used to calculate spray drift losses which are 0.58% of the active ingredients applied to cropland, 0.75% and 2.68% for early and late treatment in viticulture, respectively, and 12.02% and 4.92% for early and late treatment in orchards, respectively. For field crops, a mean distance to the body of water of 2 m during the application and 5 m for vineyards and orchards was assumed (Huber *et al.*, 2000). The drainage density, i.e. the frequency of surface waters per unit area, was computed on the basis of the digital surface water net (HAD, 2000).

Modeling results

Pesticide losses into surface waters

The 11 active ingredients that are to blame for the largest input of pesticides by drainage, runoff and spray drift, calculated by means of models, are shown in Table 1. According to these approaches an input of pesticides into surface waters of ca. 14 t/year for the total area of Germany is estimated. Input by drainage which amounted to ca. 1500 kg/year for the entire area of Germany was only calculated for 6 of the 42 active ingredients clearly, and was dominated by isoproturon. For most parts of the country only negligible amounts of pesticides are leached to 0.8 m according to model results.

The input via runoff is calculated as 9060 kg/year active ingredients. The largest part of the total runoff input is caused by arable farming. For active ingredients applied to row crops, in particular to sugar beet, relatively high outputs were calculated, e.g. metamitron contributes more than 25% of the total input. With respect to arable farming, on the whole very low losses via spray drift are calculated, which amounted to an annual input of 1–3 mg of active ingredients per hectare. In total, the input by spray drift in arable farming amounts to ca. 90 kg/year for the entire area of Germany. The input by spray drift from fruit culture adds up to ca. 3100 kg/year. This input is limited to a few regions of Germany characterized by a high density of receiving bodies of water, i.e. the “Alte Land” in the north of Hamburg. In viticulture the input by spray drift is estimated to amount to ca. 120 kg/year of active ingredients. Maps showing the regional distribution of pesticide input into surface waters are given in Huber *et al.* (1998a, 2000) and Bach *et al.* (2000).

PELMO calculations give high leaching rates in the northern lowland areas of Germany, where sandy soils prevail and autumn applications to winter grain, particularly treatments with isoproturon, are more common than in other parts of the country. However, in some regions, where a considerable leaching potential is predicted, a high tile drain density is encountered. Thus, resulting surface water pollution is much lower than the leaching potential.

Modeled surface water input compared with measured river loads of active ingredients

In general, it is difficult to compare modeled pesticide loss on a single pathway with experimental data because plots and even small catchments studied in a short period may not be representative for an entire region. In this way only long-term catchment studies should be used to prove reliability of predicted losses. Additionally, experimental data should cover the main application periods and the most frequently applied active ingredients. At present, only datasets from 13 German catchments fulfill these requirements.

Table 1 Estimated input of active ingredients into surface waters in Germany according to model approaches (reference year 1994)

Active substance ^a	Tile drainage		Runoff		Spray drift		Total amount
	Input (kg)	Percentage of application quantity (%)	Input (kg)	Percentage of application quantity (%)	Input (kg)	Percentage of application quantity (%)	
metamitron	1	0.0	2420	0.23	11	0.0	2432
isoproturon	950	0.04	1280	0.06	20	0.0	2250
propineb	120	0.05	100	0.04	1230	0.50	1450
ethofumesate	80	0.07	1030	0.42	1	0.0	1111
dichlofluanid	110	0.09	380	0.25	390	0.25	880
terbuthylazine	0		880	0.18	3	0.0	883
mancozeb	0		5	0.0	780	0.20	785
dichlorprop-P	0		630	0.05	8	0.0	638
dithianon	0		12	0.0	550	0.40	562
metolachlorine	0		510	0.18	1	0.0	511
bentazone	110	0.03	300	0.10	1	0.0	411
total ((42 a.i.)	1490		9060		3350		13,900

^aExtract from the list of the 42 active ingredients (a.i.) modeled, the volume of sales of which had been the largest in 1994

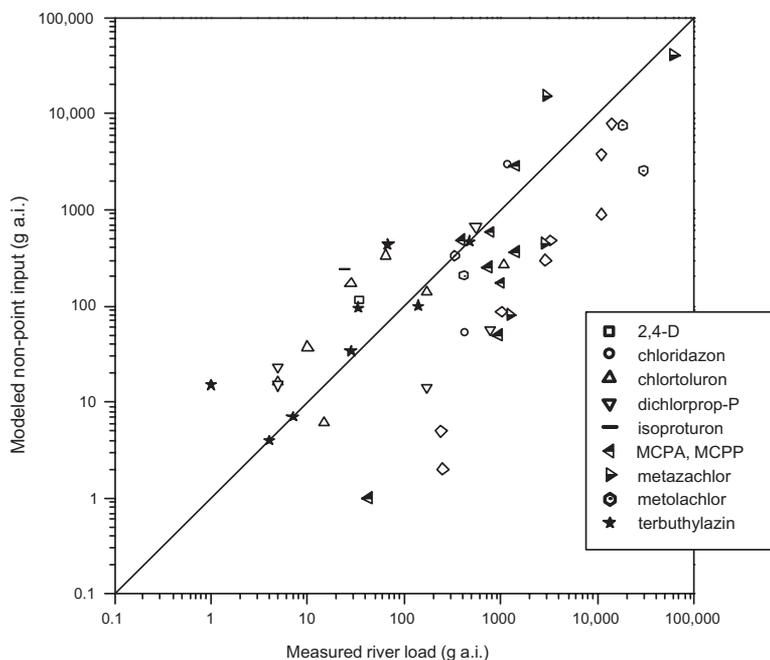


Figure 1 Comparison between modeled diffuse pesticide inputs (reference year 1994) and measured river loads (different years, different sampling periods) of six frequently analyzed active ingredients (a.i.) in 13 catchments in Germany

A major limitation of regional scale modeling is that results can never be validated in a strict sense because measured loads also include a certain amount of pesticide which did not enter the surface water system on modeled pathways. Additional input could occur via contaminated farmyard wastewaters. Finally, the model developed in this study estimated pesticide loss to surface waters while experimental data is the load at the

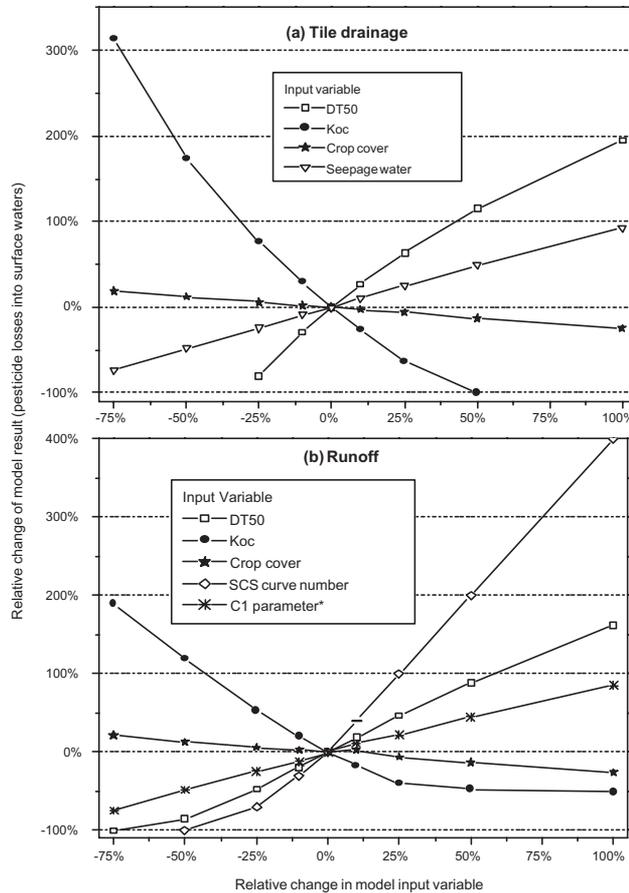


Figure 2 Sensitivity of model results to parameter variation for: (a) tile drain losses; (b) runoff losses (base scenarios, see Huber *et al.*, 1998a)

catchment outlet. Between the point of entry and the sampling station, transformation and sorption processes may occur; hence, it is probable that measured loads do not truly reflect either the total pesticide input or the input from diffuse sources. The comparison between measured pesticide loads in river and modeled diffuse input in the 13 catchments are shown in Figure 1.

Despite the limitations of the comparison, several conclusions can be drawn:

- In most cases, the model results seem to match the magnitude of pesticide pollution in surface waters. However, it is not possible to validate the prediction for a single pathway because none of the studies (except one) listed loads for each pathway separately.
- The model tends to underestimate loads in those catchments where the measured load of an active ingredient exceeds about 100 g/year. A possible explanation is the existence of point sources which are more probable in larger catchments, whereas in small catchments, point sources are often excluded by the selection of monitoring sites.
- Especially in small catchments it is likely that errors, due to the generalization of spatial input data, distort model results. For example, spatial resolution of soil data used in this study is probably too coarse to estimate pesticide runoff or leaching in catchments with an area of less than ca. 100 km².
- With respect to the limitations, both datasets show a high agreement of the order of one magnitude. Nevertheless, due to the scale of the study the estimated loads should not be

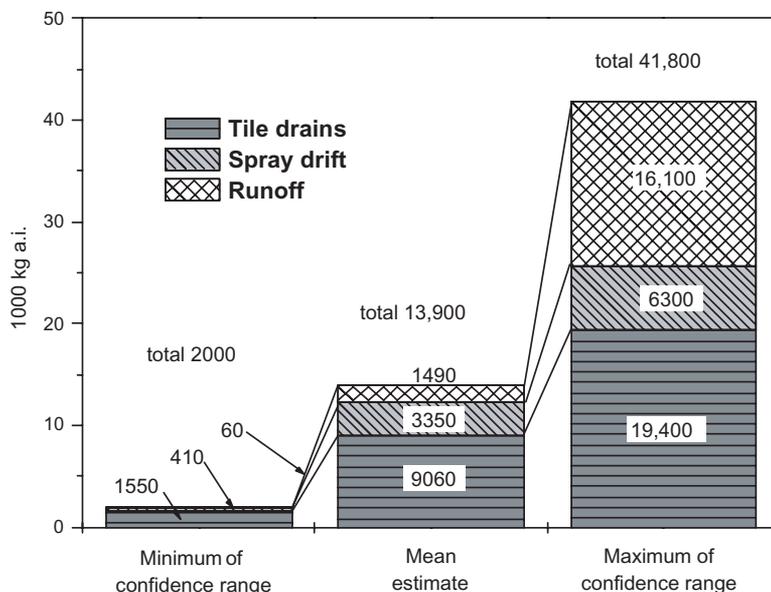


Figure 3 Mean and confidence ranges of estimated pesticide input into surface waters from diffuse sources in Germany (total of 42 ingredients, reference year 1994)

interpreted as absolute values, and only the differences between active ingredients, soil regions, climates and application periods should be focussed upon.

Sensitivity analysis

Using base information for soil and climate characteristics some parameters were varied to test the sensitivity of model-generated output to these parameters. PELMO leaching simulations show a high sensitivity to chemical properties and soil organic carbon content (Figure 2a). Therefore, model results exhibit a high variation for some active ingredients especially when the values of the most sensitive parameters, half-life (DT50) and sorption coefficient (Koc), respectively, are changed. The calculation of runoff volume is strongly influenced by the CN value (Figure 2b) followed by the pesticide properties.

Confidence range of model estimation

Model calculations for pesticide input into surface waters via surface runoff, tile drains and spray drift are summarized in Table 1. These values, however, react extremely sensitively to the assumptions that the modeling is based on. To account for parameter uncertainty inherent to all regional scale models, computed loads are given in Figure 3 together with their confidence ranges derived from sensitivity analysis. According to these approaches the mean total pesticide input into surface waters of ca. 14,000 kg/year in Germany is estimated with a range from ca. 2,000 kg/year up to ca. 42,000 kg/year (reference year 1994). The magnitude of variation for pesticide input is different for every active ingredient as well as for each pathway.

Conclusions

The crucial issue in the development of concepts to improve water quality is the determination of the most important pathways of entry of pesticides into waters. No regional-scale model is able to calculate the exact amount of pesticide loss to surface water because transport processes are of a complex nature and can only be described in a simplified form.

However, it seems possible to differentiate regions according to relative importance of three relevant paths of pesticide migration into the aquatic environment. Model runs show that both active ingredients, as well as, regions, crops or application periods, need a differentiated assessment with regard to risk of surface water pollution. The importance of non-point source pathways varies both with specific conditions under which pesticides are applied and the reasons for transport along a specific pathway.

According to model results surface runoff is the dominant non-point source pathway for pesticide input into surface waters in Germany. The model clearly shows that chemical transport with surface runoff is a more frequent phenomenon than losses via tile drains or spray drift, particularly in regions with a high spraying intensity like in loess areas of central Germany, along the lower Rhine and the Danube river. The highest annual dissipation rate of 5 g/ha was modeled for vineyards in the River Mosel region and along the upper and middle Rhine. Contrastingly, in vineyards where fungicides are also subject to runoff transport, pesticide runoff in field crops consists nearly exclusively of herbicides. Cumulated input, after all the calculated treatments, varies between 0.42% of application rate for ethofumesate to less than 0.01% for more strongly bound or rapidly degradable active ingredients. In the case of isoproturon, the most frequently used herbicide in German agriculture, calculated runoff loss is about 0.06% of the application rate.

Comparing model results with measured pesticide loads in continuously monitored catchments proves indispensable for assessing model performance, even though the modeler should always be aware of limitations inherent in any validation procedure for regional-scale models. The model approaches for the calculation of diffuse input of pesticides into waters by drainage, runoff and spray drift at a macroscale (river basins) generally provide convincing results, which nevertheless have to be validated. Despite its limitations, the application of a regional-scale model may contribute to the knowledge about the regional importance of pathways of entry of pesticides into surface waters.

References

- Bach, M., Huber, A., Frede, H.G. and Zullei-Seibert, N. (2000). *Schätzung der Einträge von Pflanzenschutzmitteln in die Oberflächengewässer Deutschlands*. [Estimation of pesticide input into surface waters in Germany.] UBA-Berichte, Umweltbundesamt, UBA-texte 3/00, Berlin.
- DWD (1997). *Parameter u/w der Extremal-I-Verteilung im 10 × 10 km² Raster (KOSTRA-Raster) für die Bundesrepublik Deutschland*. [Parameters u and w of the extremal-I-distribution for 10 × 10 km² grid cells in Germany.] Deutscher Wetterdienst, Offenbach.
- Ganzelmeier, H., Rautmann, D., Spangenberg, R., Strelake, M., Herrmann, M., Wenzelburger, H.J. and Walter, H.F. (1995). Studies on the spray drift of plant protection products – Results of a test program carried out throughout the Federal Republic of Germany. *Mitteilungen Biologischen Bundesanstalt Land-Forstwirtschaft*, **305**, Berlin.
- HAD (2000). *Hydrologischer Atlas von Deutschland*. [Hydrologic atlas of Germany.] Bundesministerium fuer Umwelt, Energie und Reaktorsicherheit (ed.), Berlin.
- Huber, A., Bach, M. and Frede, H.G. (1998a). Modeling pesticide losses with surface runoff in Germany. *Science Total Environment*, **223**, 177–191.
- Huber, A., Bach, M. and Frede, H.G. (1998b). Regional und zeitlich differenzierte Schätzung der Wirkstoff-Aufwandmengen in Feldkulturen in der Bundesrepublik Deutschland. [Spatial and temporal splitted assessment of pesticide dosage in German cropping systems.] *Gesunde Pflanzen*, **50**, 36–44.
- Huber, A., Bach, M. and Frede, H.G. (2000). Pollution of surface waters with pesticides in Germany: modeling non-point sources. *Agriculture Ecosystems Environment*, **80**(2000), 191–204.
- IVA (1995). *Mengenmaessig bedeutendste Pflanzenschutzwirkstoffe in der Bundesrepublik Deutschland 1993*. [Listing of the most sold active ingredients in Germany 1993.] Industrieverband Agrar (IVA), Frankfurt a.M.
- Klein, M. (1995). *PELMO, Pesticide Leaching Model, Version 2.01*, Manual. Fraunhofer Institut fuer Umweltchemie und Ecotoxikologie, Schmallenberg, Germany.
- Leonard, R.A., Knisel, W.G. and Still, D.A. (1987). GLEAMS: groundwater loading effects of agricultural management systems. *Trans. ASAE*, **30**(5), 1403–1418.
- Lutz, W. (1984). Berechnung von Hochwasserabflüssen unter Anwendung von Gebietskenngrößen. [Calculation of flood discharge using area characteristics.] *Mitteilungen Institut für Hydrologie und Wasserwirtschaft*, **24**, Karlsruhe.
- McCuen, R.H. (1981). *A Guide to Hydrologic Analysis Using SCS Methods*. Prentice Hall, Englewood Cliffs, USA.
- Mills, W.C. and Leonard, R.A. (1984). Pesticide pollution probabilities. *Trans. ASAE*, **27**, 1704–1710.
- Produkt und Markt (1997). *Database Agricultural Panel*. Produkt und Markt Comp., Wallenhorst, Germany.
- Willis, G.H. and McDowell L.L. (1987). Pesticide persistence on foliage. *Rev. Environ. Contam. Toxicol.*, **100**, 23–71.