Input pathways and river load of pesticides in Germany – a national scale modeling assessment

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Abstract A model has been developed which estimates the magnitude and the spatial distribution of pesticide losses from diffuse sources (surface run-off, tile drains and spraydrift) into surface waters for the entire area of Germany. The cumulative annual losses of 42 active ingredients applied to 11 field crops, orchards and vineyards are calculated for river basins in Germany based on grid maps with a resolution of 1×1 km^2. The model validation showed a sufficient degree of accuracy of the model results compared to measured pesticide loads in 13 small catchments. According to the model results the pesticide input from diffuse sources into surface waters amounted to 13.8 t in 1994 aggregated for the entire area of Germany. Input via surface runoff contributed 9.1 t while tile drainage was 1.4 t and spraydrift 3.4 t respectively. Alongside the model calculations empirical data of the pesticide load of rivers in Germany are presented. A comparison of the measured river loads with the modeled inputs from non-point sources leads to the conclusion that in most regions of Germany the largest portion of the load is due to the input from farm effluents.

Keywords Farmyard effluent; input model; non-point sources; pesticides; point sources; river load

Introduction

Water is one of the most valuable resources of today and so contamination of surface water resources with pesticides is a major issue in Europe. Pesticides are applied almost universally to municipal grounds, allotments, railtracks and in agriculture. By far the greatest contribution to the overall pesticide pollution of waters comes from agriculture, and in this study only this source has been taken into account. To facilitate the development of effective measures to minimize water pollution by pesticides originating from agriculture it is essential to know the relevance of the different input pathways.

In order to determine the importance of the various input sources three approaches have been employed.

(i)   A model has been developed with which the pesticide input into surface waters via run-off, tile drainage and spraydrift is estimated for the total cultivated area in Germany.

(ii) To gain an overview of the magnitude of point source contamination, results concerning the input of pesticides via point sources (sewage plants) in Germany were compiled from publications and evaluated.

(iii) Data for the total pesticide load of rivers in Germany were taken from monitoring programs carried out by the Environmental Agencies and water supply companies. These data were compared with the results from the model described in (i) for the individual river basins. From the relationship of the values obtained from the model for non-point sources to the total pesticide load, the contribution from non-point sources can be evaluated.

A consideration of the three approaches in combination facilitates a statement about the importance of the different input pathways for pesticide pollution of surface waters in Germany on a national scale.

Modeling of pesticide input from non-point sources

The modeling does not deal with risk assessment based on worst case assumptions, as is the case in the licensing of crop protection products. Instead the aim is to depict the actual situation of diffuse pesticide input for the entire area of Germany with a GIS-based model and a uniform calculation scheme. A set of digital maps of Germany, which contain information about land use, agroecological zones, soils, precipitation, frequency of storm events, drainage density, hydrographic network, etc., form the basis for the calculations. A database of the German Federal Environmental Agency (UBA, 1998) and compendia yielded information about the physical-chemical properties of the active ingredients (Koc, DT5O).

The modeling of the non-point input of pesticides into surface waters was then conducted separately for the three pathways: drainage surface run-off and spraydrift. Calculations were carried out for the 42 active ingredients with the greatest sales volume in Germany 1994. The quantities and the times of application of the 42 pesticides in each region were projected using a market panel (Huber *et al.*, 1998a).

Seepage water and drainage

The estimation of pesticide input into surface waters via tile drainage was carried out in two steps. Firstly it was calculated which portion of an active substance leached to a reference depth of up to 0.8 metre for the most frequent combinations of soils, climate and applicated active ingredients in Germany, based on the model PELMO (Klein *et al.*, 1997). Secondly, the area of tile drained cultivated land in agroecological zones was estimated. The input of pesticides by tile drainage was then calculated by multiplying the two results (details see Huber *et al.*, 2000a). For only six of the 42 active ingredients considered a notable input by tile drainage was calculated, amounting to a total of about 1,400 kg a^{-1} (Table 1).

A further leaching into groundwater and a possible input of pesticides into surface waters by outflowing groundwater were not taken into account. According to the current state of knowledge, pesticides in groundwater resources in Germany only occur locally. A widespread contamination of surface waters with pesticides by seepage of contaminated groundwater could not be observed.

Run-off

The model for the estimation of the outflow of active ingredients via surface run-off consists of four components (Huber *et al.*, 1998b).

- Determination of the probability of the occurrence of intense precipitation causing run-off A rainfall event is considered to produce run-off if it exceeds a volume of 10 mm in 24 h. For this purpose the German Meteorological Service provided maps on the relation between rainfall amount and rainfall duration.
- The mean time interval between the pesticide application and the intense precipitation event which is a function of the occurrence probability of the precipitation event and the dates of application.
- The run-off volume is determined using the SCS-CN-method for calculating high water flow modified by Lutz (1984) for German conditions.
- The calculation of the mean concentration of active ingredients (dissolved phase only) in the run-off is based on the GLEAMS model (Mills and Leonard, 1984) and Leonard *et al.* (1979).

For the entire agricultural land of Germany a surface water input via run-off of ca 9,000 kg a^{-1} active ingredients was calculated with the model (Table 1), the largest part of which was caused by arable farming. The highest specific outputs were calculated for active ingredients applied to row crops, in particular sugar beet. The model considers only the outflow of active ingredients in the dissolved phase. The estimation of the input of

pesticides by eroded soil material for the area of Germany would require the development of an erosion model with a high spatial and temporal resolution. Today the scientific basis for a procedure and input data are lacking for this purpose.

Spraydrift

The modeling of the input via spraydrift is founded on basic values of spraydrift supplied by Ganzelmeier *et al.* (1995). For field crops a mean distance to the body of water of two metres during the application was assumed and five metres for viniculture and orchards. The mean losses by spraydrift amounted to 0.58% of the active ingredients applied, 0.75% and 2.68% respectively for early and late treatment in viniculture, and 12.02% and 4.92% respectively for early and late treatment in orchards. Furthermore the input calculation via spraydrift requires assumptions about the mean drainage density, the width of ditches and rivers in the landscape units in Germany as well as the relative frequency of arable land adjacent to water bodies. In arable farming very low losses by spraydrift are calculated, typically 1–3 mg of active ingredients per hectare per year. In total, the input by spraydrift in arable farming approximates 90 kg a year for the entire area of Germany according to model estimations. In comparison: the input by spraydrift from fruit culture amounts to ca 3,100 kg. This higher input is limited to a few regions of Germany characterised by a high density of receiving bodies of water (e.g. the "Alte Land" in the north of Hamburg). In viniculture the input by spraydrift is estimated to approximate 120 kg of active ingredients a year.

Total of diffuse input

The eleven active ingredients that are responsible for the largest input of pesticides by drainage, run-off and spraydrift, calculated by the model, are shown in Table 1 in order of their total input quantities. According to the model approaches, a non-point source input of pesticides into surface waters of about 13,800 kg for the entire area of Germany is estimated for 1994 (a detailed description and maps showing the spatial distribution of the pesticide inputs with a grid resolution of 1×1 km^2 can be found in Huber *et al.*, 2000b, and Bach *et al.*, 2000).

Table 1 Non-point source input of active ingredients into surface waters in Germany according to model estimation (reference year 1994)

Active ingredient [a]	Tile drainage River input kg	Tile drainage Percentage of application quantity %	Run-off River input kg	Run-off Percentage of application quantity %	Spraydrift River input kg	Spraydrift Percentage of application quantity %	Total River input kg
Metamitrone	1	0.0	2,420	0.23	11	0.0	2,430
Isoproturone	950	0.04	1,280	0.06	20	0.0	2,250
Propineb	120	0.05	100	0.04	1,230	0.5	1,450
Ethofumesat	80	0.07	1,030	0.42	1	0.0	1,110
Dichlofluanide	110	0.09	380	0.25	390	0.25	880
Terbuthylazine	0		880	0.18	3	0.0	880
Mancozeb	0		5	0.0	780	0.2	790
Dichlorprop-P	0		630	0.05	8	0.0	640
Dithianone	0		12	0.0	550	0.4	560
Metolachlorine	0		510	0.18	1	0.0	510
Bentazone	110	0.03	300	0.10	1	0.0	410
Total (Σ 42 a.i.)	1,420		9,060		3,350		13,800

[a]) Extract from the list of the 42 active ingredients modeled with the largest volume of sales in1994

The largest influencing factors determining non-point source pollution are the applied quantities of the a.i., their time and method of application and their physico-chemical properties. The high input of Metamitrone, a common herbicide in sugar beet cropping, depends on the early application date (before sowing) when there is no plant cover to prevent run-off. Isoproturon, the most commonly applied active ingredient in agriculture in Germany, also contributes a large proportion to the total non-point source contamination. The highest specific emissions are calculated for the a.i. Propinep via spraydrift with 0.5% of the application quantity and for Ethofumesat via run-off with 0.42% respectively. The high input of Propinep is primarily caused by the air blast application, while Ethofumesat is a very persistent and mobile substance compared to other herbicides.

However, these results are highly dependent on the assumptions on which the model is based. For example, a variation of the respective Koc and DT5O value of an active sub-stance of ±50% changes the quantity of the input according to the model by ca ±50%. In total, the error distribution of the modeling result varies within this range.

Comparison of modeled surface water input versus measured pesticide loads in catchments in Germany

The quality of a model is commonly assessed by a comparison of the model results with empirical data. Because the model is set up to calculate the annual load, only measurements (of pesticide loads in rivers) that have been taken over a long period of time (one year) can be utilized for a comparison. Therefore only long term catchment studies should be used to prove reliability of predicted losses. Additionally, experimental data should cover the main application periods as well as the most frequently applied a.i. and the rivers have to be sampled at least once per week during the application periods.

At present, monitoring data sets from only 13 German catchments fulfill these require-ments. Values of the measured pesticides in the 13 catchments compared to the modeled diffuse input are shown in Figure 1. In most cases model results seem to match the magni-tude of pesticide pollution in surface waters: of the 64 data points in Figure 1, 47 modeled results stay within a range of 10%–1000% (one order of magnitude) of the measured result,
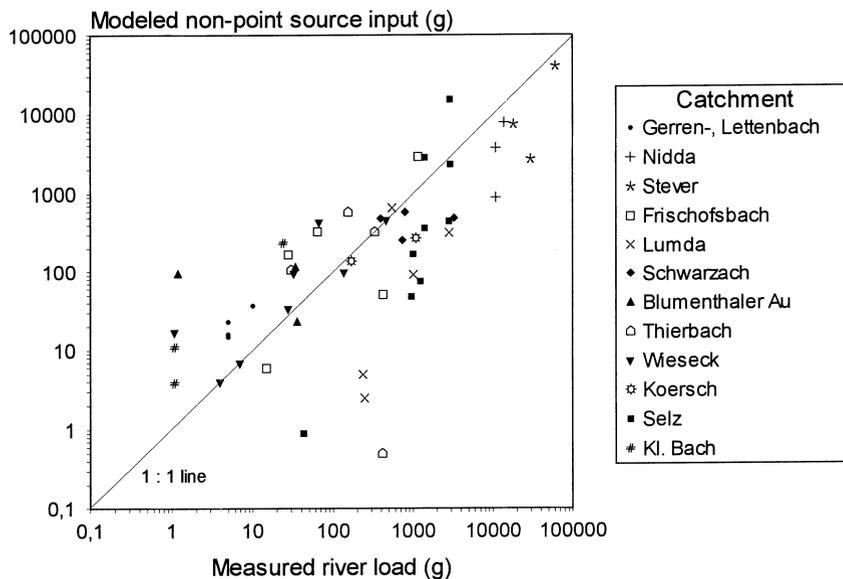

Figure 1 Model validation: comparison of modeled diffuse input versus measured river load of active ingredients for 13 river catchments in Germany (catchment data see Bach *et al.,* 2000)

Table 2 Load of active ingredients in the effluent of treatment plants with connected farms (results of seven studies regarding the input of pesticides from farm outlets and treatment plants in Germany; Bach *et al.*, 2000)

Region	Nidda river basin	Middle Hesse		Bavaria		Baden-Wuerttemberg	Muensterland
Study object (TP = treatment plant)	28 TP	4 TP	TP Hachborn[a]	1 rural TP	TP Nellingen	receiving watercourse Weiherbach	3 washing places
Period	4–5/94	9–11/96	3–12/97	3–10/96	6/95–5/96	4/93–5/94	3/94–2/95
Farms connected	ca 1,640	141	164	61	19	10	3
Total input		g of a.i. per farm (calculated) during sampling period					
Mean	32	8	80[a]	6	3	3	54
(min–max)	4–80	5–12					9–88
Number of a.i.	33	3	4	7	10	1	13

[a]) including the estimafion of the load from rain spillways

which seems to be a sufficient degree of accordance. However, it is not possible to validate the prediction accuracy for a single pathway because no study listed loads for each pathway separately. Looking at the distribution of the points in Figure 1 it seems reasonable to assume that the model tends to underestimate loads in those catchments where measured pesticide pollution exceeds about 100 g a^{-1}. A possible explanation is that the contribution of point sources to the total river load is more relevant in larger catchments, while in small catchments point sources are often excluded by the selection of monitoring sites.

Results from the input of pesticides from point sources

To gain an overview of the magnitude of point source contamination, results concerning the input of pesticides via point sources (sewage plants) in Germany were compiled from publications and evaluated. Several studies have been conducted in Germany to determine the amount of pesticides which are discharged into waters by farm outlets via treatment plants (Table 2). These pesticides are chiefly released when cleaning sprayers or by discharging the remaining spray solution onto paved farmyards. This waste water contaminated by pesticides is then discharged either into the sewage system or directly into a receiving body of water by precipitation or by rinsing water.

In the course of five studies the effluent of thirty-five treatment plants was analysed, in one study (Hachborn) the load from rain spillways was also taken into account. The load of active ingredients observed in the effluent of the treatment plant was apportioned to the number of farms connected to the treatment plant. This quotient gives an impression of the magnitude of the specific pesticide input per farm. The results of the total load of active ingredients calculated per farm are shown in Table 3.

The load of active ingredients calculated for the respective farms turns out to be extraordinarily heterogeneous, ranging from 3 g per farm to ca 80 g per farm. Possible explanations for this extreme range of the results are differences in the technical condition of the sprayers, the cropping structure of the farms, the knowledge of the users of the sprayers, and the height of retention of active ingredients in the treatment plant. Numerous other factors may also influence the results obtained. The specific causes of the respective results cannot be gathered from the monitoring. Due to the enormous variability of the results it seems inappropriate to deduce a *mean value* for the emission of pesticides from treatment plants and to carry out an extrapolation for the point source pesticide input into rivers for the entire area of Germany.

Load of active ingredients in river basins in Germany

In a third approach to estimate the relevance of pesticide pollution from point sources, empirical data of the pesticide load in rivers were compared with the results of the non-point sources input obtained from the model. From the relationship of these two values the proportion of both input sources can be evaluated. Analysis data of pesticide concentrations in rivers in Germany for the period of 1993 to 1995 were taken from monitoring programs and collected for 57 stations which had been sampled at least once a month. Based on these measurements of concentration and the run-off volume of the appropriate gauging stations active ingredients loads were calculated.

However, these loads showed an extraordinary heterogenity

- for identical stations between the years of sampling,
- for identical stations using different methods of load calculation,
- for adjacent stations (with almost identical catchments) for the same year,
- for the proportions of the load of selected active ingredients (e.g. Atrazine – Desethyl-Atrazine), which are expected to occur in a relatively stable volumetric ratio.

In general, these variances are due to an insufficient measuring method. The concentration graph of active ingredients of pesticides is highly variable in time. Statistical considerations show that thirteen or even twentyfive random samples a year are not sufficient to allow adequately precise determination of such a time-variable quantity. Further reasons are errors in the determination of river discharge and pesticide concentrations as well as different detection limits (= DL) in pesticide analyses. After a critical review, only stations corresponding to one of the following criteria were selected for the calculation of the *valid* active ingredients load:

- minimum of forty random samples a year (majority> DL), or
- continuous measuring (composite samples) over the period of a full year.

Table 3 Annual load[a] of active ingredients (in kg a^{-1}) in German river basins 1994

River	Rhine	Main	Nidda	Ruhr
Monitoring station	Köln	Bischofsheim	Praunheim	Westhofen
Catchment area	141,000 km^2 [b]	27,000 km^2	1,900 km^2	1,900 km^2
Dates of observation	95 . . . 106	25[c]	26[b]	52
2,4-DP	820		17	0
Atrazine	6,720	570	2	2
Desethyl-Atrazine	3,670	550		14
Bentazone	1,130	190	11	<DL
Isochloridazon	1,290			<DL
Chlorotoluron	440	50	1	<DL
Diuron	2,620	750	33	19
Fenpropimorph			21	
Isoproturon	6,110	1,150	49	42
MCPP	1,070		27	6
Metazachlor	50	12	1	<DL
Metolachlor	340			<DL
Simazine	1,810	40		1
Terbuthylazine	850			3
Total amount	20,900	3,300	140	110
Number of a.i.	20	10	8	34

[a]: annual load = 364/n Σ c_i*Q_i ; [b]: incl. ca 28,000 km^2 outside Germany;
[c]: composite samples; DL: detection limit

Table 4 Loads[a] of active ingredients (in kg a^{-1}) in river basins in Germany and estimated percentages from diffuse and point sources (reference year 1994)

River	Rhine	Main	Nidda	Ruhr
Monitoring station	Köln	Bischofsheim	Praunheim	Westhofen
Total load[a] measured	12,110	1,400	107	71
Subtracted load from non-point source input (according to model result)	–990[b]	–100	–18	–21
= Calculated load from point input	11,120	1,300	89	50
Percentage of point sources (calculated) of the total load	92%[b]	93%	83%	70%
Number of active ingredients	16	4	6	21

[a] From the a.i. listed in Table 3 only the a.i. were mentioned which we are registered in 1994 and used in agriculture.
[b] Non-point source input outside the German part of the catchment was not taken into account

In Germany the above-mentioned criteria are met only by four monitoring stations and river basins respectively. For these monitoring stations the annual load is shown in Table 3. When comparing the active ingredients load of the four river basins, it should be taken into account that:

(a) the monitoring programs for the four different stations do not cover the same set of active ingredients;

(b) the load decreases proportionally to the size of the river basin, the reason for which is the degradation of an increasing portion of the load due to the length of the watercourse.

Percentage of the load from diffuse and point sources

To assess the importance of point sources for the four river basins in Germany with a valid result of the pesticide load the amount of diffuse input of an active substance in the river basin as far as monitoring station was calculated using the respective model approaches. This result was then subtracted from the measured load. The difference thus obtained is ascribed to the input from point sources (Table 4). In this connection not only farm effluents via treatment plants are considered as point sources but also rain spillways and the inflow from production plants.

As shown in Table 4 the percentage of the input from non-point sources (based on model estimations) in the four river basins ranges from 30% to 7% of the total load of each of the active ingredients measured. Accordingly, the percentage of the input coming chiefly from point sources amounts to 70% to 93%. Even if an error range of ±50% for the modeled pesticide inputs via run-off, tile drainage and spraydrift is assumed, the evaluation obtains that water contamination with pesticides in the four river basins is dominated by point source inputs.

Conclusion

The results of the modeling can only be taken as tendencies because of the chosen scale and the uncertainty of the input data. The model is not suitable for producing results on a small, local scale but rather for catchment areas of at least several hundred square kilometres where meaningful results can be obtained. Nevertheless the approaches of the model are sufficiently plausible and sound to estimate the non-point source input into rivers or surface waters on a regional scale. The modeled non-point inputs stay on a relatively low level. According to the modeling results surface run-off is the major source of diffuse pesticide input in Germany. Non-point source input via tile drainage is far less important and spray-drift is only an issue in specific orchard regions.

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The crucial issue in the development of concepts to improve water quality is the determination of the most important input pathway of pesticides into waters. The presented results indicate that on a national scale point sources are of major concern compared to non-point source input of pesticide from agriculture in Germany. This outcome agrees with the results in a few small catchments in Germany where the importance of the input from treatment plants compared to diffuse input of pesticides into surface waters has been determined directly (Seel *et al.*, 1996; Bach, 1997). These studies have shown accordingly that the load was principally due to the input of pesticides from treatment plants. The percentage of diffuse input was in most cases below 10%. With the current state of knowledge, it has to be assumed that in most regions of Germany the largest portion of the load is due to the input from farm outlets. To reduce this kind of input, reliable and efficient concepts for an improved advisory service are available which could be realised immediately (Frede *et al.*, 1998).

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