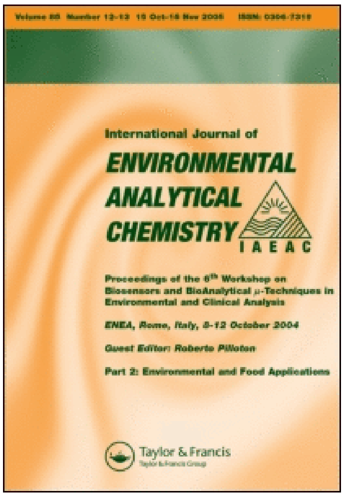

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Occurrence of Glyphosate in Surface Water

Christian Skark[a]; Ninette Zullei-seibert[a]; Uwe Schöttler[a]; Claus Schlett[b]
[a] Institut für Wasserforschung GmbH, Dortmund, Schwerte, FRG [b] Gelsenwasser AG, Gelsenkirchen, FRG

To cite this Article Skark, Christian , Zullei-seibert, Ninette , Schöttler, Uwe and Schlett, Claus(1998) 'The Occurrence of Glyphosate in Surface Water', International Journal of Environmental Analytical Chemistry, 70: 1, 93 — 104
To link to this Article: DOI: 10.1080/03067319808032607
URL: http://dx.doi.org/10.1080/03067319808032607

Intern. J. Environ. Anal. Chem., Vol. 70(1-4), pp. 93-104
Reprints available directly from the publisher
Photocopying permitted by license only

THE OCCURRENCE OF GLYPHOSATE IN SURFACE WATER

CHRISTIAN SKARK[a*], NINETTE ZULLEI-SEIBERT[a], UWE SCHÖTTLER[a] and CLAUS SCHLETT[b]

[a]*Institut für Wasserforschung GmbH, Dortmund, Zum Kellerbach 46, D-58239 Schwerte, FRG and* [b]*Gelsenwasser AG, Willy-Brandt-Allee 26, D-45891 Gelsenkirchen, FRG*

(Received 6 June 1997; In final form 5 May, 1998)

The commonly used non-selective herbicide glyphosate (N-[Phosphonomethyl]glycin) occurred in surface water of two small tributaries of the river Ruhr in North-Rhine-Westphalia (FRG) with a maximum concentration of 590 ng/l. In the examined catchment areas weed control application in rail tracks is one of the main sources of an input to surface water. The occurrence of the metabolite aminomethyl phosphonic acid (AMPA) was linked to glyphosate load rather than to a detergent inflow via municipal sewage. The observed disappearance of glyphosate was faster than the disappearance of diuron indicating a lower persistence. A final assessment of the importance of highly polar pesticides in organic contaminant of surface water needs extended water monitoring analyses and further field investigation.

Keywords: Glyphosate; aminomethyl phosphonic acid; pesticides; water quality

INTRODUCTION

Glyphosate (N-[Phosphonomethyl]glycin) is one of the most commonly used herbicides in Federal Republic of Germany (FRG) with a documented sale of more than 1000 t/a since 1991 [1]. This non-selective foliage uptaken pesticide is applied for weed control to maize and beet cultures, to pasture and forestry, to flower production as well as to settlement and industrial areas and to railway tracks. The application amount ranges between 1 kg/ha and 3.3 kg/ha active ingredient. Probably, more than 90 % of the annual tonnage is used in agriculture. In spite of the lower amount applied to non-agricultural targets application at high permeable sites like railway tracks or at sealed surfaces in private or public areas may yield to a greater environmental impact than agricultural input [2].

* Corresponding author, Fax: +49-231-544-1220, e-mail: IFW@poboxes.com.

In comparison to other pesticides glyphosate is highly polar and water-soluble (Table I). Due to these physical-chemical properties analysis of water samples is rather difficult and time-consuming. So glyphosate is not a common parameter in water quality control. Therefore, only few analysis data about the occurrence in the aquatic environment are known [3–5]. A recent research project aimed at the differentiation of pesticide occurrence and their pathways to the aquatic environment in the drinking water protection area of Dortmunder Energie- und Wasserversorgung GmbH (Figure 1). The particular interest of this study was to show the occurrence and fate of non-selective herbicides. These substances may raise problems because soil passage and linked degradation and sorption processes can fail. This may affect both groundwater and surface water quality and indirectly drinking water quality [3–9]. In regions where drinking water abstraction is based on bank filtration and artificial groundwater recharge like in the western german industrial Ruhr region good surface water quality is required to obtain drinking water according to EU and federal drinking water standards [9–12].

METHODS AND MATERIAL

In the scope of this project water samples of two small tributaries of the River Ruhr in Schwerte, North-Rhine-Westphalia, FRG, were tested for 70 pesticides (active substances and metabolites) by GC-ECD, GC-NPD or HPLC. The location of sampling points and the small catchment areas (see Table II) are displayed in Figure 1.

One of the most detected pesticides was the total herbicide diuron indicating the impact of weed control in railway tracks and settlement and industrial areas on water quality. In 1996 only glyphosate was applied on railway tracks. In each examined tributary one sampling point which had shown most often positive results in diuron was chosen for glyphosate sampling and analysis in 1996. In the northern tributary, Gerrenbach, the chosen sampling point G3 showed positive diuron results in 83 % of all samples between 1994 and 1996 (n = 99). The chosen sampling point L4 in the southern tributary Lettebach had 51 % positive diuron samples in the same period (n = 93). In L4 the ratio of positive diuron results related to the number of samples increased from 1994 58 % to 77 % in 1995 and decreased to 18 % in 1996 when no diuron was applied in nearby rail-tracks. In all sampling points the rate of positive diuron results related to the number of analyses was 53 % out of 735 samples during the period 1994 to 1996.

In comparison to diuron glyphosate has a higher affinity to water than to unpolar solvents (Table I). So the glyphosate contamination pattern in surface water

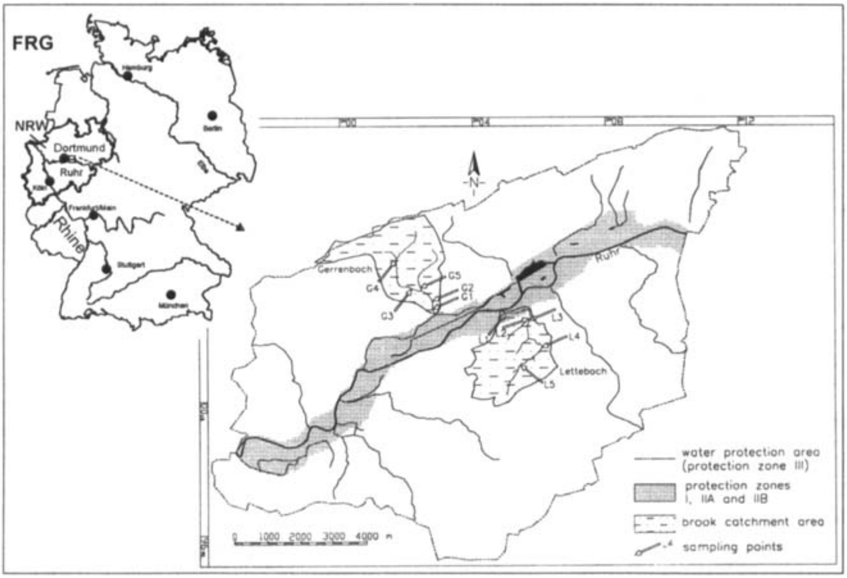

FIGURE 1 Research area NRW = North-Rhine-Westphalia

should be similar to the diuron pattern. Due to the polar interaction glyphosate adsorption by soil and sediment material exceeds diuron retardation during seepage process [14, 15, 18–20]. In Table I some physical-chemical properties of highly polar pesticides (i.e. glyphosate) are compared to moderately unpolar substances (i.e. lindane) which could also be analysed during this study.

TABLE I Physical-chemical properties of selected pesticides [13–18]

name	*substance class*	*water solubility [mg/l], [1]*	*vapor pressure [hPa], [2]*	K_{ow} *[4] [–]*	K_{oc} *[5] [dm³/kg]*
Diuron	phenylurea	35	$2,3 * 10^{-9}$	661	87 – 977 (14, 16, 18)
Glyphosate	phosphonic acid	15700	$2,5 * 10^{-5}$[3]	1	301 – 60.000 (15, 18)
Lindane	chlorohydrocarbon	7	$1,2 * 10^{-5}$	5754	251 – 3311 (14, 18)
sources		13, 17	13	13	14 – 16, 18

[1] in H_2O, 20 °C. [2] at 20 °C. [3] at 45 °C. [4] octanol/water-partition coefficient.
[5] organic carbon(soil)/water-partition-coefficient.

The extraction of glyphosate and the metabolite aminomethyl phosphonic acid (AMPA) from water samples was performed by cation exchange procedure followed by a clean-up step and chromatographic separation by HPLC with post-column-derivatization and fluorescence detection [21]. Detection limits were 25 ng/l for glyphosate and 50 ng/l for AMPA.

Flow velocity was measured by a portable magnetic-inductive velocity detector. Multiplication with streamed area yielded discharge.

RESULTS

Description of research area

In both catchment areas the soil is dominated by silty loam [22]. Carboniferous sediments are mostly shale and covered by shallow layers of quaternary terrace sediments in the Gerrenbach area which are mostly composed by sandy silts with gravel addition [22, 23]. The sequence is closed by loess. As the shale is hardly permeable the aquifer is restricted to the thin layers of porous material (thickness between 2 m and 10 m). Sediments in Lettebach area are similar, but the thickness of soft rocks rarely exceeds 6 m. The slopes in both catchment areas are slightly or little inclined.

TABLE II Land use

Catchment	*Gerrenbach*	*Lettebach*
	size in [km²]	
land use	*5,687*	*4,899*
	distribution in [%]	
settlement [1]	28	17
traffic	8	4
arable land	34	26
greenland	7	16
pasture	4	19
forestry	12	14
fallow [2]	8	3

[1] including industrial area. [2] permanent fallow.

Urban settlement, industrial and traffic areas have a part of 36 % in Gerrenbach catchment area but only 20 % in Lettebach area, so the total herbicide application is more likely in Gerrenbach area (Table II). Arable land is mostly dedicated to barley and wheat culture. Agricultural glyphosate target cultures as maize and beet are grown only subordinatedly (less than 5 % of area). Sometimes glyphosate is applied in greenland particularly in periodic fallow. Then, foliage application is performed regularly after the end of August. Therefore, the non-agricultural sphere is probably the main regional glyphosate target.

In comparison to whole catchment areas the different sampling points represent little varied land use. Particularly, Lettebach L4 sampling point was installed to monitor consequences of weed control action at a nearby railway track. In both catchments there is no outlet of a sewage plant. The municipal sewerage influence is confined to combined sewer overflows (COS) or stormwater outlets of the separate sewer system in G3 partial catchment area. The L4-catchment area is free of any of these sewerage installations.

Climatic and hydrologic conditions

Annual precipitation height was below the 40 year average in 1995 and in 1996 as well as the monthly rainfall data since October 1995, except February and August 1996, when the average was reached. From empirical hydrologic studies it is known that only storm rainfall yields in superficial run off. An estimation for storm rainfall is given by the following empirical formula

$$P \geq [5D - (D/24)\wedge 2]\wedge 0,5$$

where, P signifies the precepitation in [mm] and D the rain duration in [min] [25]. It can be calculated a run off taking place beyond rainfall intensities of 5 mm/ 5 min with a supposed frequency twice a year [25, 26]. In summer 1996 this condition was only realized once at the end of June.

Drought since autumn 1995 had led to decreasing discharge in the considered Ruhr tributaries during 1996 (Table III). The half-year mean discharge in summer 1996 was only 60 % to 80 % of 1995 values. The discharge in 1996 was highly influenced by baseflow. The contribution of baseflow to mean discharge in summer 1996 ranged between 60 % and 80 %. The discharge measurement in sampling point L4 was confined to sampling dates. In Table III therefore the data for the downstream and upstream gauging point are displayed. As it is done for the Gerrenbach catchment. In summer 1996 L4 sampling could not be performed at several days because of drought. As catchments are small direct run off induced by precipitation is discharged in less than 24 hours. Thin and tapered porous aquifer layers induce small groundwater residence time.

TABLE III Hydrologic situation

sampling point	*number of measure-ment*	*MQ 1996*	*ratio MQ(1996) to MQ(1995)*	*MQ S-1996*	*ratio MQ(S-1996) to MQ(S-1995)*	*baseflow Z(MoNQ)*	*ratio Z(MoNQ) to MQ(S-1996)*
		[l/s]	[-]	[l/s]	[-]	[l/s]	[-]
L3*	165	17,6	0,49	6,1	0,60	4,3	0,70
L5	157	3,2	0,42	1,4	0,76	0,8	0,59
G1	165	35,2	0,34	29,9	0,61	24,6	0,83
G3	173	22,4	0,33	19,9	0,85	11,7	0,59
G4	169	10,6	n.d.	7,6	0,71	4,3	0,57

MQ = mean discharge; S = hydrologic summer (May-October); Z(MoNQ) = median of monthly low water discharge; L# = Lettebach; L3* = discharge including L2; G# = Gerrenbach; baseflow determination according [27, 28]

Results of pesticides apart glyphosate

Apart diuron and glyphosate the following pesticides were detected frequently during the period from 1994 to 1996: alpha-hexachlorocyclohexane, atrazine, chlortoluron, desethylatrazine, desethylterbuthylazine, desisopropylatrazine, isoproturon, lindane, metazachlor, simazine, terbuthylazine. With some exceptions the analysed concentrations ranged between detection limits and 500 ng/l. Due to small discharge daily loads rarely exceeded 1 g/d for a single pesticide. Details of the examination of other pesticides than glyphosate are discussed elsewhere [24, 29–31].

Results of glyphosate

In the monitoring during 1995 and spring 1996 no glyphosate and AMPA could be detected except one positive result of AMPA in Gerrenbach in September 1995. All other positive results were found during summer 1996. The geometric mean of glyphosate concentration was 65 ng/l in Gerrenbach (Figure 2; considering positive results) and 160 ng/l in Lettebach. The concentration maxima reached 240 ng/l in Gerrenbach and 590 ng/l in Lettebach. In summer 1996 the ratio of positive glyphosate results compared to the number of examinations yielded 65 % in L4 (11 positive results to 17 samples) and 55 % in G3 (12 positive results to 22 samples).

An increasing concentration level was observed after weed control in rail tracks indicating a relevant contribution to glyphosate load by this application.

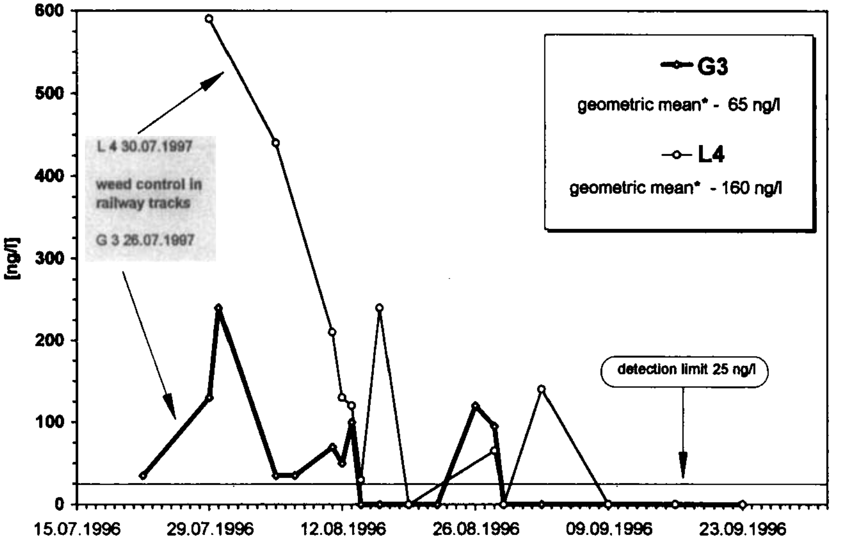

FIGURE 2 Glyphosate concentration in Gerrenbach in summer 1996 (sampling point G3, n = 19, * considering positive results)

Before the weed control action in railway tracks positive glyphosate results were due to other non-agricultural application in the settlement area because an agricultural use of glyphosate in early July is very unlikely in view of regional farming practice.

Glyphosate occurred also in days without any or very little precipitation (i.e. less than 2 mm/d, Figure 3). These results had to be the consequence of an input linked with baseflow because in small catchment areas the run off induced discharge leaves the catchment in less than one day.

Due to the drought in 1996 and low discharge, the annual load from these concentration data can be estimated less than 5 g/a [32].

Results of AMPA

The metabolite AMPA was found with a geometric mean of 70 ng/l in Gerren- and Lettebach in summer 1996 (Figure 4). The occurrence of AMPA was linked to glyphosate but did not reach the same concentration level as the latter substance. Also the ratio of positive AMPA results related to the number of examinations was lower than for glyphosate with 29 % in L4 and 18 % in G3. Except glyphosate metabolism, AMPA can be produced as metabolite of phosphonic

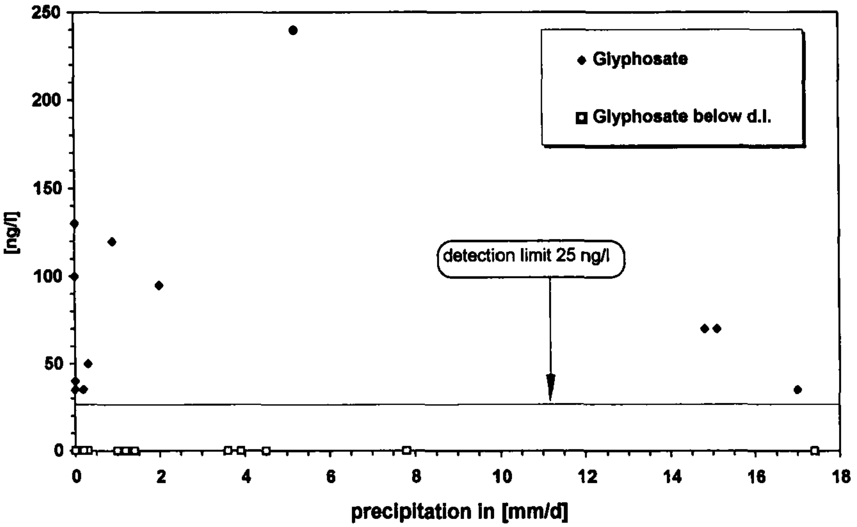

FIGURE 3 Precipitation vs. Glyphosate concentration in Gerrenbach in 1995–1996 (sampling point G3, n = 30, d.l. = detection limit)

acids in detergents [19]. Phosphonic acids like Ethylendiamine tetra(methylenephosphonic acid) (EDTMP) or Diethyletriamine penta(methylene phosphonic acid) (DTPMP) were used as detergents in large amounts in cleaning processes and can degrade to AMPA. Therefore, one can expect that AMPA concentration exceeds glyphosate concentration at a mass base as well as at a molar base, if it is produced as detergent metabolite. As in L4 catchment area there is no overflow of municipal sewer system such a pathway of AMPA production can be excluded. Municipal sewerage in the G3 catchment area is characterised by several separate sewers and only two combined sewer overflows (COS) which can yield an ephemeral detergent inflow in Gerrenbach. If a detergent input took place by COS, AMPA analyses should be positive throughout the 1995 and spring 1996 monitoring. AMPA concentrations might also exceed glyphosate concentration in this case. This failed and, therefore, Gerrenbach AMPA results have to be assumed as a consequence of glyphosate metabolism as well.

DISCUSSION

Highly water soluble substances should have a great leaching potential and their input to groundwater is expected. Adverse to this expectation chelation properties of organic phosphonates yield high sediment/water partition coefficients and

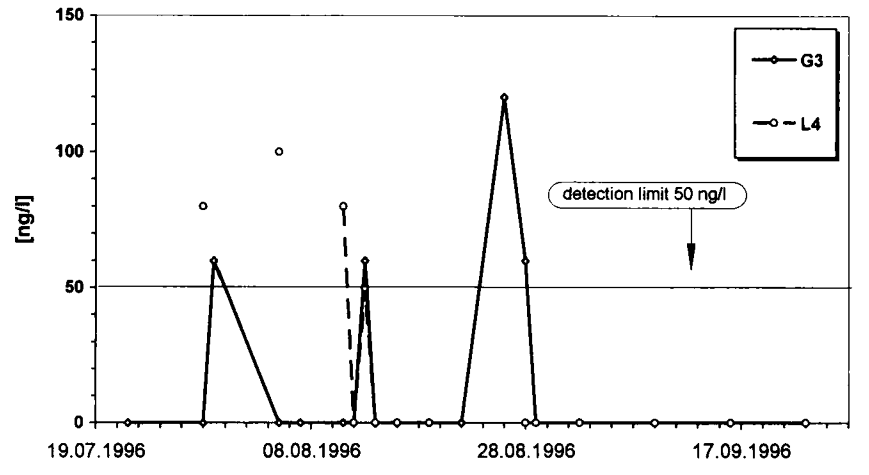

FIGURE 4 AMPA concentration in Lettebach and Gerrenbach in summer 1996 (L4: n = 17, G3: n = 19)

low mobility in soils [5, 19, 20]. Nevertheless, glyphosate occurrence at days with no precipitation indicated an input to surface water by base flow after a short underground passage. As cohesive soils tend to drought cracking one can assume that preferential flow phenomena had a great impact on this pathway through underground, particularly when glyphosate was observed soon after the application [33–35].

Fast transport to deeper underground levels has also to be expected in railway embankments. Old railway embankments constructed before 1920 were built by soil excavation so that they consist mainly out of broken carboniferous shale with an assumed median of grain size distribution in coarse gravel and a good permeability. Thus, no strong retention of seepage water and only little retardation of solutes could be expected.

From weed control experience in rail tracks the amount of applied glyphosate for this purpose can be calculated to 4.3 kg/a in G3 catchment and 1.2 kg/a in L4 catchment. The annual load estimates in Gerrenbach and Lettebach water yield 0.1 % of the amount applied in rail track weed control. Disregarding other possible targets almost 20 days after application in railway weed control glyphosate concentration fell below detection limit in both catchment areas for the first time which is a short period in comparison to the constancy of diuron occurrence in 1994 and 1995. Thus, faster disappearance of glyphosate than diuron suggests better tolerance to the aquatic environment. The occurrence of the metabolite

AMPA in the researched Ruhr tributaries has to be seen as a consequence of glyphosate application in the catchment. On the contrary, the AMPA occurrence in the river Ruhr is also caused by detergent input via municipal sewage plants [21].

The application of non-selective herbicides in housing green is restricted to small amounts [2] but house owners use total herbicides for weed control in the pavement, garage drives and similar sealed domestic area disregarding package insert or legal pesticide application regulations. No pesticide can be used for weed control in sealed areas with a run off risk to municipal sewerage according to package inserts [36]. Furthermore, in Germany the federal plant protection act as well as the regional application ordinances prohibit pesticide use in sealed areas without an extraordinary allowance by the agricultural administration authorities which can only be granted if there is public interest in weed control [37, 38]. The use in private pavement or garage drives is regularly excluded but weed control for traffic security purposes (e.g. railway tracks or airports) can be allowed. As the disregard for package insert and legal regulation by private consumer may raise problems to water quality, the access of these people to non-selective herbicides should be restricted.

In rail tracks weed control by non-selective herbicides can be allowed according to the ordinance but in the scope of this admission no quality target of the weed control extent is discussed. There is an experience based rule that rail tracks should be free of any vegetation to an extent of 90 % to maintain rail bed highly permeable and frost stable for more than 10 years. No objective criteria exists whether a vegetation restriction of 50% or 60 % might be sufficient for this purpose. An answer to this question reveals the minimisation potential of the applied pesticide amount in weed control.

CONCLUSION

Glyphosate occurred in surface water. In the examined catchment areas weed control application in rail tracks is one of the main sources for an input to surface water. The occurrence of metabolite AMPA was linked to glyphosate load rather than a detergent inflow via municipal sewerage. There are two main items for an input minimisation: As private consumers often disregard application advice their access to non-selective herbicides should be restricted. A quality target for weed control of railway tracks should be declared to keep application amount – particularly in water protection areas – as small as possible. A final assessment to the importance of highly polar pesticides in organic contaminants of surface water needs extended water monitoring analyses and further field investigation.

Acknowledgements
This study is funded by the Federal Environmental Agency, Berlin, FRG (UBA 102 02 230) and Dortmunder Energie- und Wasserversorgung GmbH. For glyphosate and AMPA analysis we appreciate Gelsenwasser AG.

References

[1] IVA (Industrieverband Agrar e.V.) 1995 – Mengenmäßig bedeutende Wirkstoffe in der Bundesrepublik Deutschland (unpublished report Frankfurt/M., 1996) 4 pp.
[2] R. von Alvensleben and H. Brinkmann Erhebung über die Anwendung von Pflanzenschutzmitteln im Haus- und Kleingartenbereich (Schriftenreihe des Bundesministers für Ernährung, Landwirtschaft und Forsten, Reihe A, Heft 395, Münster, 1991), 125 pp.
[3] R. Kozel Erfassung organischer Spurenbelastungen, insbesondere durch Pflanzenbehandlungsmittel, in oberflächennahen Lockergesteins-Grundwässern (Ph.D.-Thesis, Universität Neuchâtel 1992), 334 pp.
[4] C. Skark and N. Zullei-Seibert Erhebung über das Auftreten von Pflanzenbehandlungsmitteln in Trink- und Grundwässern.-Veröffentlichungen des Instituts für Wasserforschung GmbH und der Dortmunder Energie- und Wasserversorgung GmbH, (Dortmund, 1996), 49a, 184 pp.
[5] N.J. Smith, R.C. Martin and R.G.S. Croix, Bull. Environ.Contam. Toxicol., 57, 759–765 (1996).
[6] R. Klopp, Forum Städte-Hygiene, 44, 71–74 (1993).
[7] K. Kötter and C. Schlett, gwf Wasser-Abwasser, 135, 265–272 (1994).
[8] D. Hein and K. Vogt, Korrespondenz Abwasser, 43, 292–296 (1996).
[9] V. Neitzel and K. Döhmen, in: Ruhrwassergüte 1995 (AWWR and Ruhrverband, eds., Essen, 1996) pp. 121–160.
[10] AWWR (Arbeitsgemeinschaft der Wasserwerke an der Ruhr) Zielwerte für die Qualität des Ruhrwassers (Essen, 1995) 8 pp.
[11] EEC (European Economic Community) Drinking Water Directive (Directive 80/778/EEC, 1980).
[12] BJFG (Bundesministerium für Jugend, Familie und Gesundheit), Verordnung über Trinkwasser und über Wasser für Lebensmittelbetriebe (Trinkwasserverordnung – TrinkwV), BGBI. I, 2613–2629 (1990).
[13] IVA (Industrieverband Agrar e.V.) Wirkstoffe in Pflanzenschutz- und Schädlingsbekämpfungsmitteln.- (München, 1990), 478 pp.
[14] G. Mattheß, M. Isenbeck, A. Pekdeger, D. Schenk and J. Schröter Der Stofftransport im Grundwasser und die Wasserschutzgebietsrichtlinie W 101.- UBA-Berichte 7/85, (Berlin, 1985), 181 pp.
[15] W.F. Goure The environmental fate of glyphosate in soil and water and an assessment of its potential to contaminate surface, ground and drinking water (unpublished report Monsanto S.A., 1996), 25 pp.
[16] H. Merabet, E. Pogány and H. Schäfer Zusammenfassende Bewertung des Verhaltens von Diuron im Boden nach Anwendung von Diuron 80 aufgrund von Berechnungen mit dem Modell PELMO (unpublished report BAYER AG, 1992) 24 pp.
[17] W. Perkow Wirksubstanzen der Pflanzenschutz- und Schädlingsbekämpfungsmittel (Paul Parey, Berlin und Hamburg 1992) 2nd ed..
[18] R.D. Wauchope, T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn Beckers and J.P. Burt, Reviews of environmental contamination and toxicology, 123, 1–164 (1992).
[19] W.E. Gledhill and T.C. Feijtel, in: The handbook of environmental chemistry, Vol. 3, Part F (O. Hutzinger, ed., Berlin 1992), pp. 261–285.
[20] S.M. Carlisle and J.T. Trevors, Water, air and Soil Poll., 39, 409–420, (1988).
[21] R. Reupert and C. Schlett, gwf-Wasser, Abwasser (in preparation).
[22] GLA (Geologisches Landesamt NRW) Bodenkarte des Kreises und der Stadt Iserlohn 1 : 50.000, Karte mit Erläuterungen (Krefeld, 1976), 96 pp.
[23] GLA (Geologisches Landesamt NRW) Geologische Karte von Nordrhein-Westfalen, Erläuterungen zu Blatt C 4710 Dortmund.- (Krefeld, 1989), 64 pp.

[24] C. Skark and N. Zullei-Seibert Differenzierung des Auftretens und der Herkunft von Pflanzenschutzmittelbelastungen in einem Flussgebiet im Hinblick auf die Trinkwasserversorgung (UBA-F&E 102 02 230, in preparation).
[25] U. Maniak Hydrologie und Wasserwirtschaft (Berlin, 1993), 568 pp.
[26] J. Haider Herbizide in Oberflächenabfluß und Bodenabtrag (Ph.D.-Thesis, Technische Universität München-Weihenstephan, 1994), 231 pp.
[27] W. Wundt, Forsch.deutsch.Landesk., 104, 47–54 (1958).
[28] K. Kille, Z.dt.geol.Ges., Sonderh.Hydrogeol.Hydrogeochem., 89–95 (1970).
[29] C. Skark, N. Zullei-Seibert, U. Gatzemann and D. Schwarz, in: Ruhrwassergüte 1994 (AWWR and Ruhrverband, eds., Essen, 1995) pp 126–129.
[30] C. Skark, Proc. COST 66 Workshop, Stratford-upon-Avon, 219–220 (1996).
[31] C. Skark, N. Zullei-Seibert, U. Willme and U. Gatzemann, Vom Wasser, (in preparation).
[32] S.D. Preston, V.J. Bierman and S.E. Silliman, Water Resources Research, 25, 1379–1389 (1989).
[33] B. Lennartz, H. Hartwigsen and S. Meyer-Windel, Proc. COST 66 Workshop, Stratford-upon-Avon, 63–64 (1996).
[34] A.H. Haria, A.C. Johnson, J.P. Bell and C.H. Batchelor, J. Hydrol., 163, 203–216 (1994)
[35] A.C. Johnson, A.H. Haria, C.L. Bhardwaj, C. Völkner, C.H. Batchelor and A. Walker, J. Hydrol., 163, 217–231 (1994)
[36] PC-AGRAR (PC-AGRAR GmbH – Saphir-Verlag) Auswertungsprogramm für Pflanzenschutzmittel-Zulassungsdaten der Biologischen Bundesanstalt (BBA) Braunschweig (Ribbesbüttel, 1995).
[37] Bundesregierung, Gesetz zum Schutz der Kulturpflanzen (Pflanzenschutzgesetz – PflSchG), BGBl. I, S. 1505 (1986).
[38] NRW (Nordrhein-Westfalen), Verwaltungsvorschrift zur Anwendung von Pflanzenschutzmitteln auf Freilandflächen, die nicht landwirtschaftlich, forstwirtschaftlich oder gärtnerisch genutzt werden.- Gem.Rd.Erl. d. Ministeriums für Umwelt, Raumordnung und Landwirtschaft und d. Ministeriums für Stadtentwicklung und Verkehr, Mbl. NRW, 722–724 (1991).