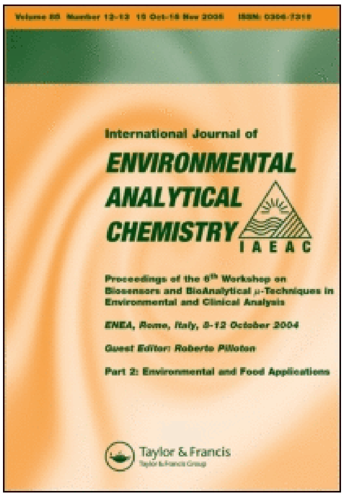

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Analysis of Pesticides and Their Degradation Products in Rainwater: A Probe into Their Atmospheric Degradation

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ANALYSIS OF PESTICIDES AND THEIR DEGRADATION PRODUCTS IN RAINWATER: A PROBE INTO THEIR ATMOSPHERIC DEGRADATION

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Rainwater samples collected in Hannover (Germany) in 1996 were analyzed for twelve pesticides. γ-HCH, metolachlor, atrazine and terbuthylazine were determined in average concentrations ranging from 19 – 63 ng/L during the application period. In addition, three degradation products of atrazine, i.e. desethylatrazine, desisopropylatrazine and desethyldesisopropylatrazine, and one degradation product of terbuthylazine, i.e. desethylterbuthylazine, were found in concentrations which were equal or even surpassed those of the parent compounds. The analysis of degradation products in rainwater represents a probe into the degradation of pesticides in the atmosphere.

Keywords: Pesticides; degradation products; rain; precipitation; triazines; atmosphere

INTRODUCTION

Pesticides are used world-wide to protect crops against pests, weeds and fungi. It has been claimed that only 1 – 3 % of an agrochemical reaches the site of action [1]. Pesticides may be transformed by chemical and biological processes or transported from the site of application by several processes including run-off, movement through the soil to groundwater, volatilization, transport on soil particles and wind erosion. One of these routes is loss to the atmosphere by volatilization, drift and soil erosion, where for many agents volatilization is the most important loss route. Volatilization rates from soil surfaces or plants can be very large with losses approaching 90 % within three days, even for chemicals with vapor pressure $\leq 10^{-3}$ mbar [2], where volatilization from the leaf surface is usu-

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ally larger than from the soil [3]. Moreover, loss of pesticides to the atmosphere may result from drift. Droplets of 10 μm may drift several kilometers at low wind velocities [4]. Droplets evaporate and become smaller as they move through the air. Transport of particle-bound pesticides may also occur by soil erosion. Little is known about this transportation path.

Pesticides released into the atmosphere may undergo photochemical transformations which, for most organic compounds, are attributed to either direct photolysis or reaction with reactive species = OH, nitrate radicals or ozone (where OH reactions often prevail). A prerequisite for photolysis is a significant overlap of the UV spectrum of the pesticide with that of sunlight, which for instance is not observed for many triazines. Thus, in this instance, degradation by OH radical reactions will prevail. In contrast to direct radiation, the chloro substituent is retained in such oxidation reactions, which usually lead to desalkyltriazines [41]. However, experimental data for the reaction of OH radicals with pesticides in the gas phase are scarce [41]. Moreover, transformation products have rarely been identified in the atmosphere.

Not only the parent pesticides released into the atmosphere but also their degradation products may be transported back to the surface by dry or wet deposition. Many polar pesticides present in the gas phase have low Henry constants. Degradation usually leads to products which are even more polar than their precursors. Thus, polar pesticides and in particular their degradation products are scavenged with high efficiency by fog, cloud or rain droplets [5]. This scavenging ratio is also high for particle-bound compounds [6]. Precipitation is therefore an important route by which airborne pesticides and their degradation products are deposited onto the soil (and surface water).

As the degradation products of pesticides are present in the atmosphere at trace amounts, their sampling and analysis is difficult. As a result of their low Henry constants, they are significantly enriched in the aqueous phase of cloud or rain droplets. Thus, atmospheric degradation products of pesticides are more easily analyzed in rainwater than in air samples, which prompted us to search for such products in precipitation.

Pesticides belonging to the group of chlorinated hydrocarbons have been detected in rain in numerous studies and will not be discussed here. As a result of their volatility and persistence, they can undergo long-range transport and have been observed even in Antarctica [7]. A variety of more polar pesticides have been found in precipitation throughout the world [8–30, 39, 50]. Organophosphate pesticides and their degradation products applied in the Central Valley in California were detected in rain samples at the foot of the Sierra Nevada mountains at concentrations reaching 7.6 μg/L for parathion [13]. Rainwater collected in Iowa was analyzed inter alia for atrazine, alachlor, cyanazine and metolachlor, where concentrations ranging from 0.1 – 40.0 µg/L were determined for the individual agents [14]. In Germany, several reports on the occurrence of pesticides in precipitation have been published [8, 10, 11, 15, 18, 21, 23, 24, 27, 39, 50]. In the most extensive study, 73 samples were collected in three sites in Southwest Germany and analyzed for 34 agents [8]. Eighteen pesticides or degradation products were found at the sampling site Schauinsland (Black Forest). Triallate, metolachlor, propiconazole and lindane were found in the highest amounts with mean concentrations ranging from 0.2 – 0.4 µg/L.

Very few reports have appeared on the occurrence of transformation products from these pesticides in precipitation where mainly desethylatrazine and desisopropylatrazine were observed [8, 15, 27].

In the present study, precipitation samples collected in Hannover in 1996 were analyzed for twelve pesticides and several of their main metabolites. The parent compounds are listed in Table I. This table also summarizes some physicochemical data and additional information on these pesticides. After the commencing of the study, we became aware that several of the selected agents are no longer permitted in Germany. However, some of these compounds were still found in precipitation.

EXPERIMENTAL

Chemicals

All pesticide standards were purchased from Riedel-De Haen with a purity of 99%; atrazine-$d_5$was obtained from Cambridge Isotope Laboratories Inc. (Andover, Massachusetts, USA) with a purity of 98%. All pesticide solutions were prepared in methanol, purchased from Baker (Deventer, Netherlands), and stored at – 20 °C.

Sampling

Rainwater was collected in Hannover in 1996 in the vicinity of the institute about 15 km away from areas with extensive agriculture. A wet-only collector, custom-made by Eigenbrodt (Königsmoor, Germany) was used. Rainwater was collected via a fused silica funnel with 0.5 m^2 sampling area in a 5 L brown glass bottle. Only individual rain events were sampled where the collected volume varied from 0.25 to 5 L per event. Between the events, the funnel was thoroughly cleaned with distilled water followed by acetone.

TABLE I Pesticides selected

Name	*Class*	*Vapour pressure (Pa) T=20°C [33]*	*Henry Constant (Pa.L.g^{-1}) [33]*	*Amount sold in Germany in 1996 (Tons)*	*Category*	*Use*	*Period of use*
Lindane	Organochlorine	$5.6.10^{-3}$	$8.0.10^{-1}$	<100 [31]	Insecticide	/	March-October
Atrazine	Triazine	$4.0.10^{-5}$	$1.3.10^{-3}$	not permitted [32]	Herbicide	Corn	April-July
Simazine	Triazine	$8.1.10^{-7}$	$1.6.10^{-4}$	not permitted [32]	Herbicide	Corn	April-July
Terbuthylazine	Triazine	$1.5.10^{-4}$	1.810^{-2}	>500 [31]	Herbicide	Corn	April-July
Cyanazine	Triazine	$2.0.10^{-7}$	$1.2.10^{-6}$	not permitted [32]	Herbicide	Corn	April-July
Terbutryn	Triazine	$1.3.10^{-4}$	$5.1.10^{3}$	<100 [31]	Herbicide	Grain	April-July
Prometryn	Triazine	$1.3.10^{-4}$	$4.0.10^{-3}$	not permitted [32]	Herbicide	General	April-July
Alachlor	Chloracetanilide	$2.9.10^{-3}$	$1.2.10^{-2}$	not permitted [32]	Herbicide	Corn	April-July
Metolachlor	Chloracetanilide	$1.7.10^{-3}$	$3.2.10^{-3}$	>200 [31]	Herbicide	Corn	April-July
Metazachlor	Chloracetanilide	$4.9.10^{-5}$	$2.9.10^{-3}$	>500 [31]	Herbicide	Rap	April-July
Propham	Organophosphorus	/	/	<50 [31]	Insecticide	/	March-October
Pirimicarb	Organophosphorus	$4.0.10^{-5}$	/	<50 [31]	Insecticide	/	March-October

Extraction and enrichment

The samples were filtered using a glass fiber filter system (Sartorius, Göttingen, Germany) and a 0.45 µm Tuffryn membrane filter (Gelman Sciences, USA). To prevent further microbial degradation, sodium azide was added and the samples stored at 4 °C until extraction.

The samples were extracted by solid-phase extraction (SPE) using cartridges filled with 200 mg Lichrolut EN from Merck (Darmstadt, Germany) after conditioning with methanol and water. After drying the solid phase with nitrogen, the cartridges were eluted with 6 ml of methanol : acetonitrile (1:1). The extract was evaporated to dryness using a gentle stream of nitrogen. After addition of the internal standard the residue was redissolved in 1 ml methanol and stored at – 20 °C until analysis (enrichment 1 : 1000). Recoveries are presented in Tables II and III.

TABLE II Concentration of pesticides in rainwater in Hannover (Germany, 1996)

Name	*Limit of quantification (ng/L)*	*Recoveries (%)*	*Range of concentration (ng/L)*	*Mean concentration (ng/L)*	*Number of events*	*Time period in which pesticides were detected (year 1996)*
Lindane	8	84	10–130	41	21	24.04–26.11
Atrazine	2	104	3–90	21	18	24.04–08.07
Simazine	1	118	0.1–2	0.7	6	24.04–20.06
Terbuthylazine	3	110	3–270	63	25	29.03–31.07
Cyanazine	10	112	n.d.	n.d.	/	n.d.
Terbutryn	2	109	n.d.	n.d.	/	n.d.
Prometryn	2	89	n.d.	n.d.	/	n.d.
Alachlor	2	96	2–30	13	3	24.05–30.09
Metolachlor	2	95	2–190	19	20	01.04–31.07
Metazachlor	10	136	n.d.	n.d.	/	n.d.
Propham	2	78	n.d.	n.d.	/	n.d.
Pirimicarb	2	89	n.d.	n.d.	/	n.d.

n.d. : not detected.

Instrumental analysis

All samples were analyzed by GC-MS using a gas chromatograph from Hewlett Packard (type 5890, series II) with a mass selective detector from Hewlett Packard (type 5972) and a column from Supelco (Bellefonte, USA) (SPB-5, 30 m, 0.25 mm i.d., 0.25 μm d_f). Samples were injected splitless. As rain water samples are heavily polluted by other organic compounds, i.e. from automobile exhaust, a retention gap preceded the analytical column. The column temperature program was: 1 min at 60 °C, to 160 °C at 20 °C/min, 5 min at 160 °C and then to 250 °C at 5 °C/min. Pesticides were identified and quantified under time-scheduled "selected ion monitoring" (SIM) conditions using two masses. Calibration was achieved using atrazine-d_5 as internal standard. The response factors relative to this internal standard were determined at one concentration (1 μg/L). The limit of quantification (LOQ) was defined as three times the limit of detection (LOD). If the ion trace was free from matrix interferences, the LOD was defined as S/N =3. In the case of interferences, the LOD was defined as the lowest unequivocally detectable concentration above the "chemical" noise.

TABLE III Concentration of atrazine and terbuthylazine and their main degradation products in rain water in Hannover (Germany, 1996)

Name	*Limit of quantification (ng/L)*	*Recoveries*	*Range of concentration (ng/L)*	*Mean concentration (ng/L)*	*Range of ratio degradation products/ parent pesticide*	*Number of events*	*Time period in which metabolites were detected (year 1996)*
Atrazine	2	104	3–90	21		18	24.04–08.07
Desethylatrazine	2	53	6–62	24	0.4–1.9	7	20.05–08.07
Desisopropylatrazine	10	86	14–107	62	0.3–15	3	24.04–04.06
Desalkylatrazine	10	15		23	0.3	1	20.06
Terbuthylazine	3	110	3–270	62		25	29.03–31.07
Desethylterbuthylazine	3	48	3–455	70	0.1–4	14	24.04–16.07

RESULTS AND DISCUSSION

Quantification of pesticides

Table II presents the range of concentrations and the mean concentration for the 12 pesticides investigated as well as some validation data on the analytical method (limit of quantification, recoveries). Cyanazine, terbutryn, prometryn, metazachlor, propham and pirimicarb were not detected, while simazine appeared to be present in several samples at concentrations < 1 ng/L, and alachlor was found only during three events at a mean concentration of 13 ng/L. Note that these compounds are either not allowed in Germany anymore or sold in small amounts. Only four pesticides could be observed frequently in rain water at elevated concentrations: lindane, metolachlor, terbuthylazine and atrazine, where only the first three agents were found at concentrations significantly higher than 100 ng/L, the limit set in the German drinking water regulations [34].

Figure 1 represents the amounts obtained during the period from April to November 1996 for lindane, metolachlor, atrazine and terbuthylazine.

Lindane, (γ-HCH), is an organochlorine insecticide used both as plant protection and wood preservation product. In spite of the relatively small amount sold in Germany (< 100 t) [31], (γ-HCH) was detected throughout the year at a mean concentration of 41 ng/L. These concentrations are in the same range as reported in other studies [8, 37]. As a result of its high vapor pressure, lindane is released into the atmosphere during application or afterwards by volatilization from sprayed plants and soils. It was reported that within 24 h 28 – 95 % of lindane (γ-HCH) is lost via this route [3, 36]. Volatilization of lindane incorporated in the soil contributes to a smaller extent to the atmospheric contamination [35]. As a result of its long lifetime (17000 h in temperate climatic zone) [36], this insecticide can be detected at sites remote from human activities.

As shown in Figure 1, metolachlor was detected repeatedly between April and July 1996 at a mean concentration of 19 ng/L. This herbicide is observed in precipitation during its application period (May-September) and has also been observed by us in rain in a previous sampling campaign in 1992, but at higher mean concentrations (~ 100 ng/L) [50].

Figure 1 also represents the results obtained for the two triazines, atrazine and terbuthylazine. Terbuthylazine was found at higher concentrations (mean 63 ng/L), and atrazine at a mean concentration of 21 ng/L. In a previous study, we found terbuthylazine at higher mean concentrations of ~ 100 ng/L [50], which is comparable to other studies [8–10]. For these two herbicides a clear correlation between the recovery in rain and the application period (April – July) is observed. Triazine herbicides are among the pesticides used most frequently throughout the world.

The main agent of this compound group, atrazine, is now found in many environmental compartments, in particular in soil and groundwater, but also in rain or fog due to its release into the atmosphere [49]. This has led to its ban in Germany in 1991. Despite banning this agent, in the present study it was still found frequently in rainwater, although in significantly lower concentrations than terbuthylazine. While the lifetime of most pesticides in the atmosphere is not known, for atrazine, both the rate constant for the reaction with OH radicals and

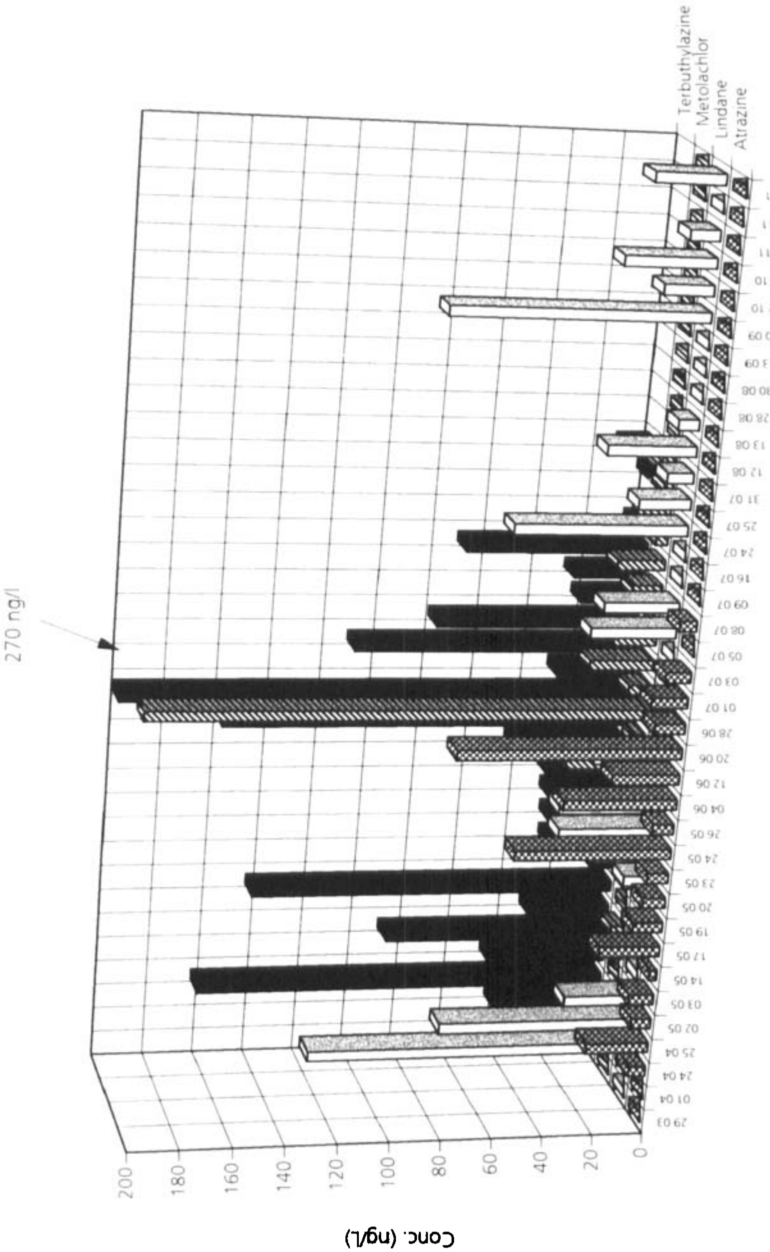

FIGURE 1 Concentration of pesticides in rain water in Hannover (Germany, 1996)

the quantum yield in aqueous solution were reported, as $k_{OH} = 14 \cdot 10^{-12}$ cm^3. s^{-1} [40] and $\phi = 0.061$, respectively [41]. These results show that the main degradation pathway is the reaction with OH radicals, resulting in a lifetime of more than one day. Thus, atrazine may be transported over longer distances. This transport may also occur in the aqueous phase (cloud droplets) leading to reduced degradation rates, longer lifetimes and thus possibly longer transport distance. Terbuthylazine is used as a substitute for atrazine in Germany. The rate constant for the reaction with OH radicals and the quantum yield reported in the literature are $k_{OH} = 11 \cdot 10^{-12}$ cm^3 . s^{-1} [42] and $\phi = 0.060$, respectively [41]. The corresponding lifetime is approximately one day due to reaction with OH radicals. Thus, also with this agent long-distance transport may occur.

Degradation products of pesticides

Knowledge about the pesticide degradation products is of interest because they may have toxicities and lifetimes different from those of the parent compounds. Triazines can be degraded by mechanisms involving dealkylation, deamination, dehalogenation and hydroxylation. Atrazine degradation in groundwater, surface water or soil is well known. Primary atrazine degradation products include hydroxyatrazine (HA), desethylatrazine (DEA) and desisopropylatrazine (DIA) which are formed through different pathways [45, 46]. The breaking of the isopropyl chain takes place slowly, in contrast to the breaking of the ethyl chain and leads to the formation of DIA which is rapidly transformed into desalkylatrazine (DAA), whereas production of this degradation product remains low when it is produced from DEA [43, 44]. The persistence of these products in soil was investigated by Winkelmann and Klaine, who determined a half-life of a few months in the soil [43]. Both DEA and DIA are phytotoxic. DEA is almost as toxic as the parent atrazine whereas DIA is five time less toxic [47]. A long persistence of these compounds was also determined in groundwater [48]. As mentioned above, atmospheric degradation of atrazine mainly involves dealkylation reactions [42].

For terbuthylazine, less degradation studies have been reported. It appears that this compound can also be degraded to several metabolites in soil, ground- and surface water both by biological and physical degradation. The main degradation products are two dealkylated metabolites, desmethylterbuthylazine (DMT) and desethylterbuthylazine (DET) and the dechlorinated metabolite, hydroxyterbuthylazine (HT). To our knowledge, the degradation products of terbuthylazine in the atmosphere have not been studied.

Like the parent compounds, the degradation products of atrazine and terbuthylazine in rainwater have also been analyzed by GC-MS. For this reason, only the dealkylated degradation products were determined, which are amenable to GC.

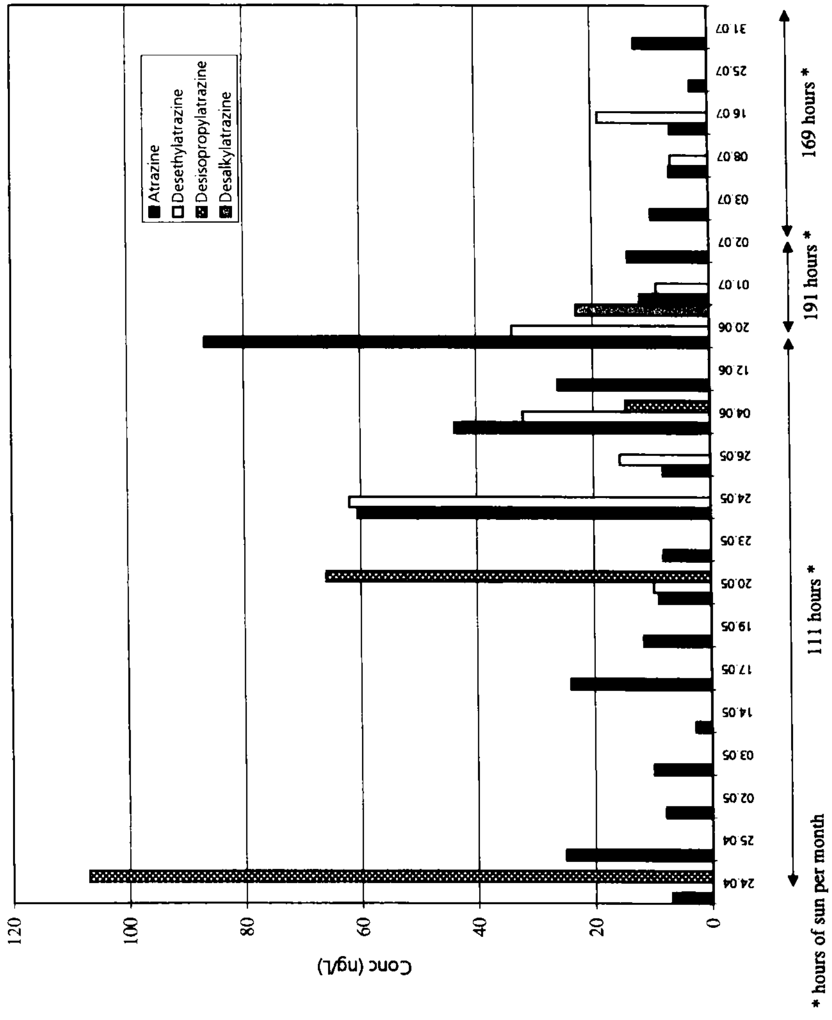

FIGURE 2 Concentration of atrazine and its degradation products in rain water in Hannover (Germany, 1996)

The results are summarized in Table III, in which the range of concentrations and the mean concentration, but also some validation data of the analytical method (recovery, LOQ) are presented. The main degradation product found for atrazine was DEA with a mean concentration of 24 ng/L. DIA was identified three times in a range from 14 to 107 ng/L and DAA found in only one sample at a concentration of 23 ng/L. These three degradation products of atrazine have been previously identified in rainwater [8, 15, 27].

Figure 2 presents for each event the concentrations found for both atrazine and its transformation products. During a first period from the beginning of April to the end of May, atrazine was found in every sample but a transformation product (DIA) in one sample only, whereas during a second period from the middle of May to the middle of July, the parent compound was accompanied by some degradation products for most of the time. The ratio between the amounts of DEA and atrazine was in the range of 0.4 to 2. A complete atmospheric degradation of atrazine has never been observed.

Figure 3 presents for each event the concentrations found for both terbuthylazine and it transformation product. Only one degradation product was investigated, desethylterbuthylazine (DET) which in this study was identified for the first time in precipitation. From 25 events in which terbuthylazine was identified, 14 samples contained desethylterbuthylazine (DET). Most of these events where both the parent compound and the degradation product were found took place between the middle of May and the beginning of July. The same concentration range was found for the two compounds, but the ratio between the amounts of DET and terbuthylatrazine varied within a wide range from 0.1 to 4. As for atrazine, no complete degradation was observed.

CONCLUSIONS

From twelve target pesticides monitored in rainwater in 1996, two could be identified only at trace levels, four (i.e. lindane (γ-HCH), atrazine, terbuthylazine and metolachlor) were determined repeatedly during the application period in concentrations ranging from ≈1 ng/L (limit of quantification) to 270 ng/L. As compared to a previous sampling campaign in 1992, a decrease in concentration was found for terbuthylazine and in particular for metolachlor. The observed concentrations are low compared to those reported in the U.S. [13, 14] which may be explained by the mode of application and the equipment used.

Although the use of atrazine has been banned in Germany, small amounts of this agent were still found in precipitation which may result from long-distance transport from neighboring countries, where this pesticide is still permitted.

The transformation products desethylatrazine, desisopropylatrazine and desalkylatrazine have been observed. Desethylatrazine was the main degradation product found in comparable concentrations of the parent compound. These metabolites have previously been identified in rainwater.

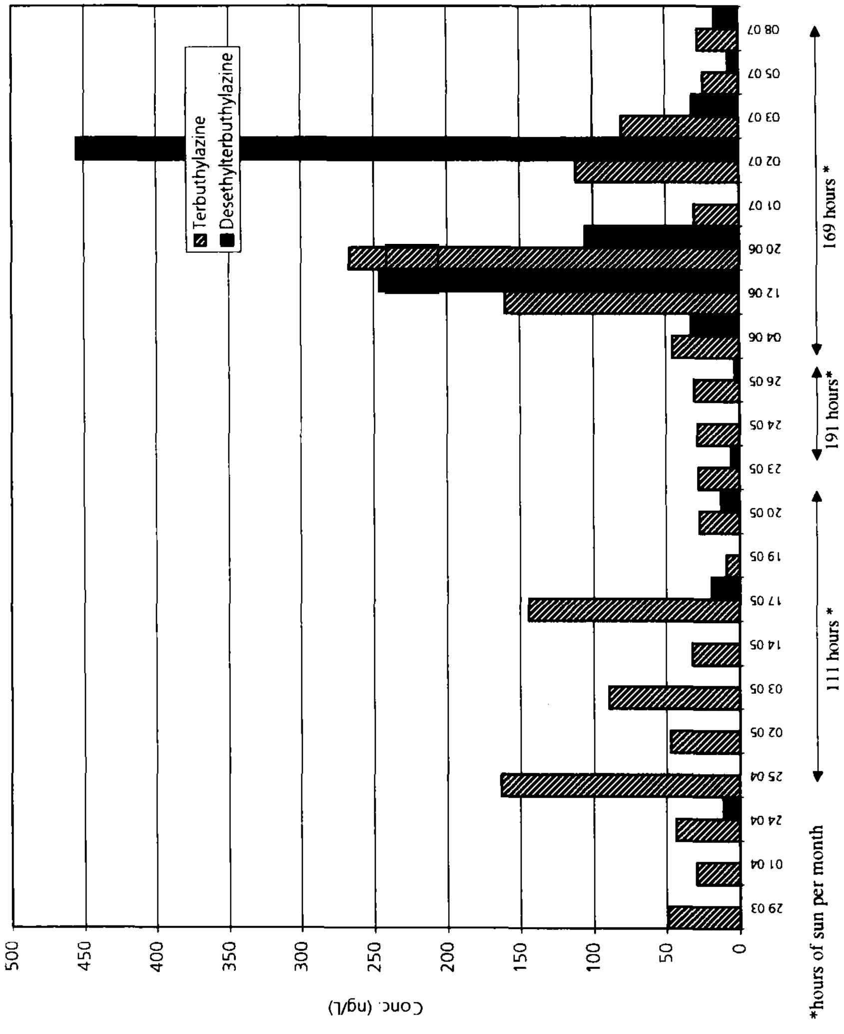

FIGURE 3 Concentration of terbuthylazine and its degradation products in rain water in Hannover (Germany, 1996)

However, a degradation product of terbuthylazine, desethylterbuthylazine, has been determined for the first time in precipitation, where the mean concentration is comparable to that of the parent compound.

As the collection and the analysis of rainwater is easier than that of air, the determination of transformation products of pesticides in precipitation may be used as a probe for the atmospheric degradation of pesticides. It is likely that the products formed by dealkylation reactions of atrazine and terbuthylazine are formed by an initial attack of OH radicals. As the concentration of OH radicals in cloud or rain droplets is low, these products will have been formed mainly in the gas and not in the liquid phase of the atmosphere, where scavenging by cloud or rain droplets occurs in a second step. As pointed out by one reviewer the degradation products of atrazine and terbuthylazine could also be formed by microbial degradation on soil followed by transport into the atmosphere as the boitic and abiotic degradation leads to the same products. Although this route cannot be excluded completely biotic metabolism is neglegible during the spraying process and of minor importance prior to or during volatilization from plants surfaces.

The study demonstrates that a substantial degradation of triazines in the atmosphere may occur. Thus, when discussing the input of pesticides into the atmosphere, their degradation products have to be taken into account.

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