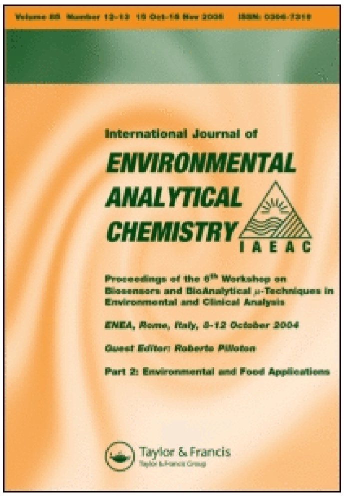

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Balancing the Fate of Terbuthylazine in a Water Catchment Area by Immunochemical Screening

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BALANCING THE FATE OF TERBUTHYLAZINE IN A WATER CATCHMENT AREA BY IMMUNOCHEMICAL SCREENING

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The extensive use of a Geographical Information System fed with analytical data gathered by immunoassays is described. The aim of the study is to elucidate the entry paths of pesticides into surface waters. The study area is characterized by sandy soils and extensive cattle breeding. Terbuthylazine, a maize herbicide of the triazine type, was selected as a model substance. The judgement of the contribution of different paths was partly based on evaluation of thematic maps set up by a Geographical Information System (GIS). The GIS was also used to achieve representative sampling, storage and handling of data, calculations and display of spatial residue information. A time-saving and cost-effective screening method for soil samples has been applied consisting of an aqueous extraction step and immunochemical measurement (ELISA). It is shown that this approach yields adequate information to judge the contribution of different migration paths of the herbicide into surface water.

Keywords: Herbicide; immunoassay; soil residue; screening; GIS; surface water

INTRODUCTION

The Frischhofsbach, a small creek, is a tributary of the Ems, lain 40 km north of Münster. The sandy aquifers in this region represent excellent ground-water occurrences. When the water needs of the surrounding municipalities grew the water supplier started with ground-water enrichment to preserve sustainability of its ground-water management. At times of high water part of the creek water is pumped to the waterworks and fed to the aquifer via infiltration bassins. This water reaches the wells at the earliest after 50 days of underground passage. Nutrients and xenobiotics that are not removed by this lead to degradation of the

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filtering layer, ground-water pollution and finally contamination of drinking water. The study area is the 32 km^2 catchment area of the surface waters upstream of the withdrawal site, however, not a water protection zone. Since 1986 the water quality is checked by continuous nitrate measurement and weekly sampling for pesticide determination. Problems with the nitrate concentration level showed up soon. To escape the whole water catchment area being declared a protected water gathering grounds in 1989 a cooperation of the water-supplier and the farmers in the area was founded.

From 1990 on the maize herbicide atrazine and later on its successor terbuthylazine and the cereals herbicide isoproturon were detected. To reduce input and loads in the creek, the cooperation set up some strategies such as reduction of the overall use of pesticides (e.g. by development of mechanical procedures), reduction of direct input (e.g. by boundary strips) and pesticide management (e.g. use of combined products). In spite of the measures taken and of declining atrazine concentrations after its ban in Germany in 1991, an increase in terbuthylazine loads occured. It was hypothesized that even by the use of the herbicides according to good agricultural practice, leaching into ground-water and subsequent discharge into the surface water might be the main contamination path of the creek. It is the aim of this study to elucidate the role and extent of the different paths.

MATERIALS AND METHODS

Terbuthylazine is a maize herbicide used extensively in Germany after the atrazine ban. It is less polar than atrazine and slightly less soluble.

GIS

A *G*eographical *I*nformation *S*ystem (GIS), the vector-oriented AtlasGIS™ by Esri Inc., was used to store, manipulate and visualize the variety of data required for calculating the residual masses, loads and fluxes in the soils of the area. For handling the data a relational database was created. To establish a geographical relationship of parameters governing the input of herbicides into surface waters, topographical maps, use maps, soil type maps, maps containing sampling sites and others were produced in the GIS starting from conventional maps available and manual input of data into the database. To analyze the data internal algorithms are applied such as data selection, generalization, data linkage, combination of layers, calculation of areas, counting and basic statistics. As an example superposition of an agricultural use map with a soil type map gives a new map with the fields subdivided in areas of identical soil type. The influence of soil type and soil texture on the residual behaviour of pesticides in soil has been described extensively, triazines being affected most by the organic carbon and clay content of the soil [1,2,3], which yet is far from constant within the plot and the profile [4].

HTS/ELISA

Residue data on terbuthylazine was gathered by a *H*igh-*T*hroughput *S*creenig (HTS) based on field sampling, aqueous elution of the herbicide and immunochemical measurements. The determination of terbuthylazine in aqueous samples was achieved by a heterogeneous competitive enzyme immunoassay (ELISA) using monoclonal antibodies (designation K1F4, refer to [5]). The procedure has been described elsewhere [6–8] and validated [9]. Water samples (ground-water, surface water) were centrifuged or filtrated, measured directly in triplicate and repeated if the relative standard deviation exceeded 15 %. Positive and negative controls were included on each microtiter plate. The detection limit was 0.03 μg L^{-1}. A weekly 2 L-sample of the surface water was enriched by a factor of 1,800 using solid-phase extraction on LiChrolut® EN (Merck, Darmstadt, FRG) and submitted to GC and HPLC analysis to verify the results and to determine all known degradation products of terbuthylazine.

On “screening sites” (see below), soil samples were taken from the plough layer (0–30 cm depth) and subsoil (30–60 cm and 60–90 cm). Sampling was done by a motor driven drilling device at 20 positions in each field. The samples were thoroughly mixed, subdivided in the field and stored in cooling boxes until transport to the lab.

The 10 × 10 m plots at the “model sites” (cf. below) were sampled using a common sampler of about 2 cm in diameter. Each drilling core of 90 cm was subdivided in 10 cm parts. The samples from 5 (later 3) drillings were combined to a single sample, homogenized in polyethylene bags and taken immediately to the lab.

The extraction of the herbicide from soil samples was done by an aqueous elution procedure set up before and evaluated to be suited to this purpose [10,11], i.e. to determine only the leachable, easily desorbable, mobile herbicide fraction [12]. In fact in samples of different soil types the recoveries may vary largely [13] and are inversely correlated to the time passed since application [14]. We found that the recovery of the aqueous elution was between 50 and 100 % and was negatively correlated to the organic carbon content of the soil. In brief, to 5.00 g of the dried (40°C) and sieved (2 mm screen) sample in an all-glass bottle, 50.0 ml of ultrapure water was added and the mixture rotated for 24 h. 10 mL of the samples were centrifuged and measured directly or after appropriate dilution with water. The detection limit of readily desorbable terbuthylazine in soils was 0.3 μg kg^{-1} of dry soil.

RESULTS AND DISCUSSION

Possible migration paths

Figure 1 summarizes different migration paths of herbicides to surface waters. Apart from these paths the countercurrent mechanisms of elimination by losses to the atmosphere and metabolization/mineralization in air, water and soil have to be judged. Two paths will be considered as of no importance: spraying over water and input via sewage. No hints on such point sources have been detected. Volatilization and redeposition has to be considered, but is not a major path with triazine herbicides [15,16]. Of greater importance could be spray drift and the formation of aerosols from treated soil particles. Dankwardt et al. [17] found up to 3 μg L^{-1} of terbuthylazine in rain water samples of rural areas, but also measurable concentrations at distant locations. An atrazine input of up to 80 μg m^{-2} y^{-1} [18] resp. 16 μg m^{-2} within 7 months [19] was calculated. In the following yet the soils that received the herbicide during application will be considered the only source for the contamination of the creek.

The variables governing solute flux in the soil can be subdivided in several groups [20]:

a. regional variables	constant (or set constant) over the entire area, e.g. rainfall, evapotranspiration
b. spatial variables	constant value within a restricted domain, e.g. area of similar soil type, individual plot
c. local variables	point data, e.g. data based on measurements at a model site
d. derived variables	based on a discrete value of another parameter, e.g. sorption depends on soil type

Regional variables: information retrieval

Water balance

Rainfall, evaporation and temperature were considered constant over the entire region. In the 32 km^2 area there are of course inhomogenities in these parameters. For the purpose of this study it seemed sufficient to take only the data of one

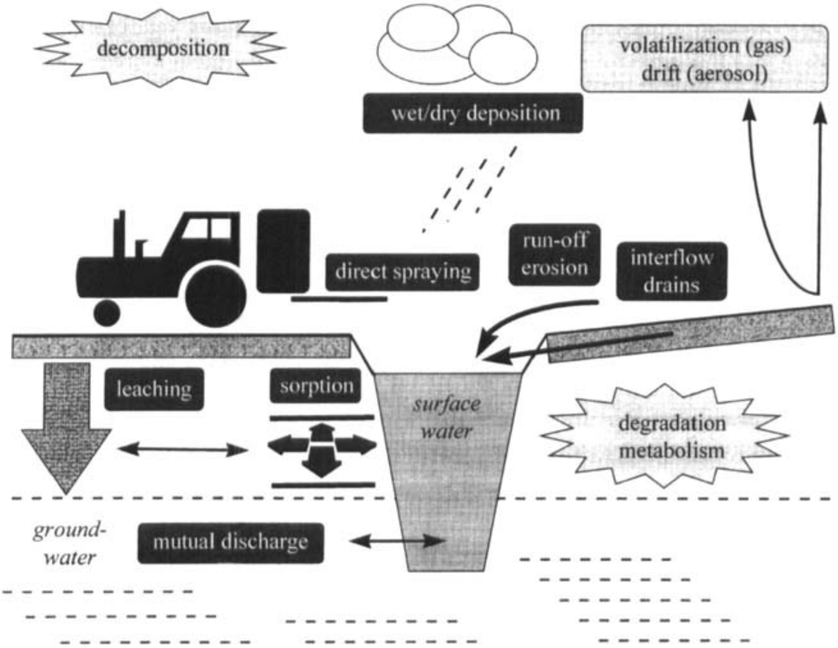

FIGURE 1 Migration paths of herbicides to surface waters. White: paths for pesticide input; black: countercurrent mechanisms of pesticide elimination

climatic station situated near the waterworks half way the length of the catchment area. The mean annual precipitation at this site is 770 mm. The study year 1995 showed 887 mm of precipitation due to a humid winter 1994/95 and 1996 was extremely dry with 573 mm of precipitation. The leachate of a pasture lysimeter was used to judge ground-water recharge and evapotranspiration. The lysimeter ran dry from July 95 to the mid of January 1996 to give seepage water of only 161 mm in this period. On the whole the ground-water recharge from precipitation under arable land thus was estimated to be less than 150 mm in the period studied.

Use pattern and pesticide input

The 3200 ha area was mapped out for the years 1995–1997 and transformed into a thematic map "use". With the GIS area calculations are done easily afterwards. The changes in use pattern were less than 1 % from year to year due to crop rotation. Arable land makes about 80 % of the study area, with 30 % maize, 27 % cereals and 20 % pasture or fallow land. All other cultivars sum up to less than

2 %. 12 % of the area is covered by woods, 3 % are open water tables, the rest is sealed territory (roads and settlement). Maize is planted every year or every second year to the same field. The GIS counted about 355 different maize plots (986 ha) and 295 cereal plots. For 12 % of the maize plots the herbicide application was revealed by the farmers. 75 % of the plots were treated with combined herbicide products ("packs") containing terbuthylazine. The average dose was 500–750 g ha^{-1} a.i. giving a total input of 370–550 kg of terbuthylazine in the area. In 1995 the application was between May, 19 and May, 24, in 1996 from May, 29 to June, 12.

Spatial variables: Evaluation using GIS-prepared thematic maps

Spatial data was derived from thematic maps. A morphological map revealed the flat relief of the area. At first sight erosion and run-off seem not to be a common problem of the study area. Nevertheless erosion grooves that reach the creek were observed temporarily. Figure 2a shows 2 other thematic maps of the region. Figure 2a points out the spatial distribution of the ground-water level below ground. Most of the soils are affected by ground-water at least during part of the year. The average level is 40–80 cm. The maximum levels are reached from February to April, the minimum from July to October. Subsurface drainage systems are required in such soils. Tubes were placed in 80–100 cm depth within about 20 % of the total area. Ditches along the fields collect the drainage water. So the creek, being a small waterbody that crosses the area at 11 km length with a maximum extension of 3 m forms a network of ditches of about 100 km length and a density of 30 m ha^{-1} covering 2.8 % of the area (Figure 2b). As pedological maps are often the only spatial information available on soil characteristics, soil types and their texture were taken from such maps with different scales and resolution and turned into a GIS map that allows for reading the soil type of each individual plot.

Local variables: sampling and measurement

Screening

In order to get spatial information on a large area, the design of the sampling program is crucial. From 1995–1997 we joined a program sampling for residual mineral nitrogen in the soils of maize fields which is performed by local authorities. The plots were selected practically at random. As the sampling campaign took place from mid of May to mid of June, part of the 147 fields sampled ("screening sites") had not been treated with a herbicide at that time. In autumn,

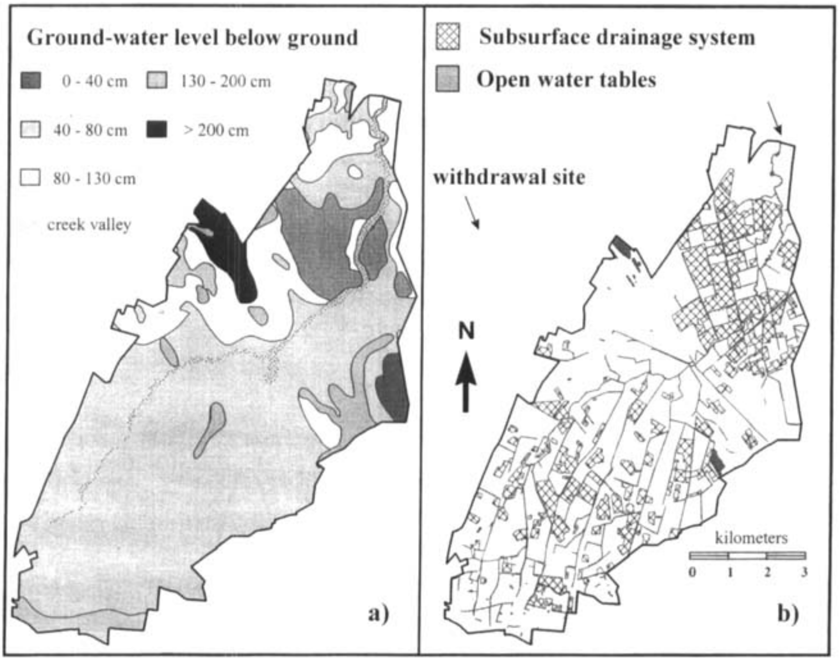

FIGURE 2 a,b Thematic maps of the study area. a) Water regime of the soils; b) Water-bearing systems in the region

after harvest, the sampling was repeated but only on 46 plots. Figure 3 shows the results of the 1995 campaign on the screening sites that were sampled twice a year. The mass concentrations were sorted, their logarithm calculated, the range of the results divided in uniform classes. The plot gives a histogram of the abundances. The logarithmic scale allows to show samples from fields treated recently and not treated in the study year ("non-treated") in the same diagram and prevents the "peaks" from distortion during the decline of the concentrations. The topsoil histogram from May 1995 shows a bimodal distribution of concentrations. The right peak corresponds to treated fields while the left distribution covers concentrations of non-treated fields. At the 95 % confidence level, fields with concentrations > 12 $\mu g\ kg^{-1}$ were classified as treated, and < 7 $\mu g\ kg^{-1}$ as non-treated. The number of fields corresponding to each peak is almost the same due to the sampling parallel to the spraying season. The distance of the maxima are close together due to the low concentrations even on treated fields. As the input from application could be 500–750 $\mu g\ ha^{-1}$ a.i., with a mean soil bulk density of 1.3 kg dm^{-3}, a maximum expectable concentration of 128–192 $\mu g\ kg^{-1}$

can be calculated. The mean value found here for easily desorbable residues is only 12–17 % of this theoretical value, mainly due to degradation, adsorption and incomplete extraction. The low but measurable residues indicate a treatment in the year(s) before or an input from spray drift. Atmospheric deposition, even assuming a value of e.g. 120 μg m^{-2}, would lead to residues below the detection limit. 4 months later our mathematical procedure was no longer able to distinguish treated from non-treated fields as the peaks fall together at a mean concentration of 4.2 μg kg^{-1}which could result from the two distributions shown. From the subsoil samples almost the same background concentration as in the top soil can be derived. The decline in concentration at this level until harvest is very small.

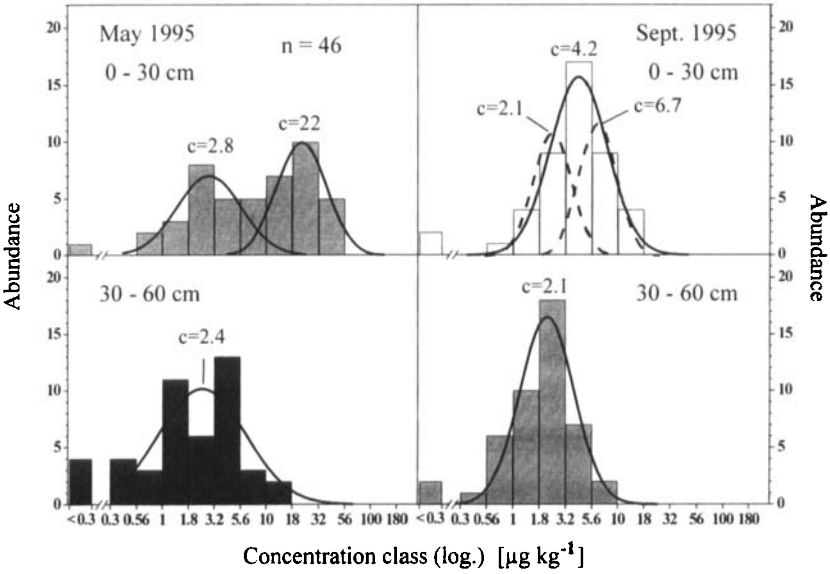

FIGURE 3 Histograms of terbuthylazine mass concentrations. Classified data from 46 screening sites; columns: sampling times; rows: sampling layers. Note the logarithmic concentration scale

In 1996 the screening was repeated with 135 maize fields sampled from mid of May to mid of June. 41 of the fields were sampled twice a year. The results from the 135 plots were not significantly different from those with the lower number. The results were well comparable to the 1995 sampling. In spring the treated fields had a mean residue of 16 μg kg^{-1}, the non-treated of 2.4 μg kg^{-1}. The concentrations declined to 5.3 and 1.6 μg kg^{-1} respectively. The subsoil mean with 4.5 μg kg^{-1} was slightly higher than in 1995 but declined to the same level until harvest (1.9 μg kg^{-1}). Another 41 samples from the 60–90 cm depth showed almost the same mean of 1.7 μg kg^{-1}. The mean concentrations of soils from treated fields was even lower than in 1995 but more treated fields (2/3 of all samples) had been sampled due to the later sampling.

Profiles

For the year 1996 model sites were selected to study the distribution of the herbicide in the profile in more detail and at 2-week intervals between application and harvest. The sampling sites ("model sites") had to be geographically referenced so they could be found again at each sampling date. Furthermore the whole set of sites should form a regionally representative soil measuring network. Both requirements were achieved by using the GIS. As an entity governing sorption, degradation and leaching, the soil type was chosen. At first, a generalization of soil types had to be done, because some of the 18 different soils were only present at a few sites. Then the model sites had to be distributed among these aggregated groups of soil types. Table I shows the results of these considerations. The Gleyic Podsol is the major soil type of the area followed by Orthic Podsol and Orthic Gleysol. Each group includes soils with different textures (sandy loams, loamy sands, etc.). The model sites were distributed – if possible – among the groups according to their area percentage to give a geostatistical sampling scheme (Table I).

TABLE I Assignment of the 19 experimental model sites to soil groups dominated by different soil types

Dominant soil type	*Area Percent [%]*	*No. of model sites**
Gleyic Podsol	41	3 M, 2 C, 1 P, 1 W
Orthic Podsol	20	2 M, 1 P, 1 W
Orthic Gleysol	17	2 M, 2 C
Plaggen Soil	8	2 M
Dystric Gleysol	4	1 M, 1 C
"no soil"**	10	–

* M = maize, C = cereals, P = pasture/fallow, W = wood
** roads, settlement, water, bog

Figure 4 shows exemplarily the depth distribution of terbuthylazine residues in 10 cm layers of one model site. The layer of 0–10 cm could not be drawn on the same scale. The field had been treated with terbuthylazine only a couple of days before. The soil is a Dystric Gleysol, its texture is of a loamy sand. The graph indicates that most of the herbicide stayed in the upper 10 cm of the soil column and was rapidly degraded there.

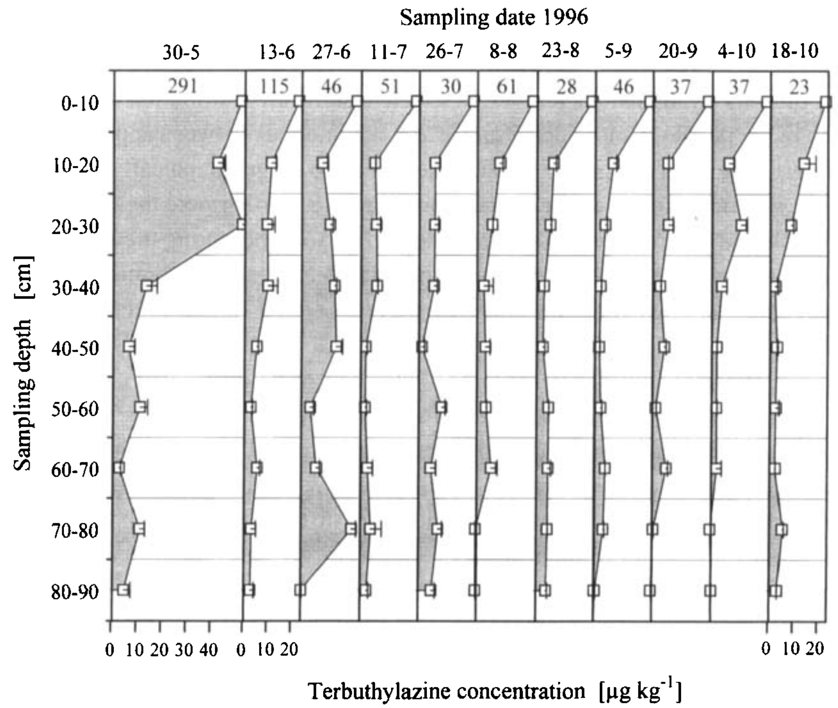

FIGURE 4 Depth profiles of terbuthylazine mass concentrations. Data from a model site (Dystric Gleysol). Note the different scaling for May, 5. The 0–10 cm layer is given by numbers. Error bars: 2 sd

The relatively low concentrations in the subsoil in autumn and the results from the screening sites indicate that the concentrations in the subsoil at the first sampling date are a consequence of the recent application. During the whole observation period, pesticide was present in almost any sample.

Derived variables: calculations and modelling

For a better insight in the processes governing leaching in the soil, the analytical data has to be analyzed by models. Assuming that disappearance of the herbicide in the soil layers of the screening sites conforms to first-order kinetics, the time for 50 % of the pesticide to disappear (DT_{50}) can be calculated. The DT_{50} values in 1995 for the 0–30 cm layer were 82 days for the residues in treated fields and 338 days for the low levels on non-treated ones. In the subsoil the DT_{50} increased to 734 days. The respective times in 1996 were 89 days for treated fields, 240 days for non-treated and 113 days for the subsoil residues. The subsoil samples seem to be unaffected from the upper layer, showing no distinct input from above and no significant further degradation of residues. This may be, however, a consequence of a combined leaching and degradation behaviour of residues from the upper layer. The data also shows the decrease in degradation rate with depth and age of residues. This is also an important hint with regard to mobility. Pätzold and Brümmer attributed decreasing mobility to the fact that the distribution coefficient between adsorbed and dissolved residues increased with time [21].

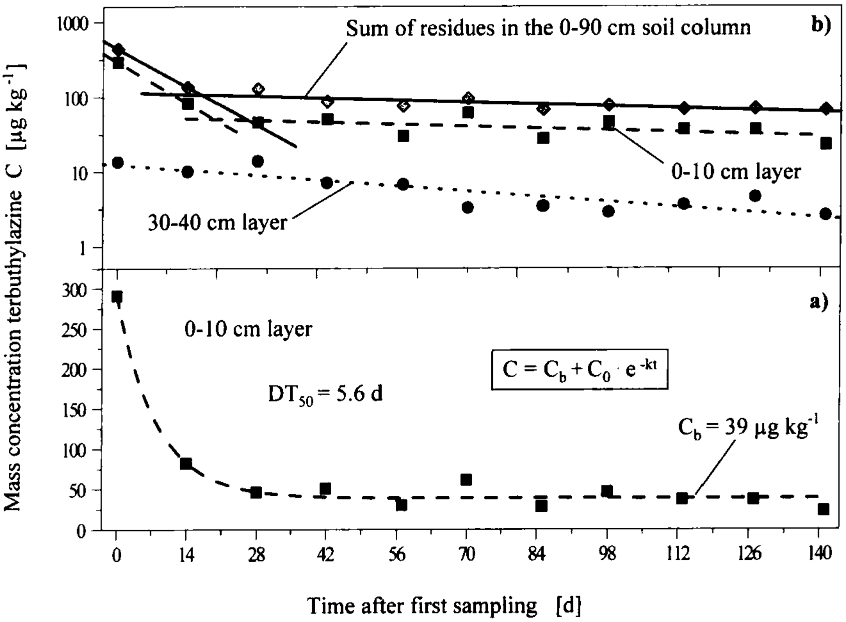

FIGURE 5 a,b Decline of mass concentrations of terbuthylazine in soil with time. Data from a model site (Dystric Gleysol). a) linear concentration scale; b) log. concentration scale. The correspondig DT_{50} values are: 0–10 cm: 7.7 and 159 d, 30–40 cm: 59 d, 0–90 cm column: 8.2 and 158 d

Figure 5 is a plot of the concentrations in the 0–10 cm soil layer at this model site. In Figure 5a the rapid decrease in concentration in the first two weeks is followed by an almost asymptotical behaviour. Assuming first-order kinetics with the formula given in the figure, an ordinate off-set of 39 $\mu g\ kg^{-1}$ representing a "non-degradable" residue can be calculated which is, however, improbable. The DT_{50} value obtained by fitting an exponential decay kinetic to the data is 5.6 days. To analyze for the kinetics more precisely the data was reassembled in Figure 5b. Plotting the concentrations on a logarithmic scale against time reveals two phases. The decrease in concentration is rapid at first, then a crease is observed to link data more or less close to a linear course. Time courses of this type have been reported before [22]. Pätzold and Brümmer [21] also found that the level of remaining residues on a long-term scale (4 years) was best represented by two combined exponential functions for the fast and slow degradation rate. The first-order half-lives were derived from the slopes of the lines of best fit obtained by linear regression analysis of the logarithm of concentration against time after application. The respective DT_{50} values are 7.7 days and 159 days respectively. Interestingly the decrease of the sum of the herbicide residue in the 90 cm soil column follows nearly the same kinetics giving DT_{50} values of 8.2 days and 158 days (Figure 5b, upper curve). As an example for the degradation rates at lower levels the course for the 30–40 cm layer is represented, too (Figure 5b, lower curve). The crease is not noticeable and the decline follows a steady first-order law with a respective disappearance time of 59 days. Walker et al. [23] calculated a change in rate with temperature change of 10°C of 2.4 and a strong influence of the nominal matric potential (factor 2.7 for a decrease from –200 to –1500 kPa) for atrazine. So a lower degradation rate should be observed in the 30–40 cm layer. This is only true for the first 2 weeks, afterwards the decline seems to remain at this level and thus is faster than in the top soil or in the whole column. As the DT_{50} does not account only for degradation we ascribe this fact to some leaching of the herbicide to lower levels. If the data from the model site and the screening sites is comparable, the half-lives of mobile terbuthylazine residues seem to be about 8 days immediately after application, then after about two weeks increase to about 80 days, become about 160 days during summer and after a year they range in the dimension of one year. In the subsoils the half-lives are longer, ranging from 60 days (probably due to leaching) to about 2 years. The DT_{50} values reported in literature for terbuthylazine are 30–90 days [24]. In the field different values for different soil horizons have been reported: 14–40 d (top soil), 350 d (40–70 cm), > 600 d(110–160 cm) [25]. In a sandy soil in field lysimeters DT_{50} values between 14 to 42 days were observed [26]. This indicates that the data from our study area fits in the range of literature data.

Estimating different contributions to river loads by rating curves

Figure 6 shows the hydrograph of terbuthylazine residues in the creek at the withdrawal site in the first sampling year. The herbicide cannot be detected at the beginning of the sampling of May, 9, 1995. It immediately appears with the beginning of the application period, the concentrations exceeding the limit of 0.1

$\mu g\ L^{-1}$ of the European Union for drinking water. In this season, the subsoils are saturated with water and most of the precipitation passes the soil column. The flux in the river was high in early spring and peaks with rain events, declining slowly, thus indicating that besides from run-off there is a ground-water component in the creek water due to effluent situations in the subsoil. Even with moderate concentrations relatively high loads of the pesticide of 2.5 g d^{-1} are reached due to the excess of water. The highest concentration was determined some time later when there is no more seeping water observed at the lysimeter station. The high concentration results from a lack of dilution. During summer heavy rainfall with more than 20 mm a day may cause run-off and input of terbuthylazine in the creek, as it may be the case with the peak on August, 28 and for some events in November, too. Moderate run-off cannot cause significant herbicide transport at this stage because the binding of the herbicide increased during summer and the concentrations usually measured in run-off are low [27]. In winter no transport of herbicide could be observed first. The soils were frozen until a storm event on February, 12 caused an enormous flush run-off from the fields as is shown by the sharp and rapidly declining flux peak on the same day. This amount of water was able to carry sediment to the creek and even with concentrations of only about 0.2 $\mu g\ L^{-1}$ the terbuthylazine load carried by the creek reached its maximum of 4 g d^{-1}. Subsequent flux peaks probably resulted from thawing of the soils because their decline is much slower and the lysimeter shows a distinct increase in seeping water. As a consequence of dilution the concentrations in the creek are not so high at this time but the carry-over of terbuthylazine is still considerable, stressing the fact that there is a need not only to determine pesticide concentrations in the rivers but also to calculate loads from hydrological data [28]. The integration of the area below the rating curve allows to calculate a rough estimate of 28 g as the amount of terbuthylazine carried out of the catchment area by the creek.

CONCLUSIONS

The overall input of terbuthylazine to the area had been calculated to 370–550 kg. So the 28 g carried by the creek is less than 0.1 ‰ (0.005 – 0.008 %) of the herbicide. This means an elimination rate of 99.99 % as required by the clearance procedure. Frank et al. [29] observed an input of 0.3–0.6 % of atrazine into ground-water in their flat catchment area where run-off was less than 0.01 %. Yet, 76 % of the herbicide applied did not show up in any of the elements of their balance. Of course it is well known that disappearance does not always mean

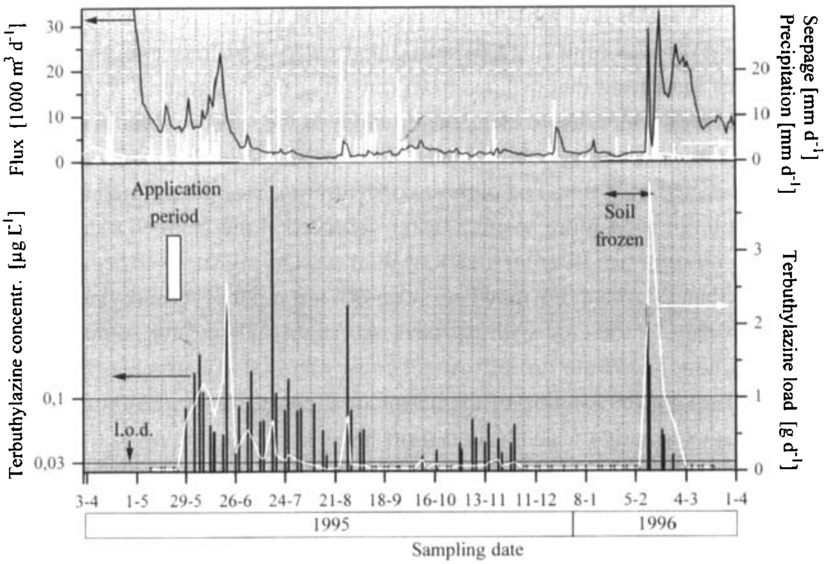

FIGURE 6 Hydrograph of the creek studied, 1995/96. Upper diagram: precipitation (white columns), seepage water at a pasture lysimeter station (white), flux of the creek (black). lower diagram: concentrations of terbuthylazine determined at the withdrawal site (black columns), calculated terbuthylazine loads carried by the creek (white)

mineralization but also strong sorption to soil constituents or formation of bound residues. Assuming a best case scenario from our data a residue of around 1.7 µg kg^{-1} can be found in nearly all samples of maize fields to a depth of 90 cm. With the mean bulk soil density of 1.3 kg dm^{-3} a content of 2 mg m^{-2} or 20 g per hectare in this 90 cm-layer can be calculated. The 150 L of seeping water passing the soil column under each square meter will thus become loaded to a concentration of 13 µg L^{-1}. On the total of 986 ha of maize the residue of 20 g ha^{-1} would give around 20 kg of residual mass of the 370–550 kg of herbicide applied (4–5 %). 450 g would be sufficient to contaminate the creek water throughout the year to a concentration of 0.1 µg L^{-1}. This shows the contamination potential of the low levels of residues found in the soils. At least two transport mechanisms are responsible for the contamination: (1) surface run-off soon after the application date and in winter when the soils are water saturated or frozen and (2) leaching and input from ground-water during effluent conditions in winter and spring.

In fact, the E.C. limit for drinking water has been surpassed several times in the creek water and part of the herbicide has been pumped to the infiltration bassins at the waterworks. This is done usually when the flux is high. It can be seen from

Figure 6 that at these intervals even with low terbuthylazine concentrations the loads may be high.

The ground-water as an important resource has not been studied directly. Pionke and Glotfelty [30] balanced a watershed area assuming steady-state conditions. Between 0.008 and 0.2 % of the atrazine applied were leached to ground-water causing concentrations 0.015 to 1.11 $\mu g\ L^{-1}$. An input of 0.04 % of the application rate would have been sufficient to exceed the 0.1 $\mu g\ L^{-1}$ limit. The authors concluded that the usually assumed retention and adsorption mechanisms in soils probably are not effective at the low residue levels observed. Preferential or by-pass flow mechanisms whereby trace levels of the pesticide are transported rapidly through the soil column withouth reaching an equilibrium with sorptive surfaces may be a main cause of this effect [31,32]. To our opinion this is also the case in the study area of the Frischhofsbach.

The significance of our results is that even when the pesticide use occurred according to good agricultural practice an input of pesticides in surface water may occur due to preferential transport and the higher persistence of aged residues.

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Terbuthylazine, 2-(*tert.*-butylamino)-4-(chloro)-6-(ethylamino)-1,3,5-triazine, registry no. 5915–41–3, P_{ow}= 1096, Solubility S(20°C) = 8.5 mg L^{-1}.

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