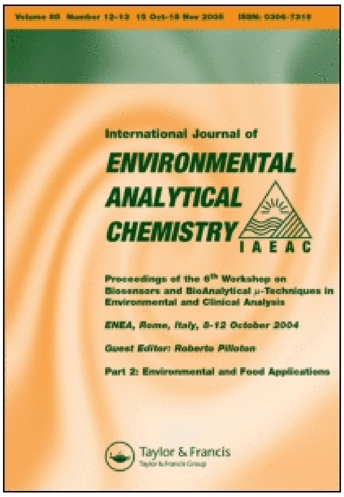

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THE OCCURRENCE OF PESTICIDES IN GROUNDWATER—RESULTS OF CASE-STUDIES

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A comparative review of pesticide survey endosing 16 waterworks in the FRG tries to increase the understanding about interferences of pesticide utilization and pesticide occurrence in ground- and drinkingwater, which includes characterization of sampling points, subsurface situation, land use and pesticide application. Between 1986 and 1991, 5772 samples were measured and led to 219094 data about the occurrence of various pesticides. 5% of these analyses showed pesticide or metabolite concentrations above the particular detection limits. This result does not vary in large extent considering groups of different characterized sampling points like groundwater dominated or surface water sampling points. As the herbicide atrazine and its metabolite desethylatrazine as well as the herbicide simazine were detected most often in all samples independent whether considering groundwater und surface water samples, this fact confirms the FRG-application ban for atrazine as well as the application restriction for simazine.

KEY WORDS: Pesticides, groundwater, risk assessment.

INTRODUCTION

Pesticides were detected in several surveying programs of environmental authorities and water supplying enterprises[1,2,3,4]. Until now interferences of pesticide application and their occurrence in groundwater had been studied in selected water catchment areas[5,6]. So these problems should be considered in a comparative review of available data within a research project supported by the Environmental Protection Agency (Umweltbundesamt) of the Federal Republic of Germany (FRG). Data about the water utilization circumstances—i.e. characterization of the subsurface situation and sample locations in the different catchment areas, about landuse and pesticide application were collected. In this study, 16 waterworks including 58 catchment sites are included, which had found pesticides content in their water without any doubt for several times. The results were expected to support the legal environmental and water protective activities.

RESULTS AND DISCUSSION

Pesticide application and water survey

Within the described case studies the agricultural administration authorities were questioned about their knowledge of land use and pesticide application in the considered water catchment areas. The available information was diversely detailed and heterogeneous, because the agricultural administration often had only approximate data about land use or they reported only regional important pesticide preparations. This problem in achieving reliable and comparable data on pesticide use is also known from other EC-members[7].

The obtained data represent mainly the recommended pesticides and application amount of the years 1990 and 1991, in some cases also older information. Sometimes the agricultural administration could provide additional data on non-agricultural use of pesticides. In total 122 active substances in use are described, including 63 herbicides (=52%). These applied pesticides represent 56% of all pesticides admitted to application in 1989[8].

Agricultural land use in FRG is dominated by corn farming. In the main part of the considered catchment areas with available agricultural land use data, more than 50% of the area with a pesticide application was dedicated to corn farming. Great regional differences in the extent of land use for various cereal crops, as wheat, rye and maize, are remarkable.

Comparing the pesticide application and pesticide analyses in water samples of 14 water catchment areas the rates of analysed pesticides are found mainly between 20% and 50% of all applied pesticides (Figure 1; Table 1). Looking at substances with an application amount of 0.5 kg/ha or more these rates are mainly increasing to 40% up to 60%. Land use and pesticide application of these 14 catchment areas are representative for further 23 catchment sites.

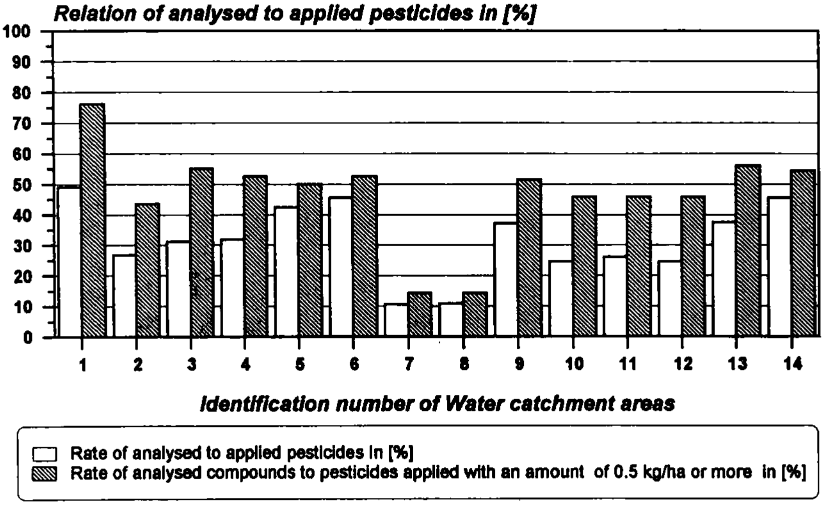

Figure 1 Relation of analysed to applied pesticides in water catchment sites

Table 1 Relation of analysed and applied pesticides

Water catchment site *Identification Number*	*Rate of analysed to applied pesticides* *[%]*	*Rate of analysed to applied pesticides with an application amount = or >0.5kg/ha* *[%]*	*Rate of analysed to applied herbicides* *[%]*	*Rate of analysed to applied fungicides* *[%]*	*Rate of analysed to applied insecticides* *[%]*
1	49	76	55	33	25
2	27	43	33	27	0
3	31	55	48	10	0
4	32	53	50	10	0
5	42	50	56	20	25
6	45	53	61	20	25
7	11	14	18	11	0
8	11	14	17	13	0
9	37	52	53	12	23
10	24	46	33	18	0
11	26	46	37	18	0
12	24	46	33	18	0
13	38	56	56	9	0
14	45	55	58	43	0

Considering different types of pesticides the analyse-to-application rate increases from insecticides to herbicides (Figure 2). As applied insecticides are often missing in monitoring programs of the waterworks, at least 9% of fungicides and 30%–60% of herbicides in use are considered. This means pesticides of important application rates are neglected in monitoring programs controlling water quality standards (raw- and drinking water).

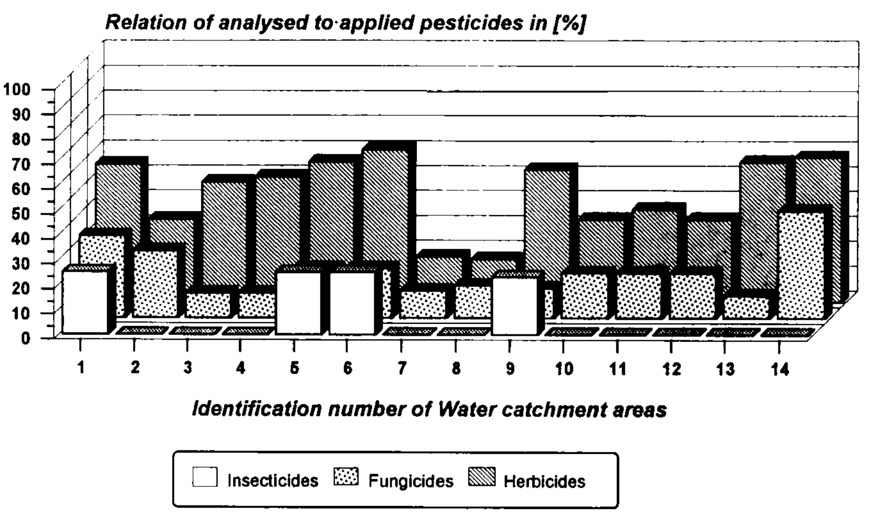

Figure 2 Relation of analysed to applied pesticides distinguishing the type of pesticide

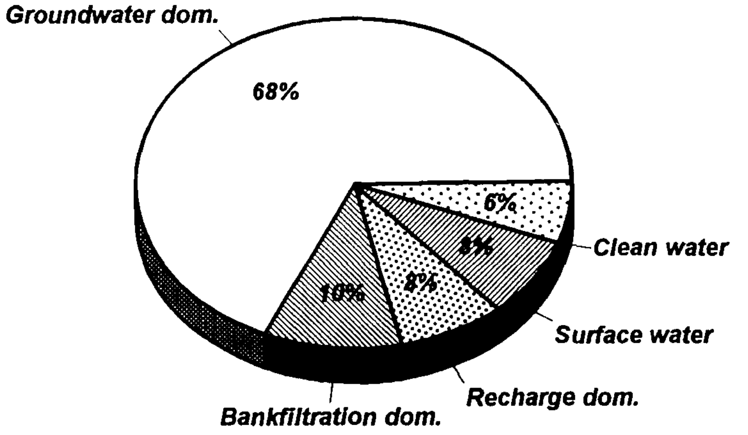

Figure 3 Character of sampling points; dom. = dominated

Characterization of sampling points

In the 58 water catchment sites samples were taken from 663 different sites. Two thirds of the sampling sites are dominated by groundwater (Figure 3), i.e. an amount of real groundwater is exceeding 50%. In almost further 20% of sampling points water is mainly influenced by bankfiltration or artificial groundwater recharge. In 8% of the sampling points surface water and in further 6% clean water was surveyed.

An aquifer type can be characterized by 570 sampling points of subsurface water. Sampling wells are mainly situated in porous aquifers (75%), while sampling points in karstic or fissured aquifers occur with 10% or 3% respectively. Mixed aquifer types can be found in 12% of all sampling points.

Agricultural pesticide application is the main contamination source for 47% of all subsurface sampling points. Further 14% of sampling points are mainly influenced by the pesticide load of surface water, while for additional 4% an effect of pesticide use on adjacent railroad banks is given. Forestry pesticide use influences 2% of subsurface sampling points. A probable pesticide input by various sources can be assumed for 33% of these sampling points. In this group several combinations of input sources can occur like agricultural use (A), pesticide load of surface water (B), application on railroad banks (C), use in forestry (D) and in private gardens (E) as well as the application on sporting grounds and sealed surfaces (F). The most frequent combinations are A-B (13% of all various sources cases), A-D (16%) and A-C-D-E (13%).

Pesticide occurrence

In total 5772 samples with 219094 analyses of single pesticides or metabolites were considered. Particular pesticide contents were found beyond the respective detection limits

Table 2 Analyses and positive results in groundwater dominated samples
Number of all samples : 2 459
Number of all single substance analyses : 94 940
Number of positive results : 4 334

Substance	*Number of analyses*	*Number of positive results*	*Rate of positive results to analyses [%]*	*Rate of particular results to all positive results [%]*	*Rate of analyses to all samples [%]*
alpha-HCH	99	1	1.0	0.0	4.0
Atrazine	2448	1493	61.0	34.4	99.6
Bromacil	1712	95	5.5	2.2	69.6
Chlortoluron	1325	6	0.5	0.1	53.9
Desethylatrazine	2420	1357	56.1	31.3	98.4
Desethylterbuthylazine	1569	16	1.0	0.4	63.8
Desisopropylatrazine	1915	51	2.7	1.2	77.9
Diuron	710	58	8.2	1.3	28.9
Hexazinone	1303	47	3.6	1.1	53.0
Isoproturon	1366	33	2.4	0.8	55.6
Lindan	415	4	1.0	0.1	16.9
Methabenzthiazuron	1296	25	1.9	0.6	52.7
Propazine	1902	74	3.9	1.7	77.3
Simazine	2446	898	36.7	20.7	99.5
Terbuthylazine	2352	113	4.8	2.6	95.6

11522 times (5% of all single substance test). Pesticide concentrations had been measured in 1% of all analyses above 0.1μg/l, the drinkingwater standard for single pesticide concentration in drinkingwater in the FRG[9].

The detected substances were mainly herbicides (32 active substances and 3 metabolites, 73% of all substances, 47% of which are triazines) while fungicides (6 substances) and insecticides (6 substances) occurred only subordinately.

Occurrence in groundwater dominated sampling points From total 5772 samples in all sampling points 2 459 (=43%) were taken in groundwater dominated sampling sites, in which the single substances were tested 94940 times. In the various pesticide analyses 4.6% of the measurements (=4334) were obtained beyond the respective detection limit. These positive results occurred in 60% of the 447 groundwater dominated sampling points. Table 2 lists inter alia substances detected in more than 15 analyses.

The positive results of the ten most often detected substances were contributing more than 97% to all detected pesticides in groundwater dominated samples (Figure 4). For the triazines atrazine, simazine and the metabolite desethylatrazine between 37% and 61% of the respective single substance tests were positive. For all the other substances this rate lay below 8%.

The most substances were tested in more than 50% of all samples except diuron (Figure 4). For 7 of these substances the median concentration was calculated below 0.1μg/l (Figure 5). On the contrary for bromacil, diuron and propazine mainly used as total herbicides[10] as well as for methabenzthiazuron and monuron the median concentrations exceed this limit.

Distinguishing different types of aquifers the rate of positive results vs. analyses does not vary in a great extent. In porous aquifers 3.6% of the respective particular analyses were

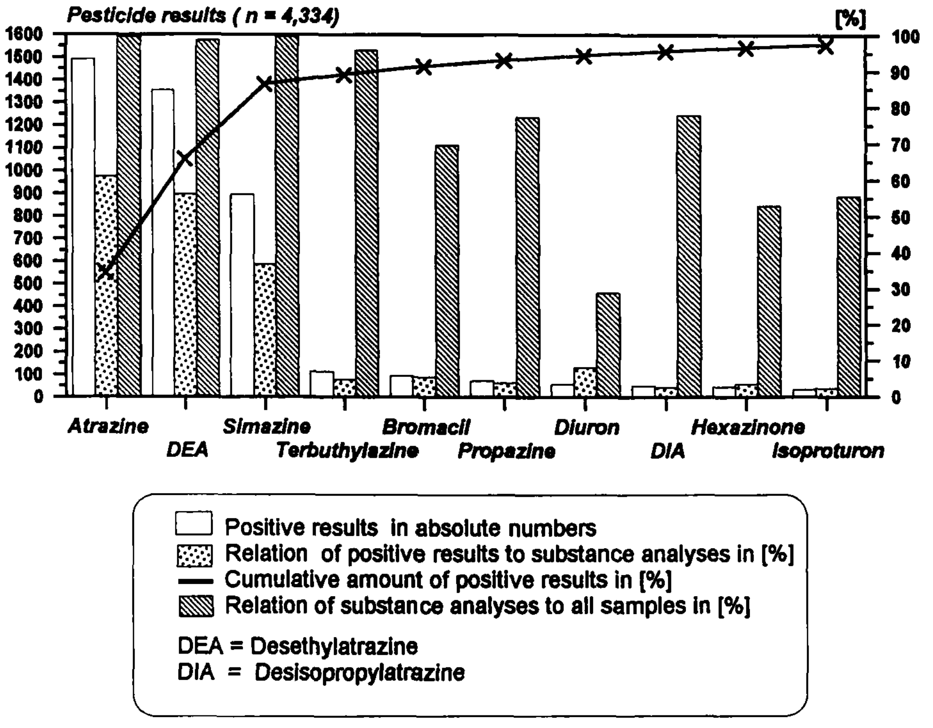

Figure 4 Pesticide occurrence in groundwater dominated sampling points listing the ten most often detected substances

positive (Table 3), whereas in karstic aquifers this rate could be obtained with 5.5%. Only in mixed aquifer types (porous/fissured media; karstic/fissured media) this rate can reach 6% or 17.5% respectively. The last both subdivisions are based only on the small amount of less than 1000 particular pesticide analyses and this can bias the result.

Occurrence in surfacewater All 52 sampling points located in surface water showed positive results. From 1331 samples (=23% of all) 53845 single pesticide data were obtained. Test results exceeding the various detection limits amount to 6% of all single substance tests.

In principle this does not vary in a large extent from the above described rate of positive results vs. analyses in groundwater. But the calculated average sampling frequency lay with 26 samples per sampling point beyond the respective frequency of groundwater dominated sites with only 6 samples. Within all of the detected substances bromacil, propazine, hexazinone and monuron could either not or less than 20 times be found. Instead of these, lindane, alpha-hexachlorocyclohexane, chlortoluron and desethylterbuthylazine were detected more than 20 times (Figure 6; Table 4). Compared to groundwater the ranking of these results does not change for atrazine, desethylatrazine and simazine representing 75% of all positive results, but for the other parameters. The pesticides median content does not exceed the concentration of 0.1 μg/l, except for chlortoluron and isoproturon (Figure 7). In the case

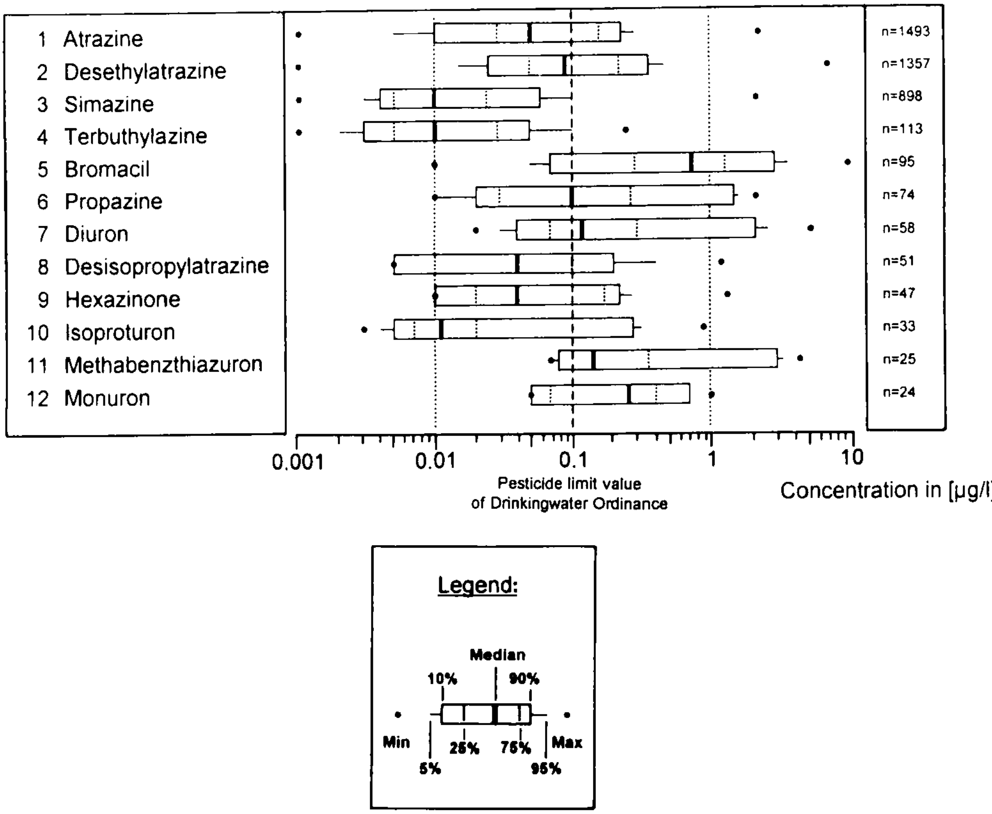

Figure 5 Calculated median concentrations of positive results in groundwater dominated samples; number of positive results n>20

of atrazine, desethylatrazine, diuron, methabenzthiazuron a lower median content compared to groundwater could be obtained in surface water.

Table 3 Analyses and positive results in groundwater dominated samples distinguished on type of aquifer

Type of aquifer	*Sampling points*	*Samples*	*Single substance analyses*		*Postive results*	
	number	*number*	*number*	*[%] 1)*	*number*	*[%] 2)*
Porous	311	1116	42022	19.2	1506	3.6
Karstic	54	521	22940	10.5	1265	5.5
Fissured	17	99	2912	1.3	68	2.3
Porous-Karstic	35	534	25055	11.4	1291	5.2
Porous-Fissured	18	93	901	0.4	54	6.0
Karstic-Fissured	11	87	748	0.3	131	17.5

1) Rate of all single substance analyses (n =219 094)
2) Rate of all single substance analyses of a subgroup

Table 4 Analyses and positive results in surface water samples
Number of all samples : 1 331
Number of all single substance analyses : 53 845
Number of positive results : 3 215

Substance	*Number of analyses*	*Number of positive results*	*Rate of positive results to analyses [%]*	*Rate of particular results to all positive results [%]*	*Rate of analyses to all samples [%]*
alpha-HCH	641	33	5.1	1.0	48.2
Atrazine	1303	1019	78.2	31.7	97.9
Bromacil	1064	9	0.8	0.3	79.9
Chlortoluron	677	84	12.4	2.6	50.9
Desethylatrazine	1299	707	54.4	22.0	97.6
Desethylterbuthylazine	709	28	3.9	0.9	53.3
Desisopropylatrazine	1181	24	2.0	0.7	88.7
Diuron	465	120	25.8	3.7	34.9
Hexazinone	163	1	0.6	0.0	12.2
Isoproturon	683	97	14.2	3.0	51.3
Lindane	658	137	20.8	4.3	49.4
Methabenzthiazuron	683	36	5.3	1.1	51.3
Propazine	1090	8	0.7	0.2	81.9
Simazine	1303	702	53.9	21.8	97.9
Terbuthylazine	1294	129	10.0	4.0	97.2

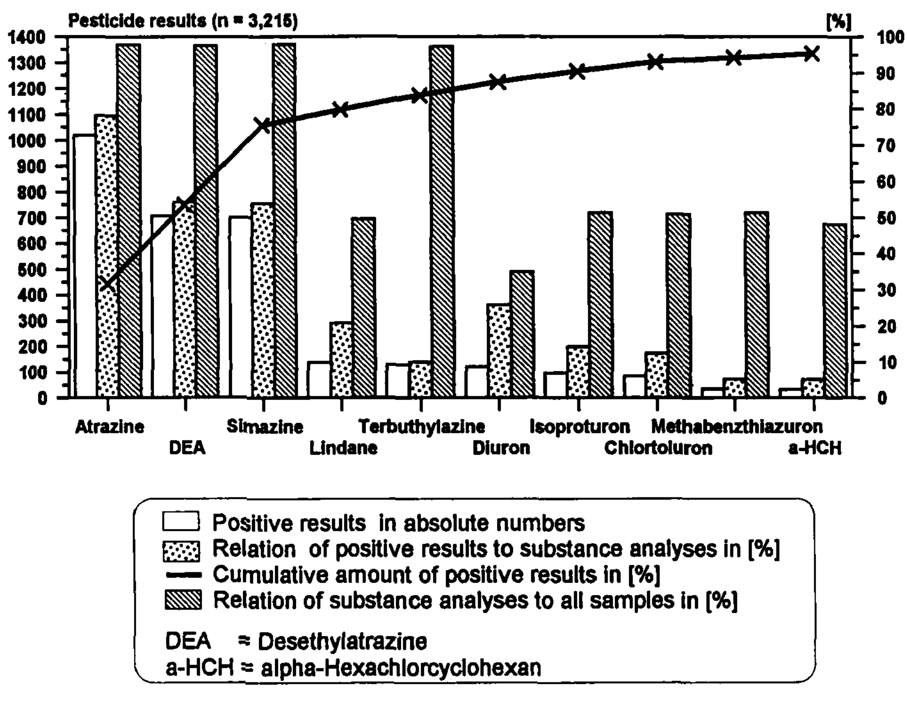

Figure 6 Pesticide occurrence in surface water sampling points listing the ten most often detected substances

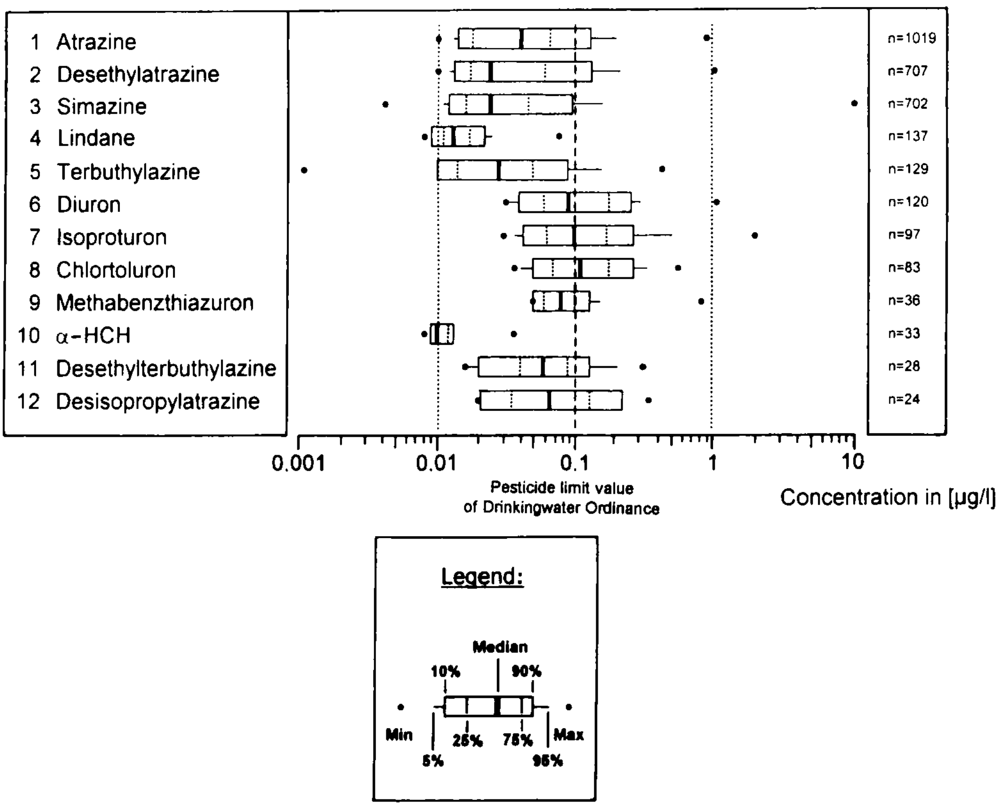

Figure 7 Calculated median concentrations of positive results in surface water samples; number of positive results n>20

CONCLUSION

Pesticide occurrence in groundwater dominated samples gives reason for a solicitude of groundwater contamination. The extent of these contaminations is not well known, because of the mostly existing lack of congruence between pesticide application and pesticide monitoring. Although one has to consider aquifer, sediment and soil conditions for pesticides risk assessment in a given catchment area[11,12,13], the most impressive factor for a groundwater contamination seems to be agricultural and non-agricultural pesticide application. Particularly, non agricultural use may rise problems, because soil passage and the coupled degradation processes in the unsaturated zone can fail. Reflecting the little influence on changing water production conditions in a given catchment site the main strategies preventing groundwater contamination has to begin in pesticide application mode[14,15]. In this context reducing applied amounts will be most effective[16,17,18,19]. As atrazine and simazine are the most often found compounds, these results are confirming the legal application ban for atrazine and respective application restrictions for simazine in the FRG, as they were announced in the recent pesticide application regulation of the FRG[20,21].

References

1. M. Roth, in: *Pflanzenschutzmittel und Grundwasser* (G. Milde and U. Müller-Wegener, eds., Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene, 79, Gustav Fischer Verlag Stuttgart, 1989) pp. 365–374.
2. H. Friege and W. van Berk, in: *Pflanzenschutzmittel und Grundwasser* (G. Milde and U. Müller-Wegener, eds., Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene, 79, Gustav Fischer Verlag Stuttgart, 1989) pp. 397–414.
3. N. Zullei-Seibert, Vorkommen und Nachweisbarkeit von Pflanzenbehandlungs- und Schädlingsbekämpfungsmittel-Wirkstoffen in Roh- und Trinkwässern der Bundesrepublik Deutschland. Veröff. Inst. Wasserforsch. Dortm. Stadtwerke. Dortmund **39** (1990), 102 pp.
4. R. Wolter, Auswertung der dem Umweltbundesamt gemeldeten Pflanzenschutzmittel-Funde. In: *Pflanzenschutzmittel im Wasser* (Fortbildungszentrum Gesundheits- und Umweltschutz Berlin e.V., eds., 18. Seminar, 1992), pp. 3–8.
5. J.-M. Rogg, *DVGW Schriftenreihe Wasser*, **67**, 81–111 (1991).
6. U. Müller-Wegener, W. Kleine, G. Milde and K. Poll, *DVGW Schriftenreihe Wasser*, **73**, 147–163 (1992).
7. A. Donati, A. Giolitti, N. Marchettini, C. Rossi, E. Tiezzi and S. Ulgiati, *Sci. Total Environ.*, **129**, 125–135 (1993).
8. W. Pestemer and H. Nordmeyer, *Wasser und Boden*, **2**, 70–76 (1993).
9. Verordnung über Trinkwasser und über Wasser für Lebensmittelbetriebe (Trinkwasserverordnung—TrinkwV). BGBI. I, S. 2613 (1990).
10. W. Perkow, Wirksubstanzen der Pflanzenschutz- und Schädlingsbekämpfungsmittel (Verlag Paul Parey, Berlin und Hamburg 1992), 2nd ed.
11. H. Vierhuff, W. Wagner and H. Aust, *Geologisches Jahrbuch*, **C 30**, 1–110 (1981).
12. W. A. Jury and J. Gruber, *Water Resources Research*, **25**, 2465–2474 (1989).
13. W. A. Pettyjohn, M. Savoca and D. Self, Regional assessment of aquifer vulnerability and sensitivity in the conterminous United States. EPA 600/2–91/043, 310 S. (1991).
14. H. Bernhardt, *gwf-Wasser-Abwasser*, **133**, 575–585 (1992).
15. D. Flinspach, *Schriftenreihe des Zweckverbandes Landeswasserversorgung*, **12**, 3–11, (1992).
16. K. Hurle, in: *Pflanzenschutzmittel und Grundwasser* (G. Milde and U. Müller-Wegener, eds., Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene, 79, Gustav Fischer Verlag Stuttgart, 1989) pp. 129–135.
17. DFG (Deutsche Forschungsgemeinschaft), *Pflanzenschutzmittel im Trinkwasser* (Verlag Chemie, Weinheim, 1990), 82 pp.
18. H. G. Hauthal, *Nachr. Chem. Tech. Lab.*, **41**, 566–570 (1993).
19. H. H. Dieter, *Bundesgesundheitsblatt*, **36**, 176–180, (1993).
20. Verordnung über Anwendungsverbote für Pflanzenschutzmittel (Pflanzenschutz-Anwendungsverordnung). BGBI. I, S. 1196 (1988).
21. Erste Verordnung zur Änderung der Pflanzenschutz-Anwendungsverordnung. BGBI. I, S. 795 (1991).