

Occurrence and Behavior of Pesticides in Rainwater, Roof Runoff, and Artificial Stormwater Infiltration

THOMAS D. BUCHELI,
STEPHAN R. MÜLLER,*
SIEGRUN HEBERLE, AND
RENÉ P. SCHWARZENBACH

Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), CH-8600 Dübendorf, Switzerland

To prevent overloading of sewer systems and to ensure sufficient recharging of the groundwater underneath sealed urban areas, collection and artificial infiltration of roof runoff water has become very popular in many countries including Switzerland. However, there is still a considerable lack of knowledge concerning the quality of roof runoff, particularly with respect to the presence of pesticides. In this work, the occurrence and the temporal variations in concentration in rainwater and in roof runoff from different types of roofs (i.e., clay tile roofs, polyester roofs, flat gravel roofs) were determined for the most important members of three widely used classes of pesticides (i.e., triazines, acetamides, phenoxy acids). It is shown that in rain and roof runoff, maximum pesticide concentrations originating primarily from agricultural use occurred during and right after the application periods. Maximum average concentrations for single rain events and total loads per year were, for example, for atrazine, 903 ng/L and 13 900 ng/(m² year); for alachlor, 191 ng/L and 5900 ng/(m² year); and for R-dichlorprop, 106 ng/L and 5100 ng/(m² year). Further, the study reveals that a major portion of the compounds washed out from the atmosphere may actually reach the groundwater, particularly if the roof runoff is infiltrated directly into highly permeable zones of the subsurface. Nevertheless, although in some cases European Union and Swiss drinking water standards (100 ng/L) were not always met in rain and roof runoff waters, for the three compound classes investigated, the groundwater contamination potential of the pesticides originating from the atmosphere can be considered of equal or even smaller importance as compared to their direct use in agriculture. The investigations also show that leaching of pesticides used as construction chemicals on roofs, that is, as roof protection agents in sealings used on flat gravel roofs, may be a much more significant source of organic pollutants present in roof runoff (see also our following paper in this issue).

Introduction

Direct infiltration of unpolluted stormwater (rainwater runoff from sealed surfaces, e.g., roads, roofs) into groundwater

has obvious advantages in that the overloading of sewer systems is prevented, and groundwater underneath sealed urban areas is recharged (2, 3). Stormwater infiltration is therefore becoming increasingly important in such regions. In fact, according to Swiss legislation, unpolluted stormwater has to be directly percolated into the ground (Swiss Water Pollution Control Law, 1992, Article 7, Paragraph 2). However, considering that stormwater may contain significant levels of pollutants, unrestricted application of this law is somewhat ambiguous, particularly because artificial infiltration systems exhibit a deliberately enhanced permeability to achieve accelerated percolation velocity, thus resulting in reduced retention and degradation of both atmospheric and road or roof-delivered contaminants in the underground.

To date, there is still a considerable lack of data concerning the quality of stormwater, especially of roof runoff waters. A few investigations dealt with trace metals in roof runoff (4, 5), but much less information is available on organic compounds, particularly on pesticides (6). Although the occurrence of pesticides and other organic compounds in rainwater (7–11), roof runoff (6), and percolating waters in agricultural areas (12–15) has been studied, comprehensive investigations focusing on the transfer of pesticides from the atmosphere to groundwater during stormwater infiltration are very scarce.

In this paper, we present data from various field studies, aimed to evaluate to what extent certain classes of widely used pesticides could pose a problem with respect to groundwater contamination due to the direct infiltration of roof runoff. To this end, several different aspects of roof water infiltration were investigated. First, the occurrence and the seasonal variations in concentration in rainwater were determined for a series of pesticides (i.e., triazines, acetamides, phenoxy acids). In addition, during selected rain events, the washout dynamics and the resulting temporal development in concentration of these compounds in roof runoff was investigated for three types of roofs, that is, a clay tile roof, a polyester roof, and a flat gravel roof. Finally, at one field site, a complete analysis of the transport and behavior of selected pesticides from rain via three different roofs into the ground has been performed.

Experimental Section

Sampling and Sample Sites. Rainwater was collected at Dübendorf (Canton Zurich), Grütze (an industrial suburb of Winterthur, Canton Zurich), and Tüffenwies (an industrial area in the north-western part of Zurich) with a 1 m² Teflon rain sampler for bulk samples, and a 5.06 m² funnel coated with a Teflon foil for sequential rainwater sampling. During dry periods, the latter sampler was covered with a plastic sheet and washed with Nanopure water and methanol prior to rainwater sampling.

The polyester and the flat gravel roof, partly covered with naturally grown vegetation, as well as the rainwater samplers were located at Tüffenwies. The clay tile roof was situated on the Werdinsel, a few hundred meters away from the other sampling site. Projected roof areas and inclinations were as follows: polyester roof, 108.8 m² and 5.6°; clay tile roof, 89.2 m² and 37.96°; and flat gravel roof, 134 m² and 0°. Sampling of sequential roof runoff was automatically performed (IMETH AG, Wetzikon, Switzerland).

The stormwater infiltration site (Figure 1) is situated in Grütze. At this site, the shallow subsurface sediments consist of a fluvio-glacial gravel. On top of a 60 cm drainage gravel layer, a 5–10 cm thick layer of humus was deposited (numbers

* Corresponding author e-mail: mueller@eawag.ch; phone: +41 1 823 54 60; fax: +41 1 823 54 71.

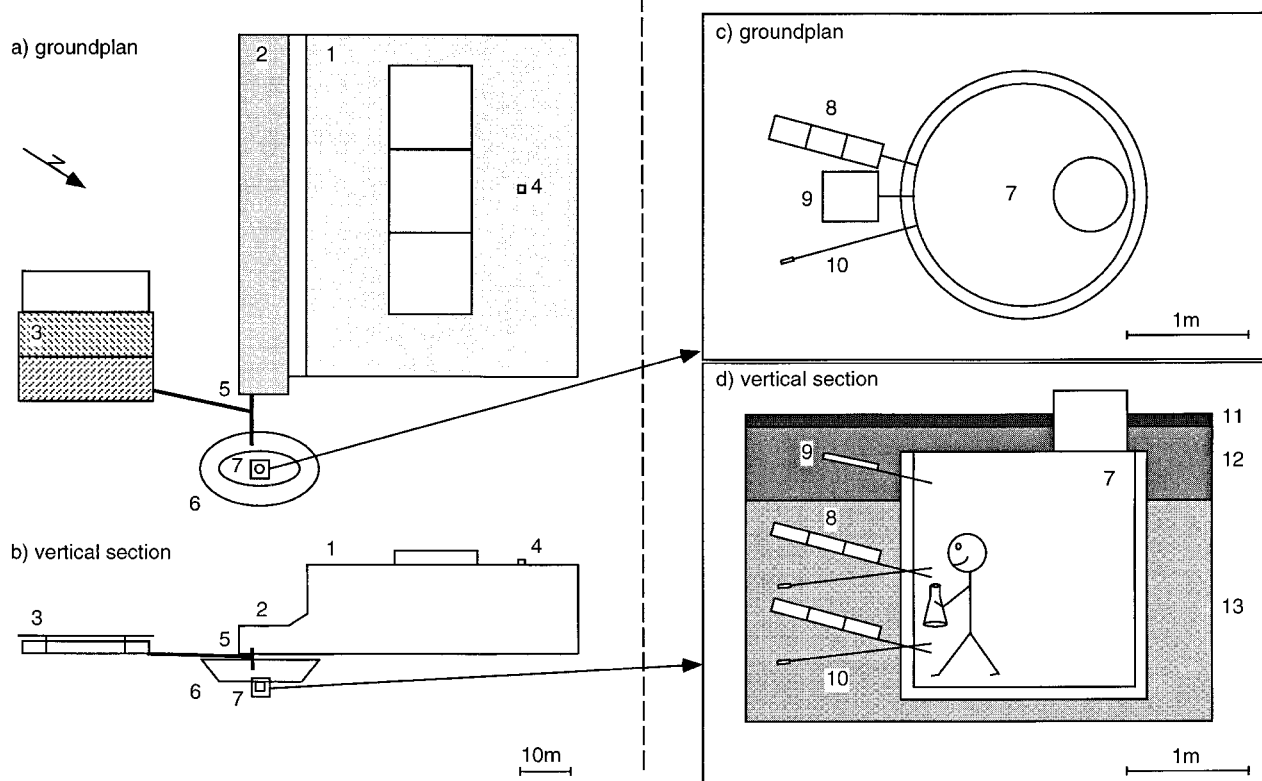


FIGURE 1. Storm water infiltration site in Grøze with groundplan (a), and vertical section (b), and enlarged sections of the sampling shaft within the infiltration pit with groundplan (c), and vertical section (d, simplified): 1, flat gravel roof; 2, flat gravel roof with rooftop planting; 3, plastic roof; 4, Teflon rain sampler; 5, roof runoff, discharged through one single pipe into the infiltration pit; 6, infiltration pit; 7, sampling shaft; 8, lysimeters (three in 100 cm, and three in 160 cm depth, each one comprising three compartments with 600 cm² each); 9, lysimeters (three in 40 cm depth with an area of 1800 cm² each); 10, suction cups (three in 100 cm, and three in 160 cm depth); 11, humic layer (10 cm depth); 12, drainage gravel layer (60 cm); 13, natural aquifer sediment of fluvio-glacial gravel.

11–13 in Figure 1). At the bottom of the infiltration pit, a shaft of 2 m in diameter and depth was inserted into the ground (number 7 in Figure 1). From within that shaft, various lysimeters (polyethylene (PE), six half pipes with areas of 3 times 600 cm² each (number 8 in Figure 1), and three single vessels with 1800 cm² each (number 9 in Figure 1) and suction cups (number 10 in Figure 1, Prenart Super Quarz; PRENART Equipment ApS, Frederiksberg, Denmark) were radial-symmetrically installed. They covered a section of $\pm 100^\circ$ around the direction of the roof runoff inflow and allowed the sequential or integrated sampling of percolating water at three different depths (40, 100, and 160 cm, respectively). Sample vessels used were made from either PE or polycarbonate. No significant sorption on lysimeter materials, suction cups, and sample equipment was found for any of the compounds investigated (data not shown). For a more detailed description of the field systems, see ref 16.

Pesticide Analysis. The pesticides investigated were determined by the method previously described in ref 17. Briefly, the compounds were enriched by solid-phase extraction on Graphitized Carbon Black, followed by sequential elution of the neutral and acidic pesticides and derivatization of the latter fraction with diazomethane. Identification and quantification of the compounds was performed with GC/MS using d₅-atrazine, ¹³C₆-metolachlor, and ¹³C₆-dichlorprop as internal standards. Absolute recoveries from Nanopure water spiked with 4–50 ng/L were 85% \pm 10%, 84% \pm 15%, and 100% \pm 7% for the triazines, the acetamides, and the phenoxy acids, respectively. Recoveries from rainwater spiked with 2–100 ng/L were 95% \pm 19%, 95% \pm 10%, and 92% \pm 14% for the triazines, the acetamides, and the phenoxy acids, respectively. The average method precision deter-

mined with fortified rainwater (2–50 ng/L) was 6.0% \pm 7.5% for the triazines, 8.6% \pm 7.5% for the acetamides, and 7.3% \pm 3.2% for the phenoxy acids, and method detection limits (MDLs) ranged from 0.1 to 4.4 ng/L.

Separation of the R- and S-enantiomers of mecoprop and dichlorprop was performed with a fused silica capillary column (FS 71 PS-086 + 20% Me- β -CD, 0.13 μ m film thickness, 0.25 mm i.d., 15 m). The oven temperature was programmed as follows: 1 min at 60 $^\circ$ C, to 165 $^\circ$ C at 15 $^\circ$ C/min, to 230 $^\circ$ C at 25 $^\circ$ C/min, and 3 min at 230 $^\circ$ C. Retention times were 7.74 and 7.84 min for R- and S-mecoprop, and 8.30 and 8.38 min for R- and S-dichlorprop, respectively. Detection limits in rain samples of the chiral compounds were around 1 ng/L (corresponding to a signal-to-noise ratio of three). Peak areas were used for the determination of the enantiomeric ratios. If only one enantiomer was present, the noise area of the respective missing compound served for calculation of the ratio. All other parameters were as described in ref 17.

All samples were kept at 4 $^\circ$ C in the dark. In earlier studies, it was found that triazine pesticides in natural water samples were stable for a few years under these conditions (17). For the main representatives of the acetamides, no significant changes in concentrations were observed within eight months after sampling (metolachlor, recovery, 96% \pm 5%, *n* = 4; alachlor, recovery, 85% \pm 14%, *n* = 4). However, the most important phenoxy acids were significantly degraded within that time period (mecoprop, recovery, 76% \pm 3%, *n* = 3; and dichlorprop, recovery, 52% \pm 40%, *n* = 5). Note that the degradation of the chiral compounds metolachlor, mecoprop, and dichlorprop may be enantioselective, and that racemization may occur (18–20). Thus, acetamides and phenoxy

TABLE 1. Pesticides in Rain Water between February and October 1996 at Grütze

	detected in <i>n</i> samples out of 41	main period of appearance ^a	concentration [ng/L]		total load ^b [ng/(m ² year)]
			median	maximum	
triazines					
atrazine	28	early May–mid July	33	903	13 900
desethylatrazine	20	mid May–end of July	29	166	5400
deisopropylatrazine	13	late May–late June	26	137	3000
terbutylazine	13	early April–late June	9	48	1800
simazine	10	late March–begin of July	10	53	700
propazine	1	mid June	7	7	10
acetamides					
alachlor	16	end of April–end of May	19	191	5900
metolachlor	16	begin of May–begin of June	15	124	4400
propachlor	12	mid May–early August	10	48	1300
dimethenamid	4	mid May–mid June	24	78	300
metalaxyl	2	late February–begin of July	14	17	100
metazachlor	1	mid September	12	12	400
phenoxy acids					
<i>R</i> -mecoprop	17	mid April–end of July	10	50	3900
<i>S</i> -mecoprop	11	mid May–late August	10	19	3000
<i>R</i> -dichlorprop	20	end of March–early June	12	106	5100
<i>S</i> -dichlorprop	2	early April–mid May	9	11	300
2,4-D	2	begin of May–early May	16	23	400
MCPA	4	early April–early May	16	27	800

^a Time span during which 10% and 90%, respectively, of the total load, was deposited; begin: 1st to 6th; early: 7th to 12th; mid: 13th to 18th; late: 19th to 24th; end: 25th to 30th day of the month. ^b Assuming no or little application and atmospheric occurrence of the investigated pesticides from November to January (see also Figure 2).

acids were only quantified if analyzed within the first three months after sampling.

Results and Discussion

Seasonal Variation in Occurrence and Concentrations of Pesticides in Rainwater. Table 1 summarizes the results from 41 subsequent rainwater samples analyzed for triazines, acetamides, and phenoxy acids between February and October 1996. In addition, for the most important representatives of each of the compound classes investigated, the specific daily and cumulative loads during this period are shown in Figure 2. From these, and from results obtained at the other sites (Tüffenwies and Dübendorf, data not shown), some general features are apparent.

For all three pesticide classes, the compounds most frequently detected are, with a few exceptions (e.g., propachlor), also the compounds most frequently used in Switzerland. Note that the same substances are also important pesticides in many other countries. Within the analyzed compound classes, pesticides not registered in Switzerland including atratone, acetochlor, 2,4,5-T, and 2,4,5-TP were never detected in any of the rainwater samples.

Most parent compounds were primarily detected during and/or right after their main application period in spring and early summer (see Figure 2, shaded areas, and Table 1, third column). Generally, there was a certain trend in that the more volatile herbicides (e.g., alachlor and metolachlor) were primarily found during the application period, while the less volatile and/or ionizable ones (i.e., the phenoxy acids or atrazine) were still present in rainwater several weeks later.

In addition to the parent compounds, some metabolites (i.e., desethyl- and deisopropylatrazine) and enantiomers of optically active herbicides (i.e., *S*-mecoprop, and *S*-dichlorprop), which are known to be formed in the environment by racemization of the active *R*-form (18–20), were found quite frequently. Maybe not too surprisingly, peak concentrations of these metabolites were observed with a delay of between two and six weeks with respect to their parent compounds. Over the season, the desethylatrazine to atrazine concentration ratio changed markedly from 0.36 ± 0.21 ($n = 12$, average atrazine concentration: 81 ± 109 ng/L) before June 30 to

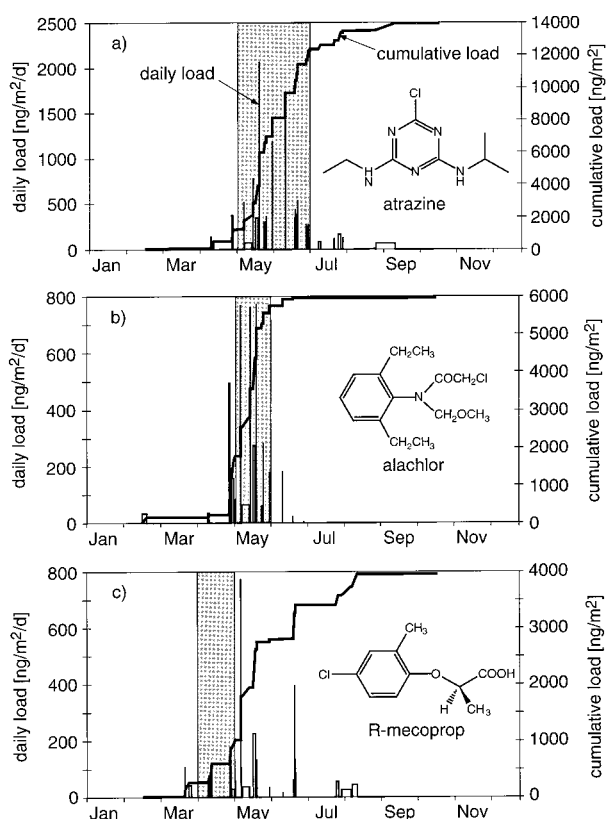


FIGURE 2. Specific daily and cumulative load of atrazine (a), alachlor (b), and *R*-mecoprop (c) from February to October 1996 in Grütze. Shaded areas indicate the main application period of the individual pesticide.

0.70 ± 0.42 ($n = 8$, average atrazine concentration: 211 ± 299 ng/L) later on. The *R*- to *S*-mecoprop concentration ratio was 2.05 ± 1.86 ($n = 17$, average *R*-mecoprop concentration: 14 ± 11 ng/L) before June 30 and 0.35 ± 0.13 ($n = 8$, average *R*-mecoprop concentration: 5 ± 1 ng/L) thereafter. These findings suggest that, after the application period, during several weeks, there was still a significant input

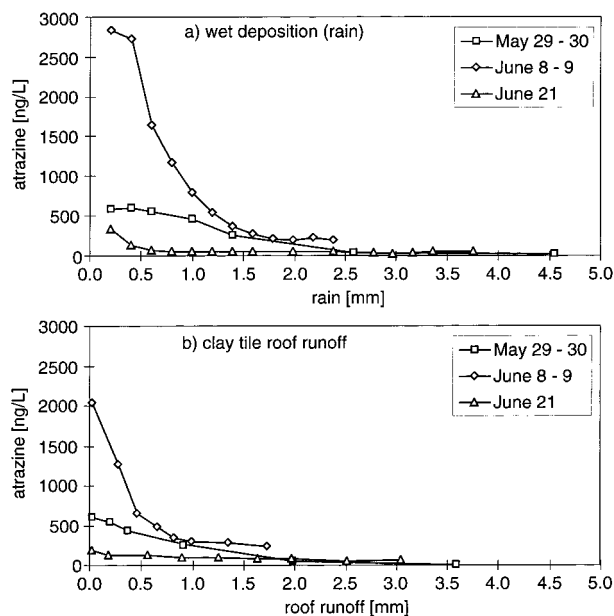


FIGURE 3. Wet deposition (rain, a) and tile roof runoff (b) dynamics of atrazine during three rain events in Tüffenwies. Rain events were sampled within the application period in 1995.

of less volatile pesticides and, particularly, of their primary transformation products, into the atmosphere.

For a judgment of the significance of the concentration levels found for the various pesticides in rainwater, it is useful to compare these values with the Swiss and European Union drinking water standards of 100 and 500 ng/L for single and total pesticides, respectively. From the data given in Table 1, it can be seen that only a few single compounds, and among them, particularly atrazine, significantly exceeded the 100 ng/L limit. Note that a certain dependence of pesticide concentrations on the amount of rain could be observed, with the highest numbers for events of a few millimeters of precipitation only. This is consistent with the observation that these rather polar pesticides are washed out quite efficiently from the atmosphere (see below). Compared to the single compounds, for total pesticides, in spring and early summer, the situation is somewhat more critical, particularly when considering that other important compound classes including, for example, nitrophenols (see refs 21, 22) and halogenated acetic acids (23, 24) must be suspected to be concomitantly present in rainwater at even higher concentrations than the ones found for the pesticides investigated in this study. Hence, during the main pesticide application times, rainwater may exhibit total pesticide concentrations that markedly exceed the drinking water standard of 500 ng/L.

Washout Dynamics of Pesticides During Single Rain Events. The knowledge on the deposition characteristics of pesticides is essential for the correct interpretation of the subsequent investigations of roof runoff behavior. As already pointed out above, because of the rather low Henry's law constants of most of the pesticides investigated ($1\text{E}-6$ to $1\text{E}-9$, dimensionless), it can be anticipated that particularly the triazines and the phenoxy acids should be readily washed out from the atmosphere if mainly present in the gas phase. Thus, a significant drop in concentration of the first few millimeters of rain can be expected for such compounds. This hypothesis was tested by the sequential sampling of rainwater from single rain events during the application period. Figure 3a depicts the concentration dynamics of atrazine for three different rain events in May and June 1995. Concentrations were found to be maximal (up to $3\text{ }\mu\text{g/L}$) at the onset of rain events and rapidly decreased by a factor of

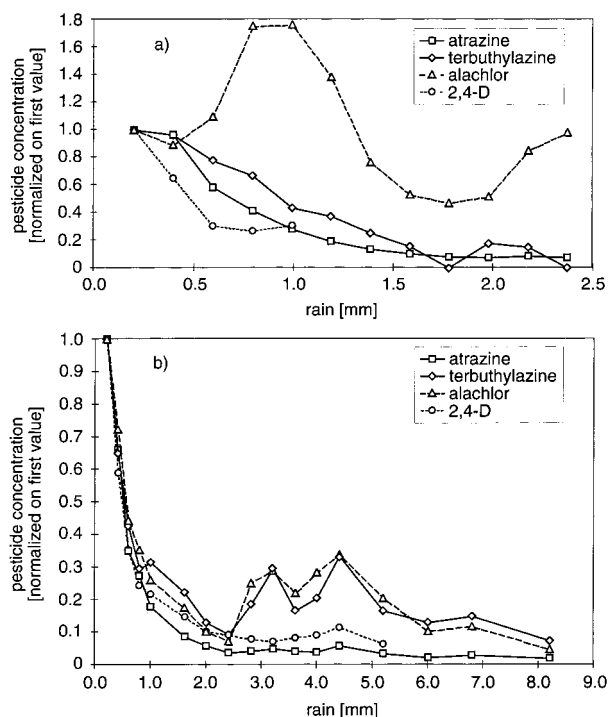


FIGURE 4. Comparison of the wet deposition dynamics of different pesticides: Variations to the normally observed first flush washout behavior. (a) Rain event from June 8, 1995 in Tüffenwies. Washout of a homogenous, more local air mass. Note that metolachlor and dimethenamid showed a washout behavior similar to the one of alachlor (data not shown). (b) Rain event from April 26, 1997 in Dübendorf. Passage of two subsequent air masses of different origin. Note, a similar washout behavior was observed for chlorinated acetic acids and trifluoroacetic acid (25) and for nitrophenols (26).

10–20 within the first 2 mm of rain. Thus, the washout of atrazine exhibited a so-called “first flush” effect, as was in general also found to be the case for the other pesticides investigated in this study, and has been reported for other pollutants in the literature (see, e.g., ref 21). However, as is shown in Figure 4, in some cases, a more complex washout behavior was observed for certain compounds.

On one hand, Figure 4a depicts a compound class-specific deposition behavior during the washout of a rather homogeneous air mass: whereas the triazines (represented by atrazine and terbutylazine) and the readily soluble phenoxy acids (represented by 2,4-D) showed a similar deposition pattern, that is, a first flush washout effect, the concentrations of the more volatile acetamides (represented by alachlor) even increased in the course of the rain event. On the other hand, subsequent scavenging of air masses with different origin led to an altered deposition pattern that was not compound class-specific (Figure 4b), but depended on the actual pesticide composition of the respective air masses. Nevertheless, in the majority of the rain events investigated, the atmospheric washout of different types of pesticides usually occurred simultaneously and immediately, and with initial concentrations up to a few micrograms per liter.

Roof Runoff Dynamics During Single Rain Events. For the runoff from roofs exhibiting a very low water storage capacity and thus a very short water residence time (i.e., the investigated clay tile and polyester roofs), the most important question is whether there is a significant additional input from previous dry deposition of pesticides on the roofs. In Table 2, the total loads calculated for various pesticides analyzed in runoff from clay tile and polyester roofs are compared to the respective loads in the rainwater. As is evident, in no case, a significant additional input of any of

TABLE 2. Relative Runoff Loads of Different Roof Types^a

	tile roof, Tüffenwies	<i>n</i>	polyester roof, Tüffenwies	<i>n</i>	flat gravel roof, Tüffenwies; minor rain events (5–15 mm)	<i>n</i>	flat gravel roof, Tüffenwies; major rain event (20 mm)	<i>n</i>	combined roof system, Grüze; major rain events (>53 mm)	<i>n</i>
atrazine	0.9 ± 0.3	7	1.2 ± 0.4	4	0.04 ± 0.02	3	0.73	1	0.93	1
desethylatrazine	1.0 ± 0.4	7	1.2 ± 0.2	4	0.08 ± 0.03	3	0.82	1		
deisopropylatrazine	0.7 ± 0.2	6	0.7 ± 0.1	2	0.10 ± 0.01	2	1.07	1		
terbutylazine	0.6 ± 0.3	6	1.1 ± 0.3	4	2.28 ± 2.79	4	2.59	1		
simazine	0.7 ± 0.3	5	0.9 ± 0.3	4	0.03	1				
alachlor	1.0 ± 0.2	2								
metolachlor	1.1 ± 0.2	2								
(<i>R,S</i>)-mecoprop	0.6 ± 0.5	2							41.0!	1
(<i>R,S</i>)-dichlorprop	0.9	1								
2,4-D	0.8 ± 0.4	2								
MCPA	1.0	1								

^a Normalized to the respective rain load; ng/m² roof runoff over ng/m² rainwater.

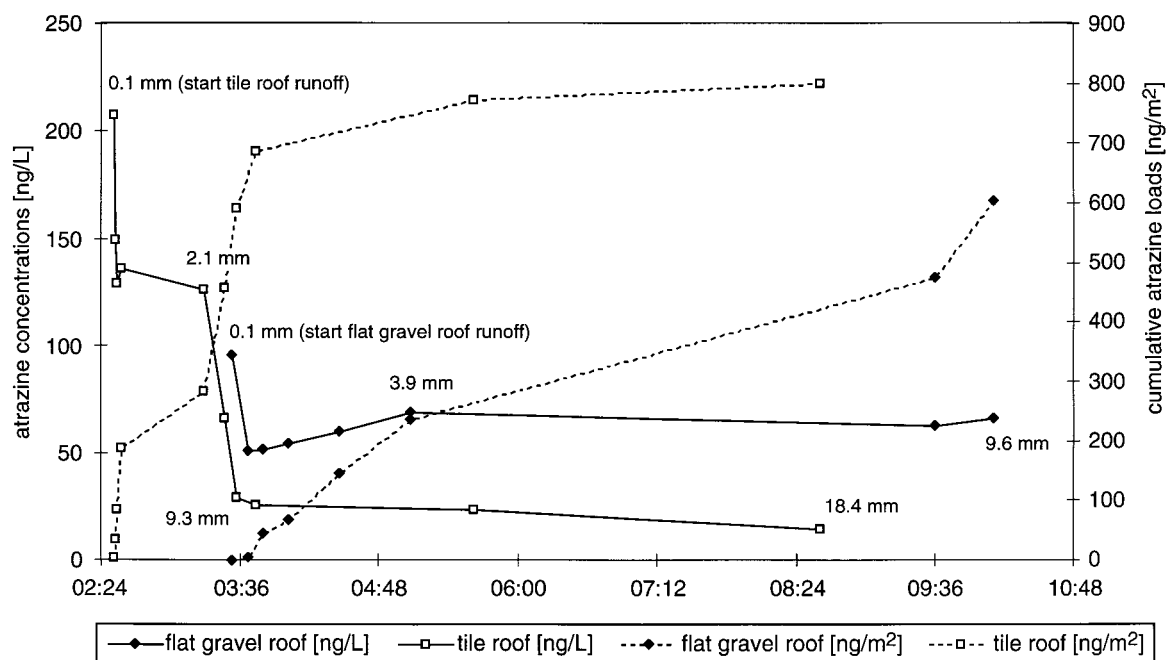


FIGURE 5. Comparison of atrazine in roof runoff from two extremely different roof types during the same rain event (July 3, 1995, Tüffenwies): solid lines, concentrations (ng/L); broken lines, cumulative loads (ng/m²).

these substances was found for these two types of roofs (relative load, 0.6–1.2; see Table 2). Thus, dry deposition was of minor importance for the compounds investigated which is in accordance with refs 27 and 28. Note that for other types of organic compounds, for example, 4-nitrophenol, which was found to be mainly particle bound (29), dry exposition has been observed (30). In some cases, even some loss of compound was observed, particularly for minor rain events, which could have been due to sorption of the compounds during initial wetting of the roof surfaces. However, as is illustrated with Figure 3b for atrazine, for clay tile and polyester roofs, in general, the runoff dynamics reflected more or less the washout dynamics of the compounds from the atmosphere.

A quite different picture was obtained for the flat gravel roofs because of their significant water storage capacity. During a rain event, compounds may be retained on the roof which may lead to a significant dampening of concentration fluctuations. This is visualized in Figure 5 which shows the temporal variations in concentration of atrazine in the runoff of a clay tile roof and of a flat gravel roof, respectively, during the same rain event. The clay tile roof runoff showed a typical first flush behavior with initial atrazine concentrations of

about 200 ng/L (Figure 5 open squares, solid line). In contrast, on the flat gravel roof, the first flush was stored and diluted by subsequent rainwater until the water storage capacity was reached, which happened about 1 h after the rain began. As is evident from Figure 5 (filled diamonds, solid line), in this case, a much less pronounced first flush behavior and a more or less constant atrazine concentration in the runoff were observed. Note that after the first 10 mm of runoff, the cumulative atrazine loads were quite similar for both roofs (see broken lines in Figure 5), and when integrating over the whole rain event (20 mm), they also corresponded reasonably well to the respective load from the rainwater (Table 2, flat gravel roof, Tüffenwies, major rain event). This indicates that no major loss of atrazine (as well as of the other triazines) occurred on the flat roof during this major rain event.

When considering minor rain events, however, the flat gravel roofs may act as a sink, that is, only minor parts of the total rainwater loads are found in the runoff (see Table 2). In such cases, in which the water storage capacity of the roof is only slightly exceeded by the total amount of precipitation, the compounds are retained on the roof. During subsequent dry periods, the compounds may then be (bio)degraded on

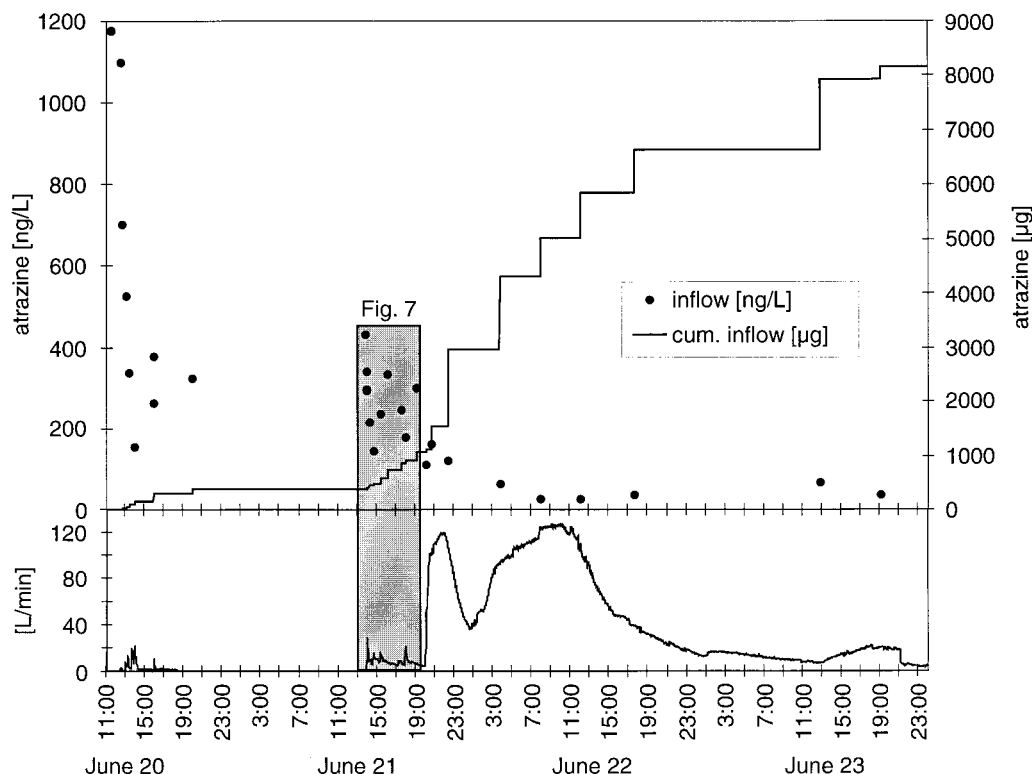


FIGURE 6. Atrazine concentrations and cumulative load in roof runoff (upper box), and runoff flow rate (lower box) into the storm water infiltration site in Grütze during two rain events from June 20, 11:00 to June 23, 24:00, 1996. The shaded area is magnified in Figure 7.

the roof, as is indicated by the generally higher desethyl-atrazine-to-atrazine ratio in flat roof runoff compared with rainwater (data not shown).

Finally, from the data given in Table 2, it can be seen that for some compounds, that is, terbutylazine and particularly (*R,S*)-mecoprop, the loads in the runoff from certain flat gravel roofs significantly exceeded the loads in the rainfall. These findings demonstrate that flat gravel roofs may also act as sources for pesticides. For terbutylazine, this additional input could have been due to the application on the roof itself or in yards nearby. In the case of (*R,S*)-mecoprop, however, the drastically higher concentrations (i.e., up to several hundred micrograms per liter) found in the combined runoff from the roofs in Grütze for both enantiomers could not be explained by the direct application of these compounds. It was found that (*R,S*)-mecoprop stemmed from the hydrolysis of Preventol B 2, a root protection agent that is added in significant amounts (about 1 wt %) to polymer modified bituminous roofing membranes used for sealing purposes. Details on the kinetics of the formation of (*R,S*)-mecoprop from Preventol B 2, and its elution from bituminous membranes, as well as the results of field studies conducted to assess the significance of this source of pesticides with respect to groundwater, for example, during stormwater infiltration and surface waters via wastewater treatment plants, are discussed in a companion paper (1).

Behavior of Pesticides During Artificial Infiltration of Roof Runoff. Figure 6 (upper box) shows the time course of the concentration of atrazine in the combined runoff of three roofs at the infiltration site in Grütze (see numbers 1–3 in Figure 1) over a period of 3 days (June 21–23, 1996) during which two rain events occurred (Figure 6, lower box). All other detected compounds (i.e., desethylatrazine, deisopropylatrazine, terbutylazine, metolachlor, dimethenamid) showed a very similar behavior, although at significantly lower concentrations. As is evident, a first flush effect was observed during both rain events because, at the onset of the rain, the roof runoff originated primarily from the plastic roof (see

number 3 in Figure 1). As soon as the two flat roofs (see numbers 1 and 2 in Figure 1) dominated the total runoff (i.e., after June 21, 15:00), more or less steady atrazine concentrations were observed.

The infiltration of roof runoff water into the subsurface was very fast and complete, that is, almost no damming up at the soil surface was observed (for details on the hydrological situation, see ref 16). However, the water mainly infiltrated through preferential flow paths, as indicated by the tremendous variability of the water yield from the individual lysimeters (see Figure 7 and explanations below). Tracer experiments revealed that the residence times of a conservative tracer (fluorescein) and atratone (a triazine pesticide) in the first two meters of the subsurface were identical and very short (i.e., between 15 and 50 min, depending on the lysimeter).

Figure 7 (enlarged section from Figure 6) compares the atrazine concentrations in roof runoff samples with those from three lysimeters of different depths and with different water flow. The length of the horizontal lines that symbolize atrazine concentrations of the percolating water equals the time required to provide a sample volume of 2 L. Note that the water flows were about 0.5 L/min for the fastest and 0.03–0.05 L/min for the slowest flow path. Irrespective of the large difference in the hydrodynamics and the different depth, the alterations in concentrations of roof runoff and percolating water were quite similar, and even minor fluctuations in runoff concentrations were still discernible in the infiltrating water. Moreover, atrazine concentrations in percolating waters were very similar to the one in roof runoff. This provides strong evidence that no degradation of atrazine occurred during the fast infiltration through macropores. A very similar result was also obtained for the other compounds (data not shown).

In suction cup water samples originating from the fine pores in the soil, atrazine concentrations were, however, significantly lower during the first rain event on June 20 as compared with the average roof runoff concentrations (79

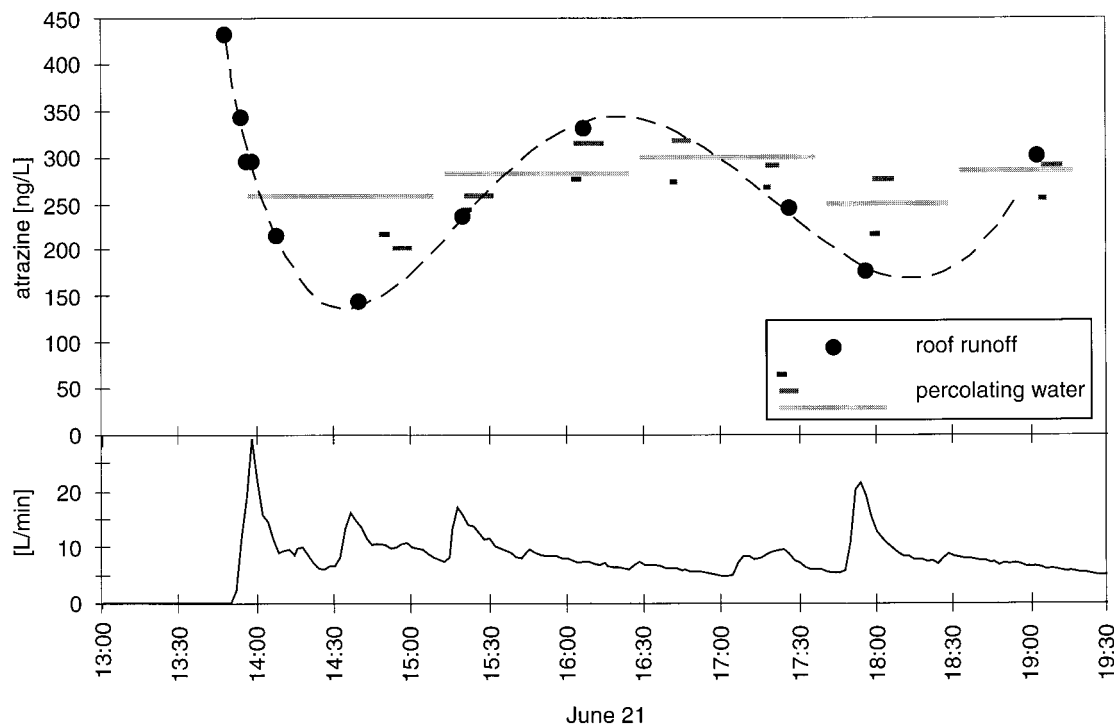


FIGURE 7. Atrazine concentrations in roof runoff and percolating waters (upper box), and runoff flow rate (lower box) into the storm water infiltration site in Grütze at the onset of a rain event from June 21, 13:00 to 19:30, 1996. Black dots indicate roof runoff samples, and the light grey, dark grey, and black bars represent water samples from three arbitrarily chosen lysimeters.

and 254 ng/L, respectively), but reached similar, or even slightly higher, concentrations later on (data not shown). Also, the desethylatrazine-to-atrazine ratio was significantly higher in the first sample from the suction cup than in roof runoff (0.9 and 0.36, respectively). Both the relatively low initial atrazine concentration and the higher desethylatrazine-to-atrazine ratio in the first suction cup sample suggest that the respective pore water originated from a previous rain event and that some atrazine degradation took place. In subsequent suction cup samples, however, the concentrations detected were more similar to the ones in the roof runoff, indicating replacement of the fine pore water by freshly infiltrating roof runoff.

Groundwater Contamination Potential of the Pesticides Present in Roof Runoff. To judge the significance of the input of pesticides from the atmosphere into groundwater when roof runoff is artificially infiltrated, not only the concentrations but also the total loads of the compounds have to be considered. As has been demonstrated by this study for three classes of pesticides, it can be assumed that, particularly during long rain events, a major portion of the compounds washed out from the atmosphere actually reaches the groundwater, particularly if the roof runoff is directly infiltrated into highly permeable zones of the subsurface. Hence, for this study, the loads calculated in Table 1 for rainwater can be used to estimate the annual input of the various compounds into the infiltration pit. As an illustrative example, at Grütze, where the total roof area is about 5100 m², for atrazine, a maximum total amount of approximately 70 mg is obtained, which, when assuming an infiltration area of 100 m², amounts to an annual load of 0.7 mg/m².

In agricultural use, which, in Switzerland is restricted to corn cultures, the maximum allowed atrazine dose is 80 mg/m². Hence, per unit area, the annual atrazine input to aquifers underneath roof runoff infiltration pits would correspond to the input expected from corn fields, if 1% of the total amount applied would finally reach the groundwater. Since this percentage is not an unrealistic estimate (for review, see ref

31), it can be concluded that in the case of atrazine, the problems related to infiltration of roof runoff are not significantly different from those related to direct agricultural application. Similar conclusions can probably also be drawn for most of the other pesticides investigated although, at present, there is not enough data available to allow sound mass balance calculations, particularly for the acetamides and the phenoxy acids.

One technical measure suggested to minimize the input of pollutants into artificial roof runoff infiltration systems, particularly of particle-bound species such as heavy metals or polycyclic aromatic hydrocarbons, is to discharge the first millimeters of roof runoff (i.e., the first flush) into the sewer systems (advanced separated sewer system; for an overview on different sewer concepts, see, e.g., ref 2). As shown by the results of this study (see e.g., Figures 5 and 6, cumulative loads), for the three classes of pesticides investigated, such a measure is only effective for roof systems with low water retention times (i.e., various types of inclined roofs). Thus, particularly in urban areas with different types of roofs, discharge of the first few millimeters of combined roof runoff into the sewer system will probably not be a very cost-effective measure to protect the groundwater from the types of pesticides investigated in this study. Furthermore, because these compounds are not retained in the ground, in contrast to the primarily particle bound pollutants, accumulation at the infiltration sites is not likely. However, due to hydrodynamic dispersion, high initial input concentrations are dampened out efficiently in the aquifer. Hence, although infiltrating roof runoffs might exceed the drinking water standards for pesticides at times, the receiving groundwaters are not likely to do so.

In conclusion, the results of this study indicate that triazine, acetamide, and phenoxy acid pesticides present in rainwater do not pose a significantly more severe groundwater contamination problem during artificial roof runoff infiltration than due to their direct application in agriculture. Furthermore, other biologically active compounds, particularly polar compounds that are formed in large quantities by

photochemical processes in the atmosphere (e.g., halogenated acetic acids, refs 23–25, nitrophenols, refs 21, 22, 26) or that are emitted to the atmosphere by fuel combustion (e.g., nitrophenols, ref 32), may be of much greater concern as compared to the compounds investigated in this study. Finally, as will be discussed in detail in a companion paper (1), sources other than the atmosphere, particularly biocides used as roof construction chemicals, may pose a much more significant threat to groundwater resources located underneath roof runoff infiltration pits.

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