Biodegradation **13:** 3–10, 2002.

Diffuse atrazine pollution in German aquifers

Wolfgang Tappe*, Joost Groeneweg & Barbara Jantsch
Research Center Jülich, Institute of Chemistry and Dynamics of the Geosphere. Institute IV: Agrosphere, 52425 Jülich, Germany (author for correspondence: E-mail: w.tappe@fz-juelich.de)*

Key words: atrazine, pollution, aquifer

Abstract

Until its prohibition in Germany in 1991, atrazine was the most frequently applied herbicide in maize cultivation. Moreover, it was used in orchards and vineyards and as a total herbicide on non-cultivated grounds (railways, factory grounds). Later on, atrazine was substituted mainly by terbutylazine. Terbutylazine and terbutryn are the only s-triazines presently permitted in Germany. Nevertheless, atrazine and its metabolite desethylatrazine are by far the most abundant herbicides detected in near surface groundwater. This might be due to wash-outs from the pools of atrazine and its metabolites from the soil into the groundwater or continuing illegal applications. Samples taken from maize fields in 1994 showed that 6.2% of 471 fields tested were treated with atrazine despite the prohibition of its use. Nevertheless, the overall trend is in fact a slow decrease in atrazine concentrations where it is detected in groundwater and, simultaneously often a slight increase in desethylatrazine concentrations. But this is not the case for all sampling points, and increasing concentrations in several aquifers are observed as well. Factors governing the adsorption, degradation, persistence and the possible transfer into the aquifer and the current situation concerning atrazine occurrence in German aquifers will be discussed.

Introduction

Among the s-triazine herbicides, atrazine played an important role in Germany as a selective herbicide for weed control in maize cultivation (~1 kg ha^{-1}). Furthermore, atrazine was applied as a total herbicide in even higher amounts (up to 9 kg ha^{-1}) on industrial sites and railroad embankments. The latter application was already forbidden in 1984 (Dörfler et al. 1997) . In Germany, the general application of atrazine has been prohibited since March 1991, because of the fact that findings of atrazine exceeded permissible concentrations in ground- and drinking water. Even ten years after the ban of atrazine, considerable concentrations of atrazine and its metabolite desethylatrazine are still found in groundwater. Biodegradation and mineralization of atrazine is reported for bacterial consortia and several pure bacterial cultures and most of these bacteria were isolated from contaminated soils (for a recent review see Ralebitso et al. (2002, this journal)). The prolonged persistence of atrazine in aquifers may be an indication of a lower microbial activity or the absence of atrazine degraders. Recalcitrant behaviour of atrazine in aquifer material (Agertved et al. 1992) could also result from concentrations being too low to induce bacterial degradation (Mirgain et al. 1995).

In this review we present trends of atrazine concentrations over time in German shallow aquifers and discuss these data in relation to possible chemical or biological resilience of the subsurface and groundwater.

Atrazine is a soil and leaf herbicide which inhibits photosythesis by interrupting the electron transport system. Other processes depending on the energy generated during photosythesis like the opening of stomata, transport of ions etc. are affected as well. Atrazine acts as selective herbicide within e.g., maize cultures because plants like maize have effective detoxification mechanisms. The solubility of atrazine in water is 30 mg l^{-1} at 20 °C and it is fairly resistant to hydrolysis at neutral pH (Burkhard & Guth 1981). In strong acid and alkaline solutions and at higher temperatures (>70 °C) atrazine hydrolyses to hydroxyatrazine loosing its herbizidal properties. Atrazine can be degraded by UV radiation (Worthing & Walker 1987).

The World Health Organization (WHO) classifies atrazine as a class III substance which means "unlikely to be hazardous in normal use". Concerning carcinogeneity, atrazine (like other s-triazines) is able to induce breast cancer in female rats, and therefore it is classified as class C, "possible human carcinogen", by the US Environmental Protection Agency. The EC directive "Quality of Water for Human Use" (1998) adopted by the German legislation as "Trinkwasserverordnung-TrinkwV 2001 (2001) sets a limit of 0.1 μg l^{-1} of individual pesticides (for aldrin, dieldrin, heptachlor and heptachlor epoxid the limit is even lower at 0.03μg l^{-1}) and a maximum of 0.5 μg l^{-1} for the sum of detected pesticides in drinking water.

The monitoring programmes on groundwater quality of the federal states of Germany showed that whenever pesticides exceeded the value of 0.1 μg l^{-1}, this was mostly due to desethylatrazine or atrazine. After the ban of atrazine, a decrease of atrazine concentrations in groundwater was expected, and taking all the data together, a slight tendency towards lower concentrations can be seen. Nevertheless, patterns of atrazine and desethylatrazine concentrations in shallow groundwater all over the country are extremely heterogeneous.

Inputs, degradation, adsorption, and mobility

Atrazine enters the ecosystem mainly by direct application for weed control. Another input pathway is the deposition of atrazine by atmospheric precipitation. The main sources for atmospheric atrazine are direct drift during application and volatilization from treated areas. Atrazine can often be detected in rain water (mainly at concentrations below 1 μg l^{-1}) and close to treated areas. There is also evidence for atmospheric transport processes over longer distances. In Norway, Lode et al. (1995) could detect up to 0.086μg l^{-1} of atrazine in rainwater. At that time, the application of atrazine was already prohibited in Norway, and the positive results were correlated with eastern winds, indicating atmospheric long-distance transport. Pollution from diffuse sources seems to be negligible when compared to the direct input from agriculture and non-farmland weed control.

Detailed knowledge has been gathered about atrazine degradation, its metabolites and bound residues in agricultural soils. The persistence of atrazine in soils depends on several chemical, biochemical, and physical factors (adsorption, mobility, wash-out, runoff, volatility, biotic and abiotic degradation, formation of bound residues, and uptake by plants). These factors are further affected by several other factors such as soil-type and climatic conditions. Whereas a certain degree of persistence is a desirable feature of herbicides, degradation products should not persist. If degradation follows first-order kinetics, a half life can be determined as an estimation for the persistence. For atrazine, estimations for the half life differ greatly with values ranging between 37 days and 3–5 years (Premazzi & Stecchi 1990). In fact, degradation does not really follow first-order kinetics, and during the experimental determination of its persistence, the methods used for analysis play an important role: Methods which include the analysis of adsorbed and bound residues detect much slower degradation velocities compared to standard-analysis procedures (Capriel & Haisch 1983; Heitmann-Weber 1992). Therefore it is important to differentiate between "degradation rate" and "removal rate" of an agent such as atrazine. Degradation in terms of mineralization seems to take place very slowly and, by no means, completely. As an example we summarize the work of Heitmann-Weber (1992) who carried out intensive lysimeter studies with radioisotopes of ^{14}C labelled triazine and desethylatrazine (triazine-ring ^{14}C). Radiolabelled atrazine and desethylatrazine were applied to lysimeters containing undisturbed soil columns of 110 cm luvisol soil. After 110 days of incubation, only about 2% of the radiocarbon was mineralized but 20–30% of the radiocarbon could be extracted as bound residues. About 30% could be extracted (water/methanol) as native substances (atrazine and desethylatrazine, respectively) and a substantial amount of hydrolyzed and dealkylized metabolites (6–15%) was found within this incubation time indicating that only a minor fraction was really mineralized. Less than 1% radioactivity of the atrazine was found in the percolate.

Due to the complex nature of soil and its living and non-living reactive compounds it is very difficult to separately record biotic and abiotic reactions, because both reactions can take place in parallel and often lead to the same reaction products. Complete mineralisation of atrazine seems to be predominantly a biotic reaction (Winkelmann & Klaine, 1991). Bacteria, cap-

Table 1. Atrazine and desethylatrazine findings and concentration ranges in shallow groundwater in four federal states of FRG and FRG (1990–1995).

State	Agent	Number of sampling points	Below detection limit	Concentrations (μg l^{-1})			Positive results (%)
				<0.1	>0.1-1.0	>1.0	
Baden-	A^*	2985	2184	674	120	7	27
Würtemberg	D^{**}	2984	2025	719	232	8	32
Bavaria	A	3471	2333	876	258	4	32
	D	3436	2219	789	420	8	35
Hesse	A	2464	2264	180	19	1	8
	D	1830	1625	170	34	1	11
Northrhine-	A	909	821	55	30	3	10
Westphalia	D	688	599	56	31	2	13
FRG	A	12101	9634	1948	494	25	20
	D	10972	8271	1877	799	25	25

A^* atrazine; D^*, desethylatrazine.
Source: UBA.

able of atrazine degradation, have been isolated from soils (see Ralebitso et al. 2002) and recently from groundwater, heavily polluted with atrazine (Patterson et al. 2002). Microcosm and column experiments showed that the addition of atrazine degrading bacteria were necessary for a successful atrazine degradation (Patterson et al. 2002). This is consistent with the findings of Shapir et al. (1998) who describe that intrinsic atrazine mineralization did not occur in the aquifer sediments sampled from a shallow aquifer receiving s-triazine herbicides for 20 years. Rapid degradation took place after the addition of 10^6 cells atrazine degrading bacteria per gram sediment. Franzmann found (cited in Patterson 2002) that the rate of degradation of atrazine generally decreased with depth through the vadose zone, largely due to lower total organic carbon levels with increasing depth.

Mobility and transport of atrazine in soil is affected by several different soil properties as well as by the mode and time of application and the precipitation intensity. Transport takes place as diffusion, mass flow, macropore flow, and even by adsorption to carrier substances (Führ 1987). Adsorption results in an accumulation of the herbicide in soil and reduces the concentration in the pore-water solution. This decreases the bioavailability and biological degradation and therefore favours the retardation of atrazine. Adsorption to low-molecular-weight humic substances and clay minerals may favour the retardation and may, to some extent, result in colloidal co-transport. Desorption makes atrazine accessible to processes such as wash out to the groundwater, uptake by plants and biotic and abiotic degradation and transformation.

Mobility is always correlated with soil organic carbon content: higher organic carbon contents in the upper soil layer cause a slow down in the dislocation rate to deeper layers (Burnside et al. 1969; Huang & Frink 1989).

Atrazine pollution of aquifers in Germany; concentrations and trends

A tremendous amount of data has been gathered by the German authorities concerning herbicide concentrations in groundwater. Most of these data are published in internal reports, which are not readily accessible. Between 1990 and 1995, about 13000 samples were taken into account by the Environmental Protection Agency (Umweltbundesamt, UBA) of the Federal Republic of Germany (FRG) and the Working Group of the Federal States on Water Problems (Länderarbeitsgemeinschaft Wasser, LAWA) for presentations on groundwater quality in Germany in terms of contents of atrazine and desethylatrazine. Differences in sampling programmes, detection limits and especially differences in the assortment of sampling sites leads to difficulties in comparability between the contamination levels of groundwater in the different federal states. Near surface groundwater is expected to be mostly endangered by contamination with pesticides. Therefore, all values given in the tables and figures refer to shallow aquifers or spring-water. In Table 1, the frequency of herbicide findings in shallow ground-

Table 2. Ranking list of positive findings of pesticides in Germany in near surface groundwater (year 2000).

Agent/metabolite	Rank	Agent/metabolite	Rank
Desethylatrazine	1	Bentazone	9
Atrazine	2	Mecoprop	10
Bromacile	3	Isoproturone	11
Simazine	4	Metolachlorine	12
Hexazinone	5	Prometryne	13
Diurone	6	Terbuthylazine	14
Propazine	7	Chlorotolurone	15
Desisopropylatrazine	8	Lindan (gamma-HCH)	16

Source: LAWA, UBA Daten zur Umwelt (2001).

water samples between 1990–1995 is given in terms of concentration ranges. Instead of a complete presentation of all states only four federal states and the values for the FRG in total are given. These four federal states represent more than 80% of all sampling sites in Germany and an area of 45% of the total area of the FRG and they are the most comparable ones with respect to the assortment of sampling sites and analytical procedures.

Most federal states differentiate at least between "basic sampling-points" (mostly natural or low anthropogenic impact), "trend sampling-points" (potentially polluted) or sampling points most likely to be polluted and with proven pollution. The selection of sampling points as well as the numbers and positions of sampling points are crucial for the results and for the comparability. However, differences in selection procedures of data by the federal states reduce the comparability of the results.

In 1998, 63% of all pesticides detected in groundwater were attributed to the s-triazines atrazine, desethylatrazine, and simazine. As shown in the "ranking list" (Table 2), even now, ten years after the prohibition of atrazine, atrazine and its metabolite desethylatrazine are the most abundant single substances detected in groundwater samples followed by bromacil and simazine. Since the metabolite desethylatrazine is found more frequently than atrazine itself, the assumption that most of the findings refer to inputs prior to the prohibition of atrazine in 1991 is supported. However, the hysteresis between application and occurrence of atrazine and its metabolites in groundwater becomes obvious.

From the data presented in Table 3, for the FRG a significant decrease in atrazine concentration in groundwater can hardly be stated and desethylatrazine concentrations seem to be constant or even increase.

Figure 1 summarizes atrazine/desethylatrazine findings in Bavaria between 1990 and 1999 and shows a quite similar trend when compared to the FRG data. A slight decrease in the frequency of atrazine findings (at least for concentrations above 0.1 μg l^{-1}) is accompanied by a minor increase in the frequency of desethylatrazine findings.

Focussing on single sampling points, the picture becomes even more complicated. There are sampling points with distinct trends towards decreasing concentrations. One example is given in Figure 2: A clear drop in atrazine and desethylatrazine concentrations in spring water (Bayerisches Landesamt 2001) was measured. Strikingly, this trend already began 3 years prior to the prohibition of atrazine.

Baden-Württemberg is one of the federal states where an early decrease in atrazine concentration became apparent (Figure 3A). But within the same time period, there is no significant drop in desethylatrazine concentrations (Figure 3B).

Actual results from 1999 confirm this trend with the difference, that now both atrazine and desethylatrazine were found with significantly lower frequencies in 1999 compared to the 1998 data, and compared to the mean values from 1990–1994 (LFU Baden-Württemberg 2000, data not shown).

In Figures 4 and 5, the concentrations of atrazine and desethylatrazine are given for two sampling points within the same catchment area of a waterwork in Baden-Württemberg near the city of Freiburg. There is a strong difference between the trends as well as in the ratio of atrazine/desethylatrazine. Within the same catchment area, there are also several wells free of any pesticide. Considering these extremes within a small scale of only a few square kilometers, the differences on a larger scale are not surprising.

There are even examples for sampling points first showing a clear trend towards lower concentrations, followed suddenly by a return to increased levels. Atrazine and desethylatrazine concentrations of such a sampling point are given in Figure 6 for a well in North Rhine-Westphalia, near the city of Bonn. For the average of all the sampling points in North Rhine-Westphalia, a slight decrease of atrazine findings was reported. This decrease was especially notified for wells influenced by surfacewater and situated in areas with intensive agriculture (UBA 2001).

In two catchment areas belonging to the waterworks of Freiburg (Baden-Württemberg) mainly dif-

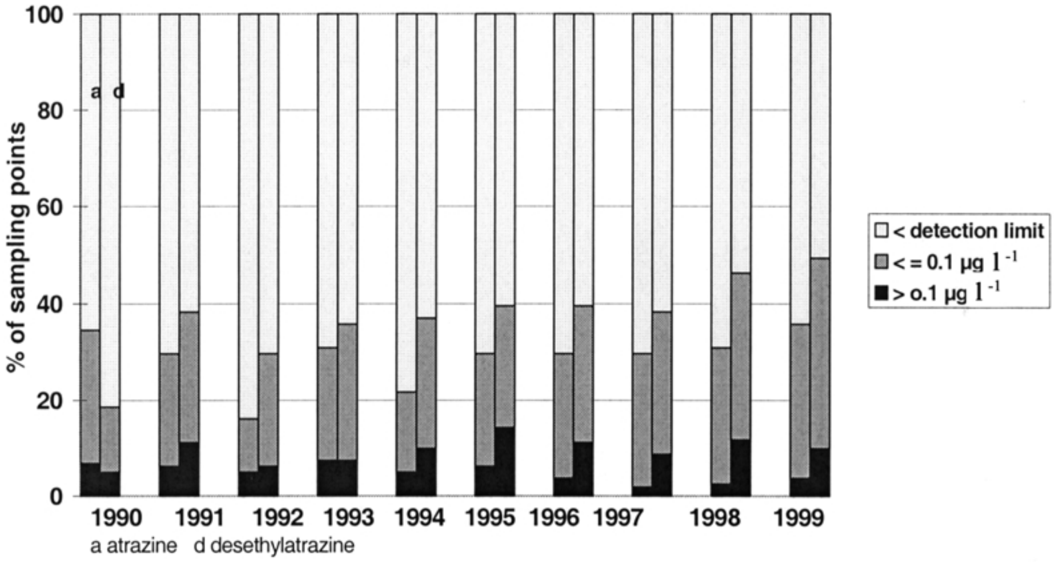

Figure 1. Groundwater quality in Bavaria concerning atrazine and desethylatrazine between 1990 and 1999. Source: Bayerisches Landesamt für Wasserwirtschaft (2001).

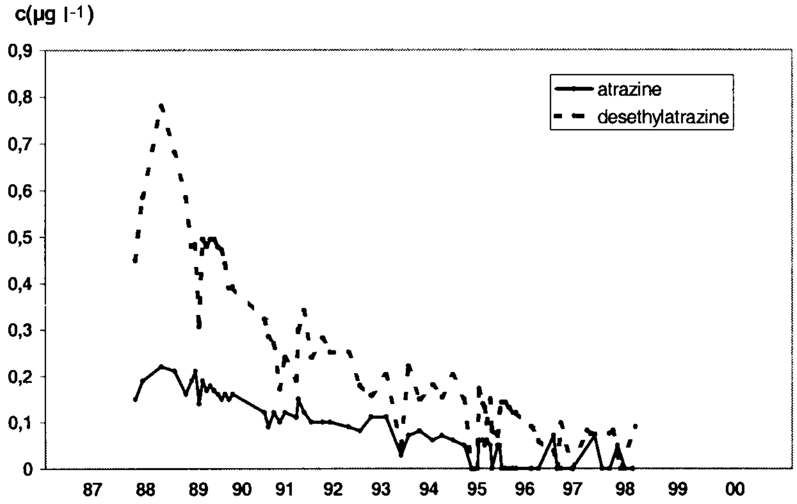

Figure 2. Atrazine and desethylatrazine concentrations in spring-water (anonym) in Bavaria.

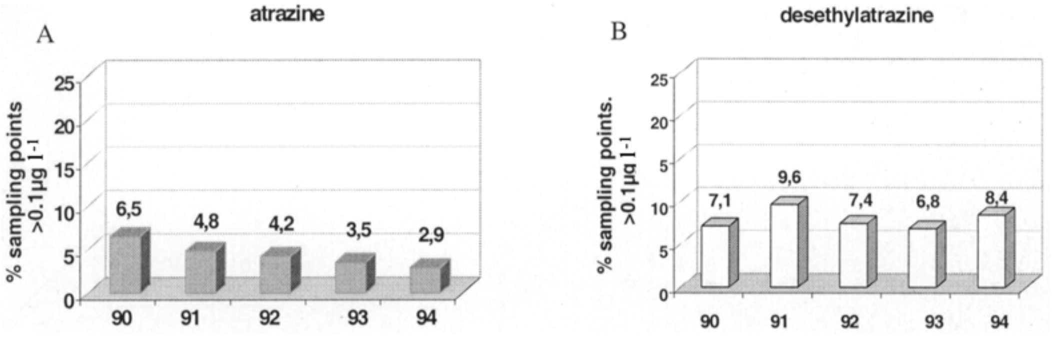

Figure 3. (A) Atrazine and (B) desethylatrazine findings in shallow groundwater of Baden-Wüttemberg from 1990 until 1994 (percentage of sampling points with concentrations $>0.1\ \mu g\ l^{-1}$). Source: LAWA (1997).

Table 3. Trends in atrazine and desethylatrazine concentrations in near surface groundwater in FRG from 1996–1999.

Year	Agent	Number of sampling points	Above detection limit		$>0.1\ \mu g\ l^{-1}$	
			Number	(%)	Number	(%)
1996	A*	8472	1978	**23.3**	536	**6.3**
	D**	8636	1595	**18.5**	273	**3.2**
1997	A	5198	1118	**21.5**	326	**6.3**
	D	5350	868	**16.2**	143	**2.7**
1998	A	3850	1068	**27.7**	332	**8.6**
	D	3980	804	**20.2**	143	**3.6**
1999	A	4711	777	**16.5**	110	**2.3**
	D	4678	1080	**23.1**	251	**5.4**

A*, atrazine; D**, desethylatrazine.
Source: UBA Daten zur Umwelt.

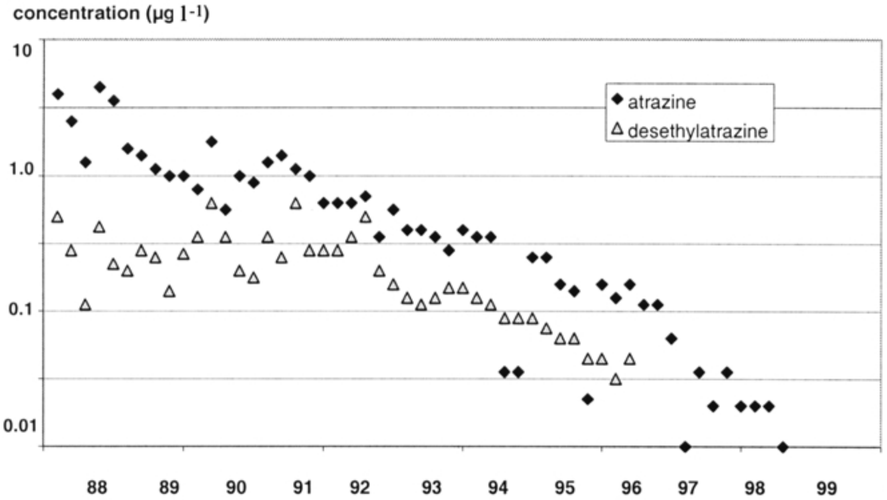

Figure 4. Atrazine and desethylatrazine concentrations in groundwater of a single sampling point (NH5) in the catchment area of a waterwork near Freiburg (Baden-Württemberg).

fering in the renewal times of groundwater, long-term monitoring revealed that besides year to year variations the decrease in atrazine and desethylatrazine positive findings was strongly correlated with the renewal-time of the groundwater (Figure 7).

As pointed out by Herwig et al. (2001), s-triazines, once adsorbed in the mineral horizon of the soil persist there over long periods and desorb only gradually, thus being translocated into deeper soil layers and ultimately into the groundwater. Annual differences in concentrations of atrazine and desethylatrazine in groundwater can be explained by desorption processes influenced by the amounts and intensities of rainfall. Providing that biological degradation of low concentrations of atrazine in subsoils and groundwater is not implicated, the main reasons for the decreasing trends in atrazine concentrations in groundwater could simply be the exhaustion of atrazine pools in soils and dilution effects.

Final remarks

Ten years after the prohibition of atrazine in Germany, concentrations above 0.1 $\mu g\ l^{-1}$ can still be detected at several groundwater sampling points. There is a trend towards a slow decrease in atrazine concentrations as well as in the frequency of positive findings, but this trend is by no means common to all sampling points. Increasing concentrations are observed in certain wells, sometimes even within the same catchment areas. Despite the prohibition of atrazine, an appreciable amount of atrazine seems to be applied illegally.

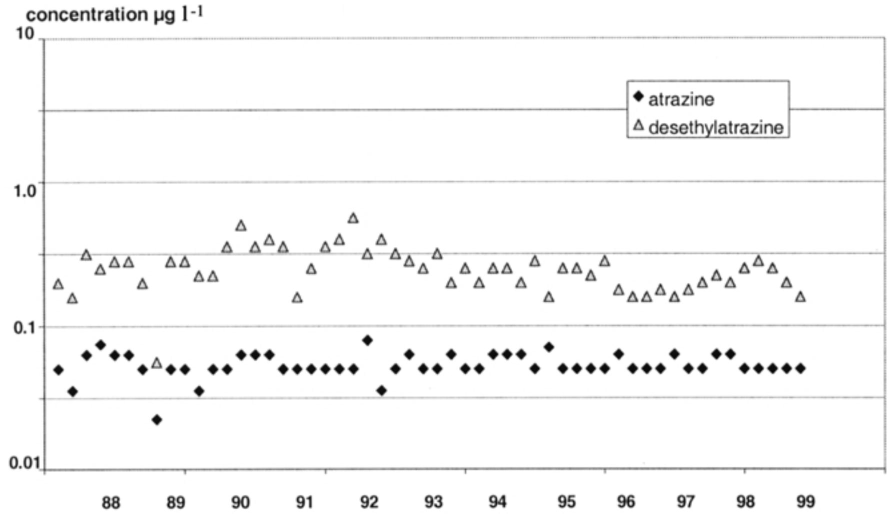

Figure 5. Atrazine and desethylatrazine concentrations in groundwater of a single sampling point (NH44) in the catchment area (the same as in Figure 4) of a waterwork near Freiburg (Baden-Württemberg).

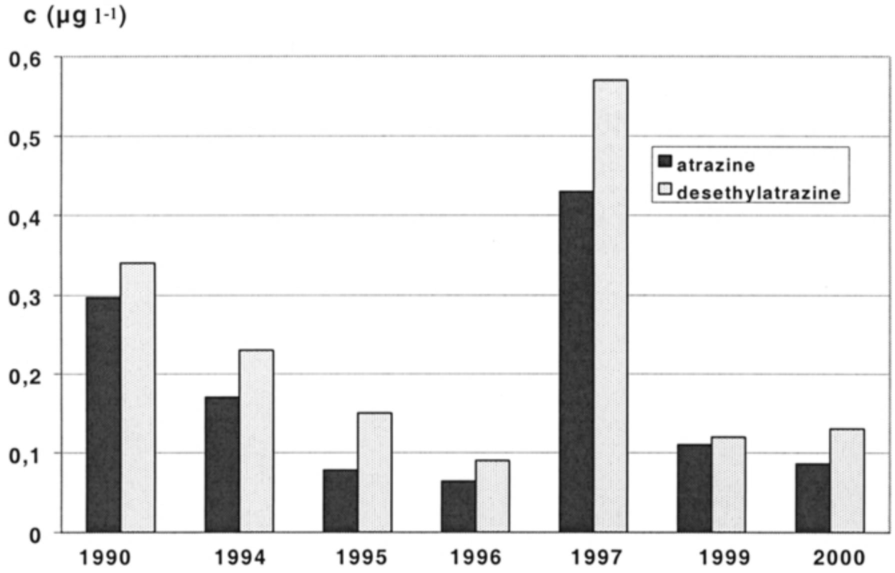

Figure 6. Atrazine and desethylatrazine concentrations in near surface groundwater of a sampling point in Lessenich/Bonn (North Rhine-Westphalia) from 1990 until 2000.

Samples taken from agricultural soils in Bavaria indicate that still in 1999, 1–3% of the maize fields were treated with atrazine.

Strong variations in spatial and temporal concentrations are frequently observed. These observations lead to the conclusion that not the whole aquifer but more or less large parts of the aquifer are contaminated and that these plumes seem to move, depending on e.g., precipitation intensity.

Some federal states (Brandenburg, Saxony and Thuringia) have already reported pesticide findings in deeper aquifers (LAWA 97). At present, this seems to be restricted to very sensitive areas, but for the future, the penetration of contaminations from shallow into deeper aquifers cannot be excluded.

The transport of atrazine to aquifers depends on soil and subsoil properties and hydrogeological conditions, and therefore it can take considerable time until it appears in the groundwater. Restrictions to applica-

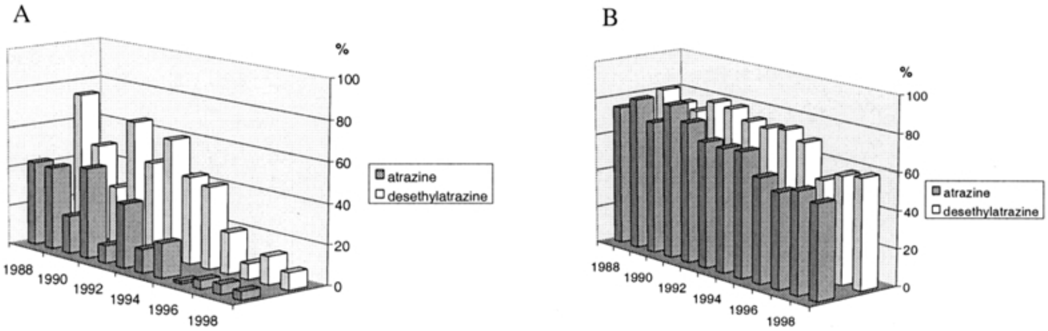

Figure 7. Frequency of positive findings of atrazine and desethylatrazine in wells of two different catchment areas of water works in Baden-Württemberg. (A) Renewal time of groundwater: 2–8 years. (B) Renewal time of groundwater: 10–25 years. Source: Rogg & Betting (2000).

tion or prohibition of certain pesticides do not guarantee a rapid disappearance of the respective agent from groundwater, once it has been detected there.

References

Agverted J, Rugge K & Baker JK (1992) Transformation of the herbicide MCPP and atrazine under natural aquifer conditions. Ground Water 30(4): 500–506

Bayerisches Landesamt für Wasserwirtschaft (2001) personal communication, data presented in this article were kindly provided by L. Friedmann

Burkhard N & Guth A (1981) Chemical hydrolysis of 2-chloro-4,6-bis(alkylamino)-1,3,5-triazine herbicides and their breakdown in soil under the influence of adsorption. Pestic. Sci. 12: 45–52

Burnside OC, Fenster CR, Wicks GA & Drew JV (1969) Effect of soil and climate on herbicide dissipation. Weed Sci. 17: 241–245

Capriel P & Haisch A (1983) Persistenz von Atrazin und seiner Metaboliten in Boden nach einmaliger Herbizidanwendung. Z. Pflanzenernähr. Bodenk. 146: 474–480

Dörfler U, Scheunert I, Viswanarhan R & Zsolnay A (1997) Standortgerechte Berwertung von s-Triazinen in Böden. GSF-Bericht 22/97. GSF-Forschungszentrum für Umwelt und Gesundheit, GmbH

EC directive (1998) 98/83/EC Nr. L330, 32 pp

Führ F (1987) Non-extractable pesticide residues in soil. In: Greenhalgh R & Roberts (Eds) Proc. 6th IUPAC Congress of Pesticide Chemistry, Pesticide Science and Biotechnology (pp 381–389). T.R. Oxford

Guth JA (1972) Adsorptions- und Einwaschverhalten von Pflanzenschutzmitteln in Böden. Schr. Reihe Ver. Wasser- Boden-Lufthyg. Berlin-Dahlem, 37, Stuttgart

Heitmann-Weber B (1992) Untersuchungen zu Abbau, Bindung und Verlagerung von Atrazin und Desethylatrazin in einer Pseudogley-Braunerde im Vergleich zu einer Parabraunerde – Labor- und Lysimeterversuche nach praxisgerechter Applikation zu Mais. Dissertation Univ. Bonn, Berichte des Forschungszentrums Jülich, 2683

Herwig H, Klumpp E, Narres H-D & Schwuger, MJ (2001) Physicochemical interactions between atrazine and clay minerals. Appl. Clay Sci. 18: 211–222

IVA, Industrieverband Agrar e.V. (1993) personal communication with U. Dörfler. In: Dörfler U, Scheunert I, Viswanarhan R & Zsolnay A (1997) Standortgerechte Berwertung von s-Triazinen in Böden. GSF-Bericht 22/97. GSF-Forschungszentrum für Umwelt und Gesundheit, GmbH

Ivey MJ & Andrews H (1965) Leaching of simazine, atrazine, diurone, and DCPA in soil columns. Proceedings of the Southern Weed Conference 18: 670–684

Huang LQ & Frink, CR (1989) Distribution of atrazine, simazine, alachlor, and metochlor in soil profiles. Bull. Environ. Contam. Toxicol. 43: 159–164

Landesamt für Umweltschutz Baden-Württemberg (2000) Grundwasserüberwachungs-programm, Ergebnisse der Beprobung 1999, Karlsruhe

Landesumweltamt Nordrhein-Westfalen (2001) personal communication, data presented in this article were kindly provided by S. Kempkes

LAWA, Länderarbeitsgemeinschaft Wasser (1997) Bericht zur Grundwasserbeschaffenheit – Pflanzenschutzmittel. Kulturbuchverlag Berlin GmbH

Lode O, Eklo OM, Holen B, Svenson, A & Johnsen, AM (1995) Pesticides in precipitation in Norway. Sci. Total Environm. 160/161: 421–431

Mirgain I, Green G & Monteil H (1995) Biodegradation of the herbicide atrazine in groundwater under laboratory conditions. Environ. Technol. 16: 967–976

Premazzi G & Stecchi R (1990) Evaluation of the impact of atrazine on the aquatic environment. EUR 12569 EN. The Office for Official Publications of the European Communities, Luxemburg

Ralebitso TK, Senior E & van Verseveld HW (2002) Microbial aspects of atrazine degradation in natural environments. Biodegradation 13: 11–19

Rogg JM & Betting D (2000) Pestizidreport Nr. 4 Freiburger Energie- und Wasserversorgungs AG

Trinkwasserverordnung (2001) TrinkwV Bundesgestzblatt 2001, Teil 1, Nr. 24, Bonn

Umweltbundesamt (2001) Daten zur Umwelt, Der Zustand der Umwelt in Deutschland 2000. Erich Schmidt Verlag, Berlin

Winkelmann DA & Klaine SJ (1991) Degradation and bound residues formation of atrazine in a Western Tennessee soil. Environ. Toxicol. Chem. 10: 335–345

Worthing CR & Walker SB (1987) The Pesticide Manual. British Crop Protection Council