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Occurrence of Pesticide Residues in Water

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1 *Problem statement and study approach*

Since the early 1980s, considerable public attention has focused on the pollution of surface and groundwater by pesticides. Broad discussion of the pesticide problem started roughly simultaneously in North America (USA and Canada) (e.g. *Cohen et al., 1984)* and Europe *(e.g. Milde & Friesel, 1987)*. The present study examines the various reasons for this situation. It also provides as up-to-date a summary as possible of pesticide occurrence in water in a number of EU Member States.

In the EU, large-scale public debate on the subject of "pesticides and water" resulted initially from the discovery of isolated groundwater traces of these substances. This led to establishment of an EU drinking water limit for individual substances of 0.1 µg/l. The limit value of 0.1 µg/l is designed above all to indicate that the synthetic substances involved are considered not acceptable in drinking water. Their specific effects on health are not taken into account. This approach differs fundamentally from a toxicological view of limit values, for example in the area of foodstuffs. As a result, the EU Guidelines set a limit value which for many substances was at that time below the analytical detection level. Whereas this limit value aims above all to protect man as the consumer, the very low permissible value also protects the aquatic ecosystem. The present assessment largely focuses on human water usage.

In the first decades of pesticide use, scientists and others assumed that soil prevented the passage of pesticides into groundwater. This view was based on the fact that pesticides were microbially degraded in upper soil layers and clung to soil particles for lengthy periods. Pesticide registration therefore also focused on the chemicals' behaviour in the soil. Users' primary concern was that pesticides should not harm crops. Application form, volume and frequency were thus often determined by the registration authorities.

The discovery of pesticides in groundwater caused a considerable shift in perspective. All the EU-countries involved have altered their pesticide registration procedures. This development has led to an overall reduction in the number of products registered in the EU. Some pesticides were banned in a number of countries.

Supervision of such rules requires analytical methods capable of detecting any excess values. Over the last 25 years, improvements in apparatus have greatly refined environmental analysis, particularly of organic compounds. Above all the combination of gas chromatography with mass spectrometry offers a highly sensitive method of detecting synthetic organic compounds. Numerous pesticides can now be traced in water at levels well below 0.1 µg/l. However, when evaluating pesticide monitoring data, it should be remembered that even with sophisticated technology, ultratrace analysis still poses major problems. There is a high risk of false positive findings because of analytical interferences with natural organic substances during the measurement. Thus the analyses` results should be checked with plausibility criteria (*Häfner, 1994*).

It is very likely that pesticide residues entered groundwater before those found in the 1980s. Lack of appropriate technology simply made them impossible to detect. Increasing analytical sensitivity thus went hand in hand with the emergence of a "pesticide problem" in water. Were this development to continue, the number of "positive probes" could keep on increasing despite a whole series of preventive measures. A "zero concentration" approach to limit values is wholly impracticable due to rapidly falling detection limits.

The present study aims to evaluate the significance of pesticide residues in different watertypes. The data have to be reviewed for their usefulness in assessing how critical the probes are in total (excess values as a percentage of total probes), and what a value above 0.1 µg/l means for an individual site or region. The 0.1 µg/l drinking water limit value thus becomes a 0.1 µg/l tolerance value. This is the usual procedure in Switzerland, and is a feature of official practice elsewhere (e.g. in France).

Pesticides form a very heterogeneous group of substances. They can be grouped by use (herbicides, fungicides, insecticides, etc.), or by chemical structure (triazines, phenylureas, carbamates, etc.). Which substances are the current focus of attention? One quick answer is: "atrazine". A large number of "positive" findings in ground, surface and drinking water have led to a ban on this herbicide in several EU countries. The whole atrazine story thus offers helpful perspectives on possible causes of water pollution *(e.g. Gießl, 1988, Zullei-Seibert, 1990).* In the following study we examine which other pesticides are of interest and why.

A chemical's behaviour in the environment is in part determined by its structure, and illustrated in many laboratory and field studies. Knowledge of these studies as well as of substances' structure and physico-chemical characteristics is therefore of great importance for an assessment of their potential threat to water quality. These investigations enable scientists to estimate processes both of environmental transfer (e.g. solution, vapourization, particle accumulation) and transformation (hydrolytic, photochemical and microbial degradation, mineralization) *(Schwarzenbach et al., 1993).* Investigation is required of the correlation between substances' specific characteristics and their occurrence in water.

Another important aspect of this discussion is the form, intensity and frequency of application. The available statistics usually differentiate only broadly, for example between "farming" and "other" uses. It would, however, be valuable to describe the actual form of use. The question arises of whether water pollution is related to a specific application strategy. Usage volumes can only be estimated from the sales figures, and in such cases have to be averaged out per local area. The term "Good Agricultural Practice" covers a range of measures designed to limit pesticide emissions from farm use. *(see e.g. Hurle, 1989, Fördergemeinschaft Integrierter Pflanzenbau, 1996).* The measures' effectiveness remains a matter of debate.

Pesticide residues in water are known often to result from non-agricultural use (e.g. along railway lines), and from inappropriate application or disposal. Suitable preventive measures must be discussed.

Each region has its particular climatic, geological and morphological features. Each also has its own pattern of plant growth and human settlement. These may well contribute to the occurrence of pesticides in water. Unlike climate, geology or morphology, land use is readily alterable. Agriculture and settlement often determine how seriously a particular case of pollution is taken, and how the authorities react. Regional factors lead to widely varying pesticide problems within the EU. We have therefore selected Member States which differ in their regional characteristics: Denmark, United Kingdom, The Netherlands, Germany, France, Italy and Spain. The bulk of available data refers to United Kingdom, The Netherlands and Denmark, whereas no compiled data were available for Italy and Spain.

A major aspect to be borne in mind when interpreting the data is the number and choice of sampling sites, as well as the sampling strategy. Monitoring sites may be randomly or systematically chosen. Alternatively, the initial test programme may include a degree of pre-selection. The same is true for the choice of substances to be analysed, and for the sampling frequency. Many studies are designed with (1) potential water pollution as a criterium for the choice of measuring sites, (2) a targeted selection of substances and (3) periodical retests of polluted sites only. Unfortunately, the literature rarely contains a precise description of the strategy employed.

The following chapters offer country-by-country summaries of the data investigated. These then provide the basis for an overall assessment of the situation. Discussion of the data with experts from different countries and with different point of views at a workshop in Kiel supported many aspects of the conclusions and the outlook in the last chapter.

Three institutes in Dortmund, Germany, recently completed an extensive pesticides study for the European Commission DGXI *(Heinz et al., 1995).* This study examined a considerable volume of data from a number of viewpoints. These included an economic assessment. Our work makes frequent reference to the

Dortmund study, whose data research was of considerably wider scope than our own. The two publications, however, serve different purposes. The EU study is primarily a reference data source. Our work concentrates on a discussion of current problems, the assessment of monitoring data and the relevance of the pesticide problem.

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Completion of this study was only possible with the generous help of many European and local institutions. Our hearty thanks are due to all those involved, for their recommendations, information and data. We would also like to thank the experts (listed with name and adress in the Appendix) for their contributions to the study's final version at the workshop in Kiel, which was instigated by Professor Karl Aurand. The study was made possible by a financial grant from Ciba (now Novartis, Basel, Switzerland). We are greatly indebted to Professor Horst D. Schulz, who kindly enabled work to be carried out at the University of Bremen, Germany.

2 Situation in selected EU countries

2.1 United Kingdom

Geographical situation

The United Kingdom can be roughly divided into two types of landscape: a cool, moist, rugged highland and island zone in the west and north and a hilly lowland zone in the east and south. Annual precipitation is around 1000 mm on average, but considerably higher on the Atlantic coast and in the mountainous areas. The lowland zone has a moderately warm and relatively dry climate. Agricultural use of the two types of landscape differs considerably. Whereas extensive grazing predominates in the west and north, the east and south are used for intensive arable farming.

Source of data

The following data on the presence of pesticides in water are based largely on the results of the in some respects extensive monitoring programmes of the NRA (1995) which is now part of the Environment Agency (EA). By comparison, relatively few data are available for Scotland or Northern Ireland.

Registration of pesticides

Responsibility for the testing and registration of pesticides for use in agriculture, forestry, and horticulture in the UK lies with the Pesticide Safety Directorate (PSD) within the Ministry of Agriculture, Fisheries and Food (MAFF). Registration of pesticides for veterinary use is the responsibility of the Veterinary Medicines Directorate, while registration of pesticides for non-agricultural purposes is the responsibility of the Health and Safety Executive (HSE). Somewhat more than 450 pesticides are currently licensed by the MAFF and the HSE (*Eke et al., 1996*), most of these being proprietary products for agricultural use.

Use of pesticides

According to the *FAO (1994)*, some 31,100 t of active substance were sold in the UK in 1992. This amount consisted mostly of herbicides (around 63%), followed by fungicides (around 21%) and insecticides (around 4%). The remaining approximately 12% were accounted for by growth regulators and other types of product. In 1992 and 1993 somewhat more than 90% of pesticides were used in agriculture and horticulture and a total of some 10% in industry, forestry, land care, and domestic hygiene (*Heinz et al., 1995*). Pesticide sales figures for the period 1990 to 1992 were more or less static overall, though insecticides showed a pronounced fall and herbicides a slight rise (*Heinz et al., 1995*).

Occurrence of pesticides in water

A research programme ("Harmonized Monitoring Programme") incorporating nationally standardized sampling techniques and analytical methods, was set up as long ago as 1974 (*Eke et al., 1996*). Its principal task was to evaluate the long-term trends of pesticide occurrence in surface water in a series of defined water catchment areas. Surface waters are continuously tested for, among other substances, the insecticides aldrin, dieldrin, γ-HCH (lindane), heptachlor, and certain DDT and DDE isomers. Over the past ten years there has been a marked fall in the number of positive findings, particularly of dieldrin, the use of which is now prohibited in the UK, and a less pronounced fall in the number of positive findings of lindane, which is still used (*Eke et al., 1996*).

Responsibility for monitoring residue levels in inland and coastal waters in England and Wales lies primarily with the EA. The main focus of the monitoring programmes is naturally the very vulnerable surface water, which supplies some 72% of the raw water for the UK's drinking water supplies, whereas only 28% is derived from groundwater (*Heinz, 1996*). As criteria for the description and quantification of residues of pesticides in water the EA monitoring programmes include both nationally and internationally established limit values as well as non-legally-binding environmental quality standards including those established by the EA itself. The limit and reference values for pesticide content in surface and coastal waters for the year 1992/1993 are summarized in *Table 2.1*.

These values are based on different notions. Maximum levels, annual means, and 95th percentiles are given as toxicologically and ecotoxicologically based values. Thus, the table *2.1* contains the UK limit values for eight pesticides included in List 1 of EC Directive 76/464/EEC. The Department of the Environment (DoE) also publishes reference values for 15 other pesticides included in List 2 of EC Directive 76/464/EEC and the "Red List" commonly used in the UK. In the case of the List 1 substances lindane, DDT, pentachlorophenol, aldrin, isodrin, endrin, and hexachlorobenzene, the EA is legally responsible to the DoE for control, monitoring, and notification. Pollution of water with List 2 substances is covered by a continuous monitoring programme characterized in particular by measurement sites downstream of known sewage input sites. The following bar chart showing levels of pesticides in the various categories of water is based on the extensive data collected by the NRA in 1992/1993 (*NRA, 1995*). The 450,000 individual measurements taken at some 3,500 sites were analysed in terms of some 120 different pesticides, metabolites, and isomers. The proportion of measurement sites at which the limit and reference values for

List 1 pesticides were exceeded was less than 1%, or approximately 4% when all named limit and reference values are considered. These data nevertheless do not cover pesticide residues in drinking water, as the quality of this is generally monitored by the water supply companies themselves.

Table 2.1: NRA limit and reference values for pesticide content in surface and coastal waters for the year 1992/1993 in µg/l (modified from NRA).

Substance	Inland water			Coastal water		
	Maximum level [µg/l]	Annual mean [µg/l]	95th percentile [µg/l]	Maximum level [µg/l]	Annual mean [µg/l]	95th percentile [µg/l]
HCH [1) 2)]		0.1 [5]			0.02 [5]	
p,p-DDT [1) 2)]		0.01 [5]			0.01 [5]	
Total DDT [1) 2)]		0.025 [5]			0.025 [5]	
Pentachlorophenol [1) 2)]		2 [5]			2 [5]	
Total aldrin + dieldrin + endrin + isodrin [1) 2)]		0.03 [5]			0.03 [5]	
Endrin [1) 2)]		0.005 [5]			0.005 [5]	
Hexachlorobenzene [1) 2)]		0.03 [5]			0.03 [5]	
Atrazine + simazine [3)]	10	2		10	2	
Azinphos-methyl [1) 3)]	0.04	0.01		0.04	0.01	
Dichlorvos [3)]		0.001			0.04	
Endosulfan [3)]	0.3	0.003			0.003	
Fenitrothion [3)]	0.25	0.01		0.25	0.01	
Malathion [3)]	0.5	0.01		0.5	0.02	
Trifluralin [3)]	20	0.1		20	0.1	
Diazinon	0.1	0.01		0.15	0.015	
PCSDs [4)]			0.05			0.05
Cyfluthrin [4)]			0.001			0.001
Sulcofuron [4)]			25			25
Flucofuron [4)]			1			1
Tributyltin (TBT) [4)]	0.02			0.002		
Triphenyltin (TPT) [4)]	0.02			0.008		
Permethrin [4)]			0.01			0.01

1) not registered in the UK
2) "List 1"
3) "Red list"
4) "List 2"
5) legally stipulated limit value

Surface water

In terms of the number of substances considered and the frequency of sampling, pesticide occurrence in surface water is best measured by the EA monitoring programmes. In 1993 inland water was analysed for 112 different substances; 83 of these were found, with 59 present at concentrations above 0.1 µg/l (*Fig. 2.1*).

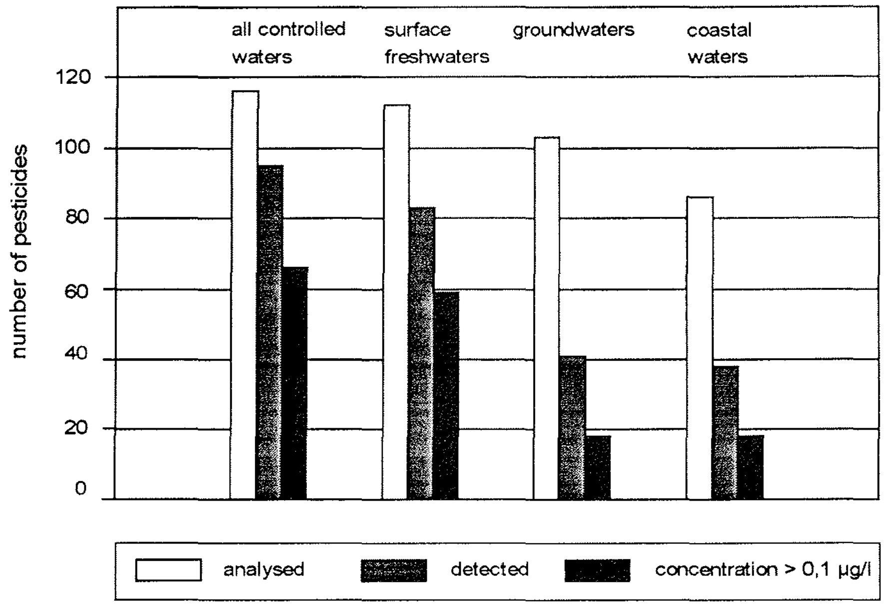


Fig. 2.1: *Number of pesticides found to be present at concentrations of > 0.1 µg/l in the various categories of water in England and Wales in 1993 (data from NRA, 1995).*

Fig. 2.2 shows the substances that were most commonly found. Most common of all were the herbicides mecoprop (phenoxycarboxylic acid derivative), which is used in agriculture, and the herbicides diuron (urea derivative) and atrazine (triazine derivative), which were used mostly for non-agricultural purposes. Noteworthy is the increased frequency with which diuron was found in 1993 as compared with 1992, whereas the proportion of cases in which atrazine was found at concentrations above 0.1 µg/l fell in the same period (*Fig. 2.2*). This was probably due to the prohibition on the use of atrazine and simazine for non-agricultural purposes that came into effect in September 1993. Even before it came into effect, this ruling seems to have resulted in a marked reduction in the use of atrazine and a corresponding increase in the use of diuron. In view of the small sample size involved, the frequent occurrence of chlorpropham (a substance used as an antisprouting agent in the storage of potatoes) that was reported in a substance-specific study in 1993 cannot be regarded as conclusive. The same observation applies with reservations to the fungicide carbendazim and the herbizide bentazone. The latter substance was first included in the monitoring programme in 1993, after its occurrence in the surface water of certain water catchment areas had been predicted on the basis of mathematical models. In the case of carbendazim it must be borne in mind that the studies concerned were performed exclusively at sites at which the substance was known to be used. It must also be remembered that sampling was performed shortly after application of the substance.

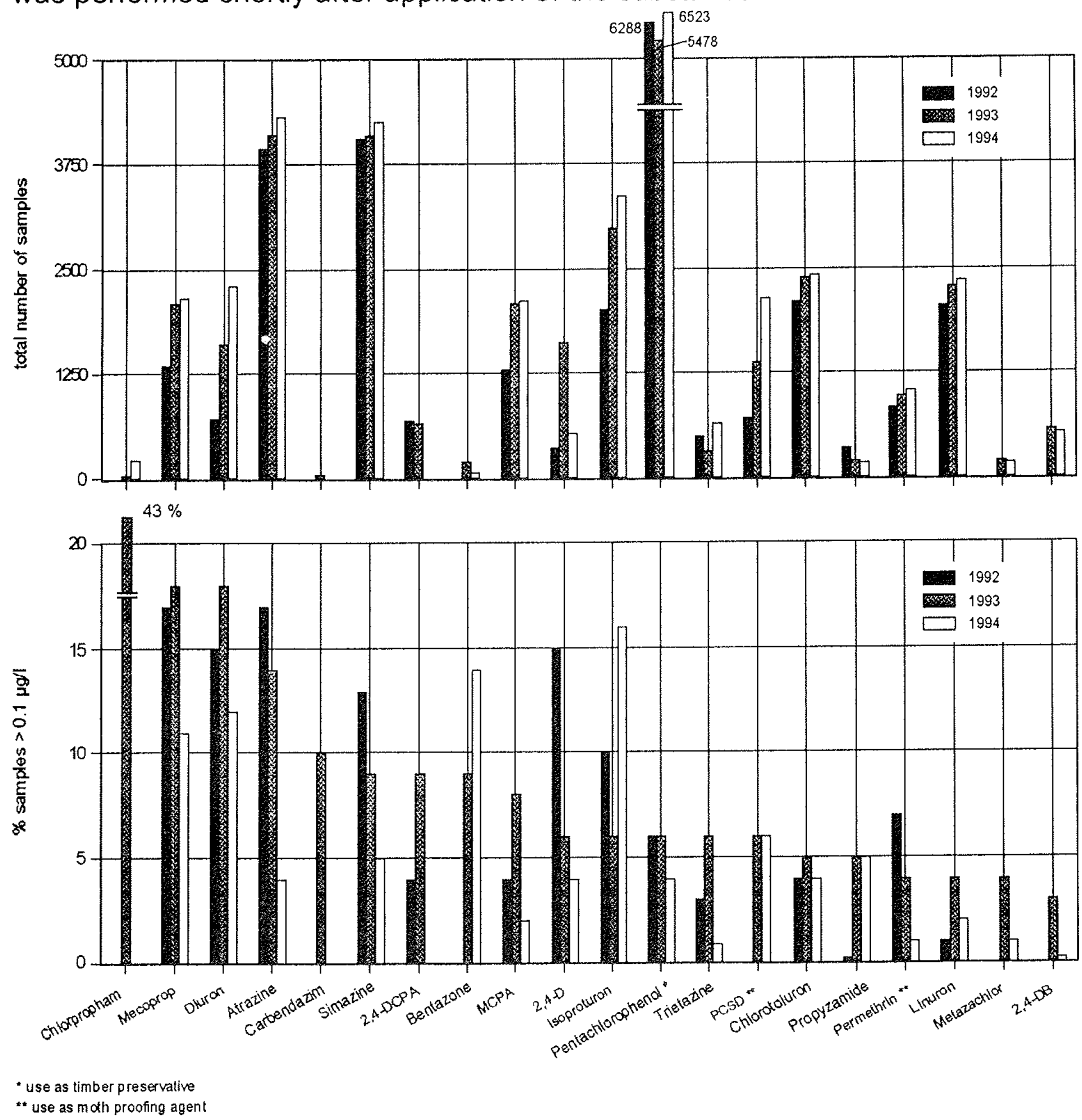
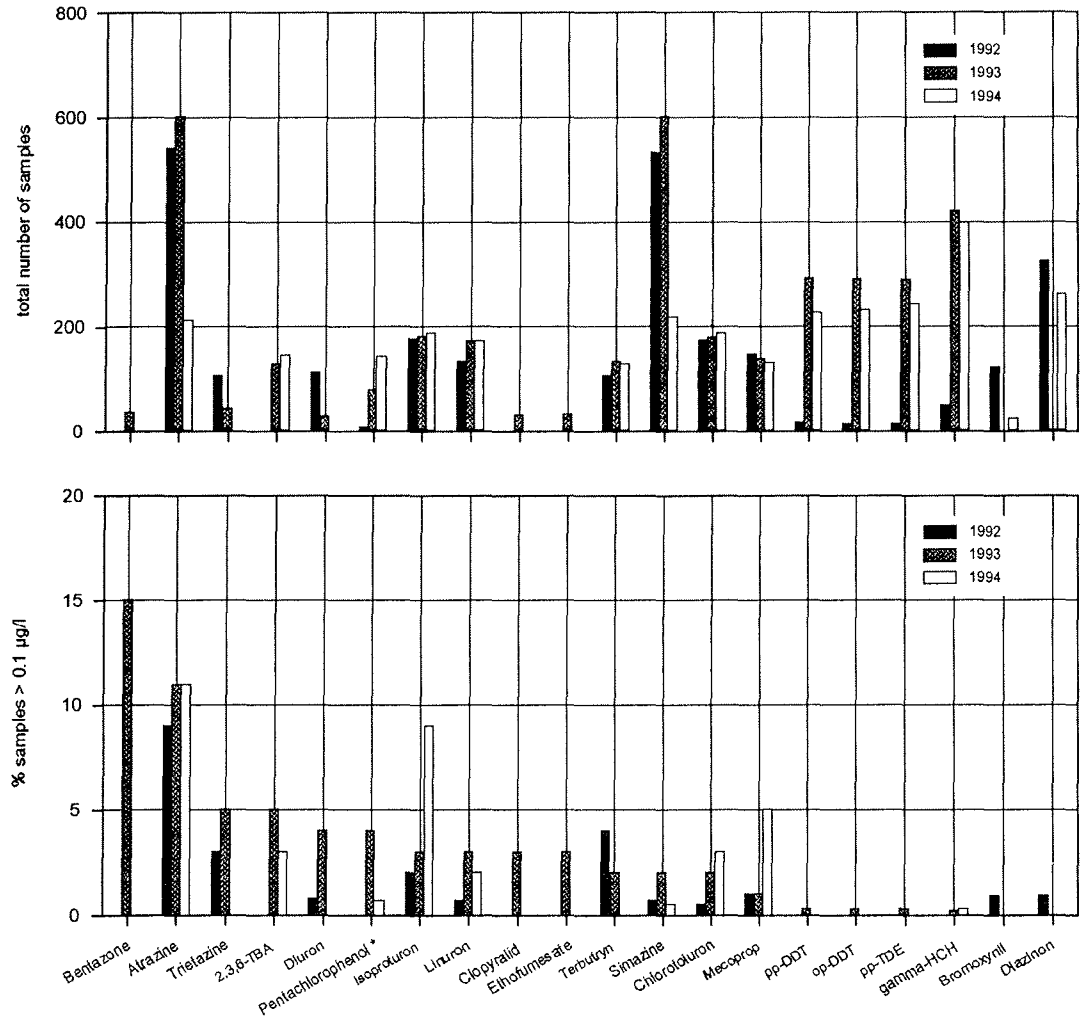


Fig. 2.2: *Number of analyses and proportion of analyses with concentrations of > 0.1 µg/l of the 20 pesticides most commonly found in surface water in England and Wales between 1992 and 1994 (data from EA, 1996).*

By contrast, inland water residues of phenoxycarboxylic acid and urea derivatives, which are generally applied extensively as agricultural herbicides, has been clearly demonstrated on the basis of relatively large sample sizes. Thus, as in the cases of mecoprop and diuron, a notable proportion of analyses for the phenoxycarboxylic acid derivatives MCPA and 2,4-D and for the urea derivatives isoproturon, chlortoluron, and linuron revealed concentrations above 0.1 µg/l.



* use as timber preservative

Fig. 2.3: *Number of analyses and proportion of analyses with concentrations of > 0.1 µg/l of the 20 pesticides most commonly found in groundwater in England and Wales between 1992 and 1994 (data from EA, 1996).*

Groundwater

Groundwater is used for drinking water supplies mostly in the eastern and southern parts of England. The aquifers present here include in particular chalk formation, which as a fissure aquifer and to some extent also a karst aquifer is at particular risk of pesticide input. As monitoring of groundwater withdrawal for use as drinking water is primarily a responsibility of the water supply companies themselves, the EA has only a limited monitoring programme in this respect.

Groundwater was analysed for around 80 individual substances in 1992 and for around 100 in 1993 (*Fig. 2.1*). It contains considerably fewer individual pollutants than surface water. Thus, in 1993 the NRA found 41 different substances in groundwater, of which around half were present at concentrations above 0.1 µg/l (*Fig. 2.1*). *Fig. 2.3* provides a summary of the pesticides most commonly found in groundwater at concentrations above 0.1 µg/l.

Most of these substances are herbicides. The substance most commonly found in groundwater at concentrations above 0.1 µg/l was bentazone. Here again, however, account must be taken of the fact that the number of samples was small and the monitoring programme was investigating a specific question. Like surface water, groundwater was first analysed for bentazone in 1993 and the input of this substance into groundwater was predicted on the basis of a mathematical model. In contrast to the situation with surface water, atrazine was found in groundwater more often in 1994 and 1993 than in 1992. This increase was probably due to the considerable increase in the area of maize cultivation in southwestern England during this period (*Eke et al., 1996*). In the case of the remaining substances, a large proportion of which were triazine and urea derivatives, the proportion of findings in which the concentration was above 0.1 µg/l was between around 1 and 5% (*Fig. 2.3*).

Drinking water

Data on pesticide occurrence in raw water of drinking water supplies are summarized in the reports of the *Drinking Water Inspectorate* (1992, 1993) referring to monitoring data from the 37 British water companies. The number of pesticides monitored by each company varies according to the pesticides used in the catchment area. The data are given as total pesticides and individual pesticides detected in the supply zones with concentrations exceeding the drinking water standard.

About 70 % (69.4 to 72.1%) of the water supply zones (1993: 2 323) complied with the individual pesticide standard in the years 1990 to 1993. 85 to 88 met the total pesticide standard. These data indicate a slight decrease of pesticide residues in the raw water. In the case of 30 % supply zones which are non-compliant, it should be considered that of only one or very few samples from a supply zone exceeded the drinking water standard concentration. Usually of the total number of pesticide samples of more than a million, 2.1 % exceeded the limit for individual pesticides in 1993.

The occurrence of pesticides in surface water systems that are used for the supply of drinking water merits particular attention. Well-known examples include the presence of relatively high atrazine residues in raw water from the river Avon, and the finding of isoproturon at concentrations of several µg/l in the

Eastern Yar River (Isle of Wight) in March 1994, a circumstance that led to shutdown of the local water supply plant (*Eke et al., 1996*). In both examples, the occurrence of the pesticides could be referred to point source contamination arising from mixing and loading of sprayers rather than spraying of the maize crop. *Court et al. (1995)* refer to concentrations of pesticides exceeding the permissible limit in the raw water used by the water supply company Severn Trent Water. The pesticides most commonly found are the herbicides mecoprop, isoproturon, MCPA, and diuron as well as atrazine and simazine, which are found especially in lowland surface water, though also in groundwater. The percentage of positive analyses for atrazine and simazine in which the concentration exceeded the limit value of 0.1 µg/l fell from 10–20% to less than 5% between 1990 and 1994. Over the same period the corresponding figure for mecoprop fluctuated between 10 and 20%, while that for isoproturon fluctuated between 10 and 30%.

Reactions of authorities to contamination of water with pesticides

Where contamination of water with pesticides is found, the primary responsibility of the EA is to take samples and to adequately check analytical findings. The EA is also required to investigate the cause of the contamination and where possible to undertake a comprehensive environmental risk assessment. These measures are mostly taken in response to individual sources of contamination reported to the EA by industrial concerns, pesticide users, or the public or police.

Of the various long-term measures aimed at preventing contamination of water with pesticides, the ongoing development of environmental quality targets by the EA is worthy of special mention. In its capacity as a water authority the EA is making increasing efforts to gain influence in relation to the registration of pesticides and the designation of water protection areas. Efforts of this kind led to the banning of atrazine and simazine for non-agricultural use. Another important aspect of long-term strategy is the public relations work of the MAFF and the EA: via programmes involving explanation, counselling, and education this aims principally to improve the way in which pesticides are used (*Ministry of Agriculture, Fisheries and Food, 1991*).

Principal areas of research

The task of the EA makes it fundamentally concerned with quantifying and predicting the outcome of contamination of the aquatic environment with pesticides. The EA's current research activities therefore include further development of new analytical methods and improvement of risk prediction in terms of expected concentrations of various pesticides in water. Below is a list of selected current and proposed EA projects designed to provide information on the effects of pesticide use. These research projects deal in particular with the following points:

- Fewer than half of the pesticides currently registered in the UK can be detected at sufficiently low concentrations using presently available analytical methods. This is particularly true of fungicides and pyrethroid insecticides. Special efforts are therefore being made to improve and develop suitable gas-chromatographic and mass-spectrometric methods to detect pesticides and their metabolites whose presence can be predicted via mathematical models. Similarly, efforts are also being made to construct a database of relevant metabolites and byproducts.

- Another project is to develop methods for estimating the risk of damage from individual sources of contamination such as leaks and accidents. The emphasis here is on the development of methods that permit quantitative predictions of surface water contamination.

- Together with other research institutions, the EA is helping to develop the POPPIE (Prediction Of Pesticide Pollution In the Environment) computer system. This is designed to help predict the risk from pesticide residues in groundwater and surface water, and as an aid to monitoring programmes. It also offers better management of pesticide use in water catchments, and thus helps to minimise water pollution. A similar model called CATCHIS is used by Severn Trent Water for this purpose. The system combines GIS (geographical information system) with mathematical models of groundwater and surface water flow. These are based on input from various databases on amounts and physicochemical properties of pesticides used, land use, soil-science and hydrologic data. It is designed both for regional use and as an aid to national monitoring programmes. There are also plans to use the model to derive suitable reference values for pesticide concentrations in groundwater and surface water.

- There are also plans for quantitative assessment of the potential for further reduction in the use of pesticides as a result of improvements in their application.

2.2 The Netherlands

Geographical Situation

The Netherlands are formed by low coastal plains around the mouths of the Rhine, Meuse and Scheldt. Groundwater is therefore usually not far from the surface. In large sections of the country, agriculture is only possible thanks to the system of dykes. Agricultural land accounts for about 70% of the total surface area, waterways for another 18%. The climate is one of cool summers and mild winters. Annual rainfall is between 550 and 850 mm.

Source of data

A number of Dutch authorities and institutes run pesticide/water monitoring programmes. In particular, the RIZA (National Institute for Inland Water Management and Waste Water Treatment) keeps a regular nationwide watch on inland water. The National Institute of Public Health and the Environment (RIVM) conducts periodical investigations of pesticide residues in groundwater. The Rhine and Meuse Waterworks Association (RIWA) and other water companies continually check drinking water sources.

The overview provided below of pesticide occurrence in Dutch water is based on data in *Tas et al. (1996) and Teunissen-Ordelmann & Schrap (1996)*. The former publication is a summary of numerous public and internal reports collated by a range of state and other institutions between 1987 and 1994. It can be assumed that the various monitoring programmes had differing aims. The data are correspondingly heterogeneous, and permit only limited comparisons. In some substance-specific studies, for example, the occurrence of particular pesticide was deliberately investigated immediately after application. Other substances were simply noted in the course of routine monitoring programmes. Nonetheless, these data at present appear a suitable guide to the degree of ground- and surface water pollution by pesticides.

The summary by *Teunissen-Ordelmann & Schrap (1996)* is based on RIZA investigations into the occurrence of 103 different pesticide substances in surface and groundwater. Three criteria were used to select these pesticides from the total of about 270 such substances on the Dutch market: (1) valid registration status in 1991; (2) estimated 1991 application volumes over 10 t/a, and (3) active concentration well below the water solubility mark. The substances thus chosen represented only 38% of those registered, but about 70% of total usage volumes. They belong to 14 different chemical groups. The majority can be classified either as organophosphates (n=16), phenylurea herbicides (14), carbamates (11), dithiocarbamates (9) or triazines (10). The

103 substances are composed of 39 herbicides, 31 insecticides, 29 fungicides and four nematicides.

Registration of pesticides

About 270 pesticide substances are currently registered for agricultural use in the Netherlands. The approval procedure includes an environmental risk assessment. Hitherto, this has largely involved laboratory studies of toxicity, persistency, degradation behaviour and physico-chemical properties. A more objective impression of the ecological risks posed by pesticides requires investigation of substances' actual use and their concentrations in different environmental compartments.

Use of pesticides

In 1995, 10,923 tonnes of active substance were sold in the Netherlands. Fungicides formed the single largest category, with 36.5% of the total application volume (*Tab. 2.2*). Herbicides had about 28% of the market, and nematicides some 22%. The year's sales figures *(NEFYTO 1996)* show that about 51% of fungicides were dithiocarbamates (e.g. mancozeb, maneb). Carbamates (e.g. carbaryl) and organophosphates (e.g dimethoate, parathione, dichlorvos) accounted for more than half of the insecticides and acaricides. Phenoxycarbolic acids (e.g. MCPA, mecoprop P), triazines (e.g. atrazine) and urea derivatives like isoproturon and linuron form roughly 40% of herbicide sales by volume.

Figures for Netherlands sales of pesticides up to 1993 are supplied by members of the "Dutch Foundation for Phytopharmacy" (NEFYTO). Actual sales are estimated to be about 7% higher *(Brouwer et al., 1994)*. *Table 2.2* shows a noticeable decline in pesticide volumes. This is particularly true of nematicides, which until 1992 were the country's best-selling substance group in volume terms. Insecticides/acaricides and herbicides show a drop between 1988 and 1995 of 18% and 20%, respectively. Fungicide sales remained virtually unchanged.

Soil and crop differences mean that pesticide use in the Netherlands shows marked geographical variety. Hard data are rarely available on regional pesticide choice or application volumes. An indication of the differences emerges from variations in soil and natural land use. On the largely sandy soil in the northeast, farmers chiefly grow potatoes and sugar beet. This area sees particularly heavy nematicide use. To the immediate south and west are corn-growing and pasture areas, where herbicides are the dominant pesticides. The coastal regions of the northern and southern Netherlands have a mixture of sandy and clay soils low in humus. Here, large-scale ornamentals production necessitates intensive use of nematicides and fungicides. Further inland, to the south, fungicides and to a lesser extent insecticides are used in greenhouse farming of vegetables and ornamentals.

Table 2.2: Annual pesticide sales for agricultural use in the Netherlands (NEFYTO (1996) (1) and Brouwer et al. (1994) (2)). For the period 1984-1988 average annual sales figures are given.

Active substance (x 1000 kg)	1984-1988(1)	1989 (2)	1990 (2)	1991 (2)	1992 (2)	1993 (1)	1994 (1)	1995 (1)	% drop 1984-95
Herbicides	3854	3330	3468	3312	2987	2796	2678	3070	20
Fungicides	4039	4052	4140	4281	4192	4007	3883	3990	1
Insecticides/ Acaricides	603	745	731	594	557	471	439	497	18
Nematicides	10247	9830	8937	7679	6762	2587	2535	2374	77
Other	1218	1189	1559	1440	1423	1900	1634	992	19
Total	19961	19146	18835	17306	15921	11761	11169	10923	45

Occurrence of pesticides in water

Dutch legislation demands an especially close watch on the occurrence in water of "attention substances" regarded as particularly harmful to the environment. These include 30 pesticides for agricultural and three for other uses, as well as the insecticides aldrin, dieldrin, endrin, endosulfan and isodrin, which are all banned in the Netherlands *(Tas et al. 1996)*.

In addition, the Netherlands authorities apply a series of ecotoxicological test values for the presence of pesticides in surface and groundwater. These environmental standards are not yet legally binding, but are clearly necessary. According to *Tas et al. (1996)*, only some 40% of the pesticide substances in surface and 50% of those in groundwater appear in the list of "attention substances".

Surface water

The Netherlands authorities survey four categories of surface water: (1) coastal waters, (2) international waterways like the Rhine, Meuse and Scheldt, (3) sovereign inland water areas (Ijsselmeer, Markermeer, etc.) and (4) regional inland water areas (smaller lakes and rivers, canals). *Tas et al. (1996)* report investigation of 140 pesticide substances and metabolites, of which 68 were found to be present *(Fig. 2.4)*. 59 substances appeared at concentrations above 0.1 µg/l. The highest values were recorded in lakes and canals, not in the rivers, some of which are used for drinking water *(Tas et al., 1996)*.

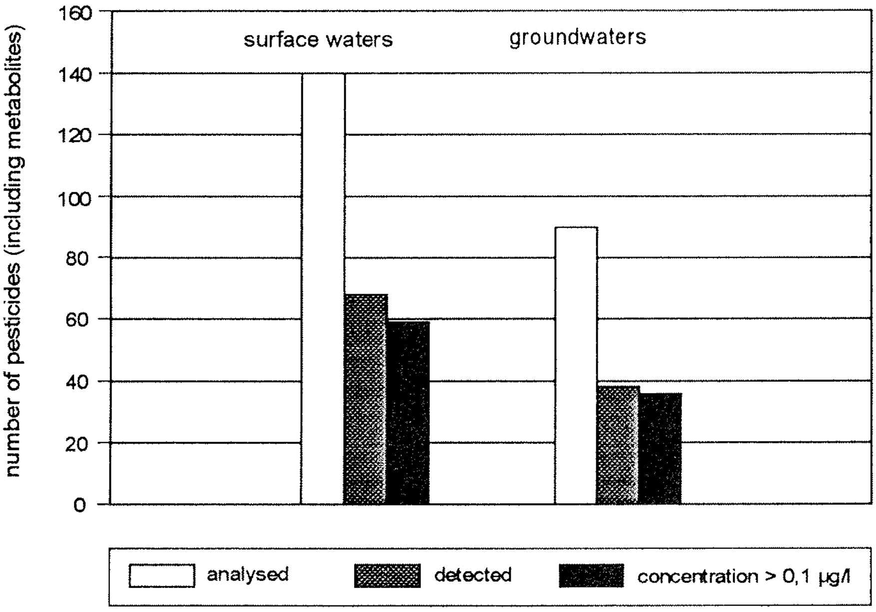


Fig. 2.4: Number of pesticides analysed, found and present at concentrations > 0.1 µg/l in Dutch surface- and groundwater between 1987 and 1994 (data from Tas et al., 1996).

The data collated by *Teunissen-Ordelmann & Schrap (1996)* demonstrate that regional waterways downstream from areas of intensive agricultural activity contain the largest spectrum of traceable pesticide substances. Regional distribution of results from surface water monitoring in 1993 are shown in *Figure 2.5.* Results from several measuring sites within each region have been combined. It is noticeable how few substances were analysed in the Provinces of Utrecht and North-Brabant (central and southern Netherlands), where high fungicide use, e.g. on greenhouse vegetables, would be expected to generate more residues. In the northern and northeastern areas of intensive cereal, sugar beet and potato farming (in Flevoland and southeast of the Ijsselmeer), a relatively large number of substances were investigated. A high proportion of the substances was found; between 20 and 60% exceeded the test values. *Figure 2.6* shows the ten pesticides which most frequently exceeded the test values in the four categories of inland water. Almost all of them are herbicides (chiefly phenylureas, phenoxycarbolic acids and triazines) or insecticides (organophosphates and carbamates). The herbicides diuron, mecoprop and MCPA as well as the insecticide dichlorvos appear to a marked degree in all four categories. Mevinvos, malathion and atrazine are each seen with high frequency in three sections.

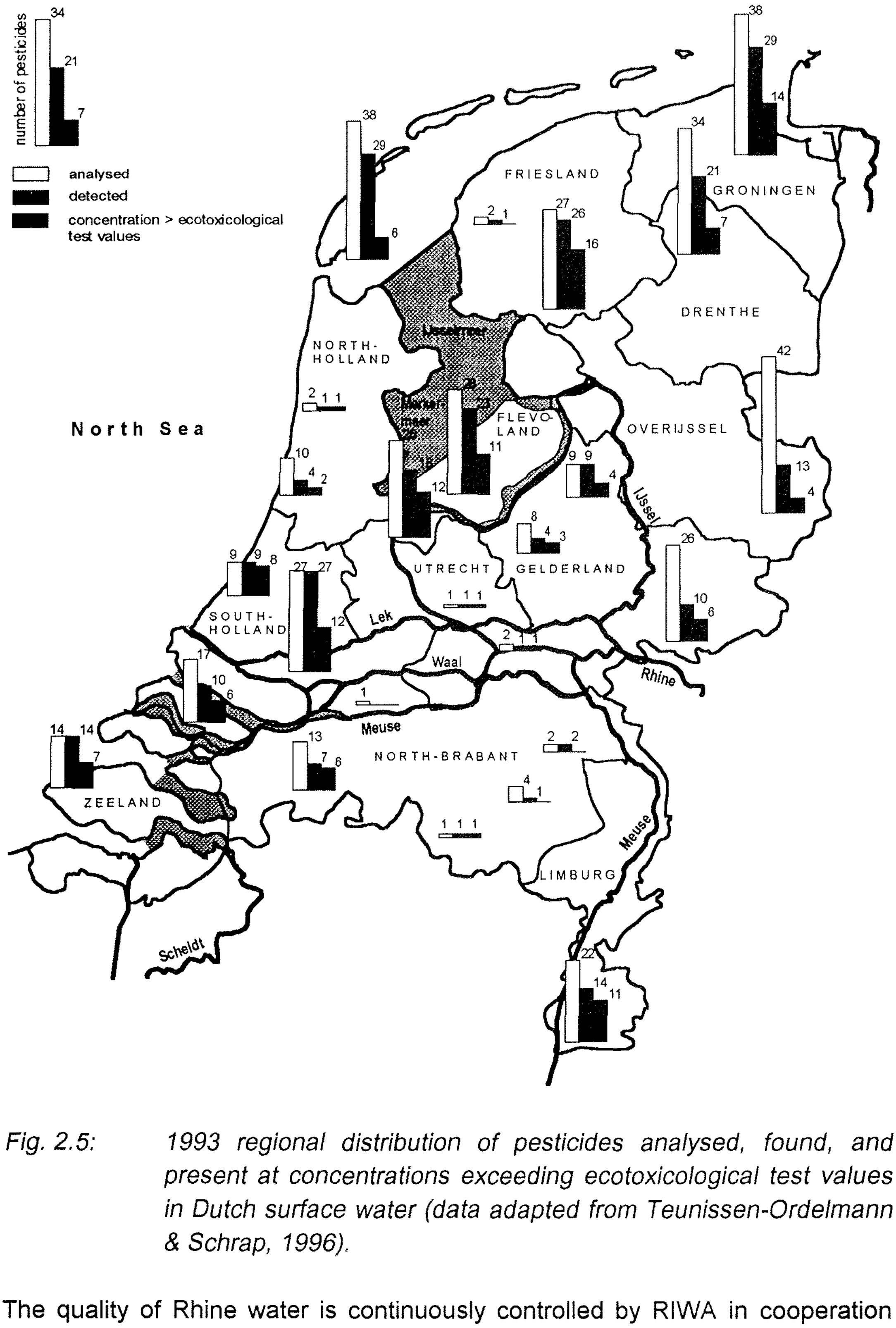


Fig. 2.5: *1993 regional distribution of pesticides analysed, found, and present at concentrations exceeding ecotoxicological test values in Dutch surface water (data adapted from Teunissen-Ordelmann & Schrap, 1996).*

The quality of Rhine water is continuously controlled by RIWA in cooperation with RIZA. The criterion to evaluate water quality is the standard for raw water of drinking water supply. In 1994, residues of atrazine, simazine, diuron and isoproturon measured at four locations in the Rhine catchment area exceeded the drinking water limit (*RIWA, 1996*). These data were attributed to diffuse input by agricultural use and application of these pesticides in municipal gardens. In april 1994, the drinking water supply in Lobith was stopped for a month due to concentrations of 0.5 µg/l isoproturon in Rhine water.

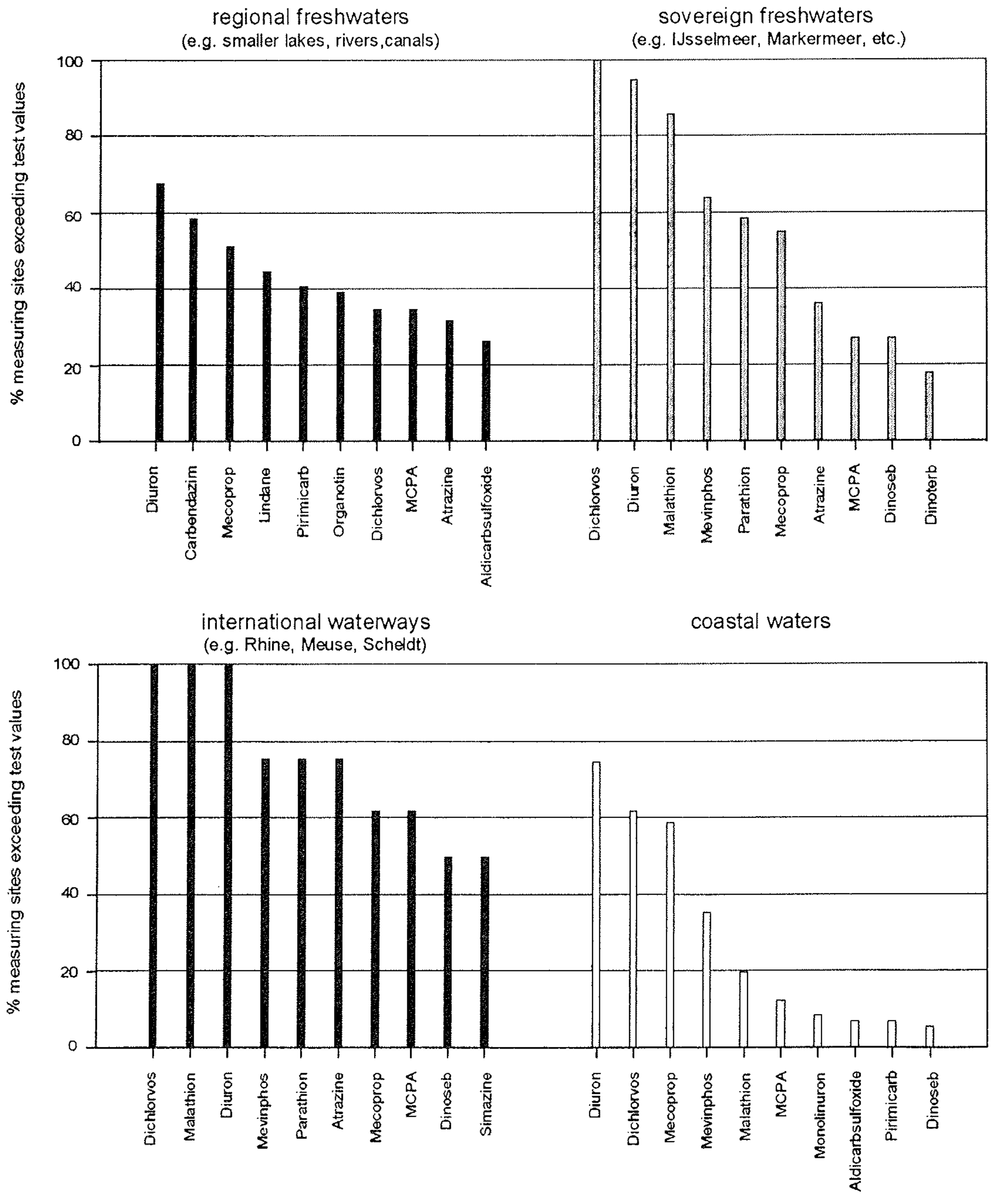


Fig. 2.6: *Pesticides most frequently exceeding ecotoxicological test values in various surface water categories (data from Teunissen-Ordelmann & Schrap, 1996)*

Lobith is situated a few kilometers west of the German border near Emmerich. The development of pesticide residues in Rhine water from 1988 to 1992 (*Fig. 2.7*) indicates a decline of atrazine and simazine concentrations, related to the atrazine ban in Germany in 1991. The data base for lindane is complete over a period of 20 years (*Fig. 2.8*). Lindane concentrations also declined to ultratrace levels following reduction in use in Germany.

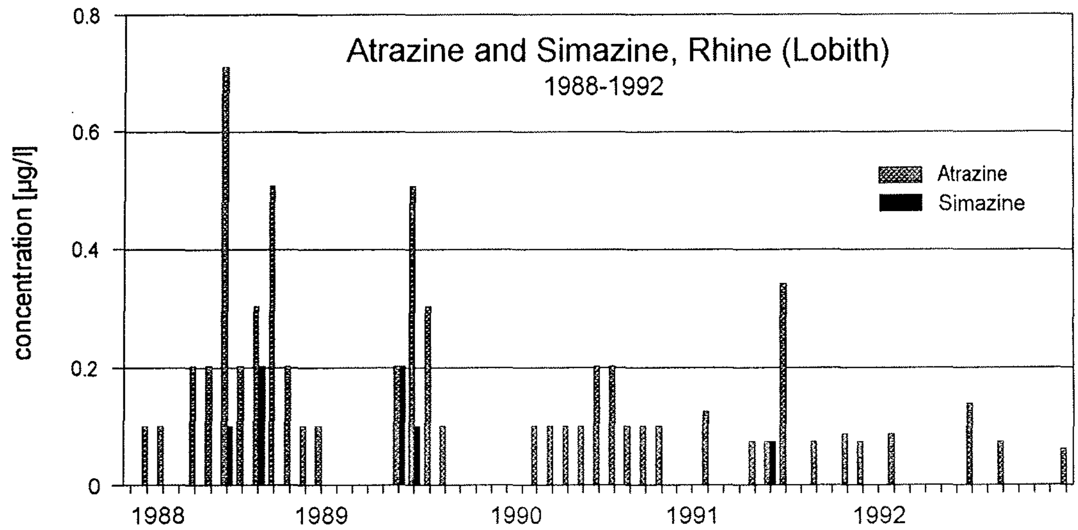


Fig. 2.7: *Development of atrazine and simazine concentrations in Rhine water from 1988 to 1992 measured at Lobith (data from Teunissen-Ordelmann et al., 1993 and Breukel, 1993).*

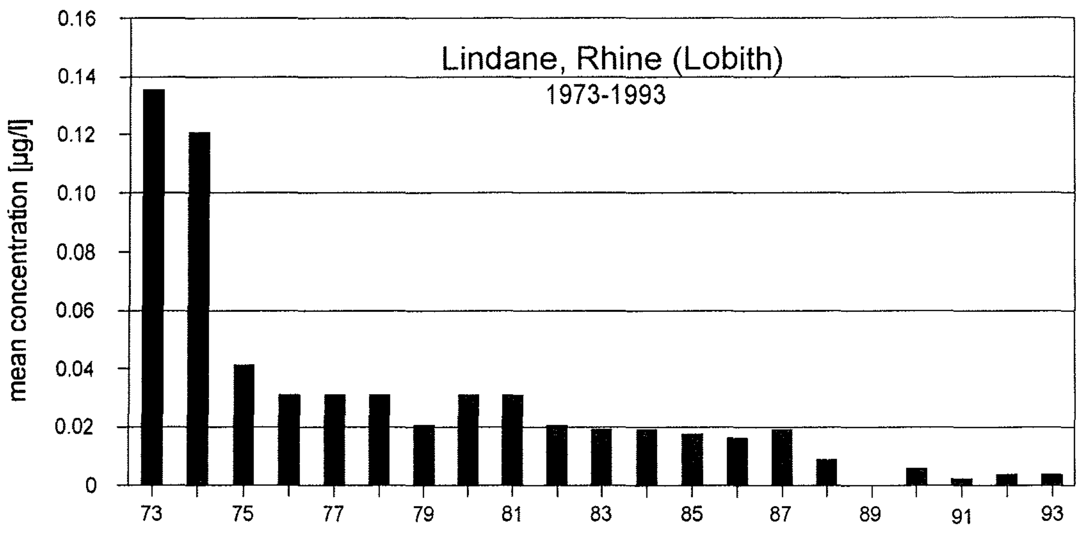


Fig. 2.8: *Development of lindane concentrations in Rhine water over a period of 20 years measured at Lobith (data from Teunissen-Ordelmann et al., 1993).*

Groundwater

In the Netherlands, official national surveys of pesticides in groundwater are chiefly the responsibility of the RIVM. The Institute's figures for 1986-1994 are cited by *Teunissen-Ordelmann & Schrap (1996)*. The RIVM analysed considerably fewer individual substances in groundwater than in surface water (*Fig. 2.4*). Only about a quarter of the pesticides investigated in any kind of water were analysed in leachate or groundwater. The literature covered by the present study does not give any details of regional pesticide occurrence.

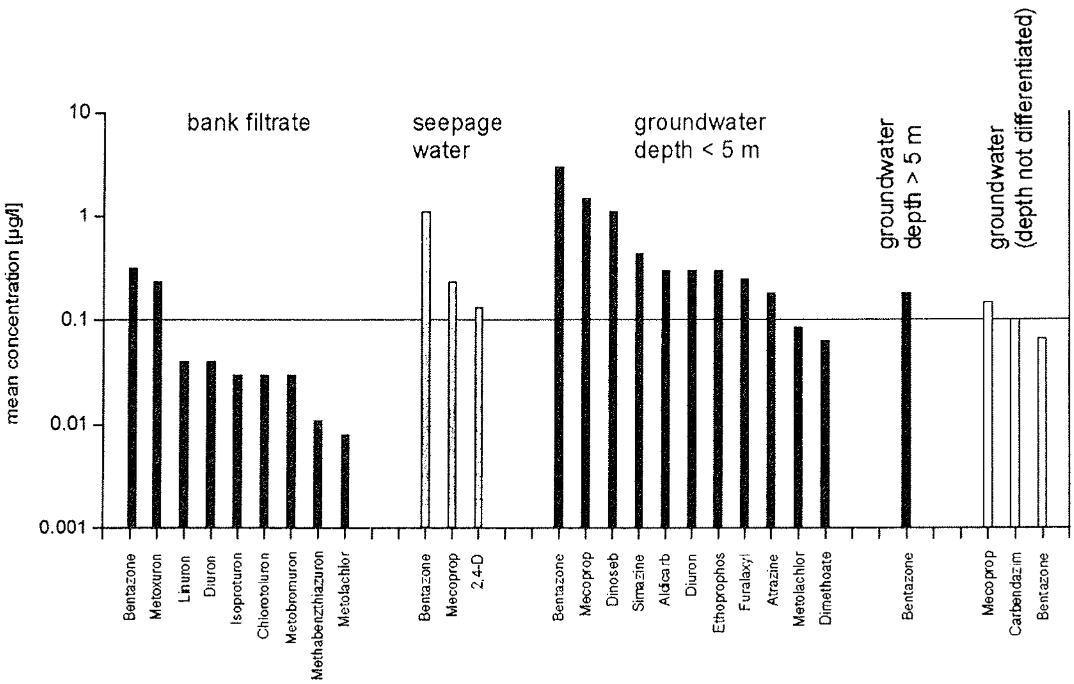


Fig. 2.9: *Mean concentrations of pesticides detected in various groundwater categories between 1986 and 1994 (data from Teunissen-Ordelmann & Schrap, 1996)*

Figure 2.9 provides an overview of the pesticide spectrum in leachate and a range of groundwater. These are based on mean concentration values, generally from several years' observation. The substances found are mostly herbicides. As would be expected, groundwater near the surface (max. depth 5 m) displays the heaviest content of pesticide residues. Deeper-lying groundwater showed traces only of bentazone. Noticeably, this substance also appears in the other water categories given. Bentazone is largely used on ornamentals in the southern Netherlands. It has been seen on a number of occasions at very high groundwater concentrations of up to 98 µg/l (*Teunissen-Ordelmann et al., 1995*).

Drinking water

Information about pesticides in Netherlands drinking water is very hard to come by. *Heinz et al. (1995)* presume that all the surface water used as a drinking water source in the Netherlands contains pesticide substances at concentrations above the legal limit of 0.1 µg/l. Between 1983 and 1993 about 110 pesticides, metabolites or related substances were found in Rhine, Meuse, Ijsselmeer and Haringvliet surface water. 80 of these compounds were used directly as pesticides *(van Genderen et al., 1994)*. The drinking water from these sources was tested for 55 substances. 19 were found, six of them at concentrations > 0.1 µg/l. This last group included the herbicides atrazine, metolachlor, TCA and bentazone.

Reactions of authorities to contamination of water with pesticides

With its "Multi-Year Crop Protection Plan", the Dutch government aims at a long-term reduction in the use of pesticides. The plan foresees a halving of 1984-1988 pesticide application volumes by the year 2000. By 1994, usage had already fallen by 44%, mainly through a reduction in nematicide use. However, no comparable reduction was achieved for insecticides and fungicides, which are considered by toxicologists to pose a particular threat to the environment. Official targets exist for pesticide levels in surface water. A problem here is that adequate quantitative data are often lacking.

Principal areas of research

Numerous Dutch monitoring programmes gear their choice of investigated substances to current legal demands and to the available analytic methods. A study commissioned by the RIZA *(van Genderen et al., 1994)* shows clearly that water and drinking water surveys have hitherto paid too little attention to toxicological criteria. Future Netherlands research projects should therefore use chemical and toxicological analyses to widen the scope of current lists of major ecotoxins. In particular, intensified research is required into the presence and behaviour of metabolites.

2.3 Denmark

Geographical situation

The landscapes of Denmark, which are characterized by moraines and glacial outwash, were formed mostly during the last glacial periods. The range of altitude is correspondingly low. The intensive agricultural use made possible by fertile soils and good climatic conditions (mean annual precipitation ranges from 400 mm in the eastern islands to 800 mm in West Jutland) is the most important factor influencing the landscape. The proportion of the total land area used for agriculture is 66% (*Vogel et al., 1995*). Grain cultivation (especially barley and wheat) and forestry (e.g. Christmas trees) each account for somewhat more than a third of this. Other regionally important crops are sugar beet, rape, potatoes, cabbage, and various types of vegetable. With the exception of the conurbation of Copenhagen, which is home to some 20% of the population, the population is fairly evenly distributed.

Source of data

Responsibility for overall monitoring of groundwater and surface water lies with the state. A national programme for monitoring pesticide residues in groundwater was set up in 1988. This now incorporates 976 groundwater measurement sites. It confines itself to the determination of groundwater levels of eight plant protection agents that are regarded as particularly environmentally relevant in view of their mobility. These are four phenoxycarboxylic acid derivatives (dichlorprop, mecoprop, MCPA, 2,4-D), two triazine derivatives (atrazine, simazine), and two nitrophenols (dinoseb, DNOC).

Drinking water is monitored by the local supply companies, which are obliged to forward their data to the Ministry for the Environment and Energy. As almost 100% of drinking water in Denmark is obtained from groundwater and as there are a large number of controlled sampling wells, analyses of drinking water also serve as a source of information on the extent of pesticide occurrence in groundwater. Results for the eight pesticides included in the national monitoring programme are available from 3,700 wells. Some wells have also been tested for the presence of other pesticides.

There are also regional monitoring programmes that consider a greater range of pesticides. The South Jutland Authority has tested for 18 pesticides and two metabolites in the groundwater of the agriculturally exploited water catchment area of Bolbro Bæk. The Vejle Authority has tested for twelve pesticides and four metabolites in the groundwater of five areas.

Mogensen & Spliid (1995) analysed the results obtained by the National

Environmental Research Institute (NERI) on the presence of pesticides in surface water. Data on pesticide concentrations in soil water and drainage water and in the rivers of three selected water catchment areas on Lolland and Zealand and in southern Jutland were analysed. The investigations were conducted over two years and considered eleven pesticides (atrazine, simazine, MCPA, mecoprop, dichlorprop, 2,4-D, dinoseb, DNOC, bromoxynil, ioxynil, isoproturon).

It must be stated that the value of the available data is generally limited by the small number of pesticides considered. The results of the studies performed in regions in which a more extensive range of parameters was considered show that the frequency of detection depends to a considerable extent on the number of pesticides considered (see below).

In evaluating the data on the pesticide residues in groundwater it must also be borne in mind that atrazine and the phenoxycarboxylic acid derivatives, which were included in the national monitoring programme, have since been prohibited (i.e. five out of eight agents).

Registration of pesticides

In accordance with applicable EU directives, pesticides in Denmark fall under the competence of the 1979 "Chemical Substances and Products Act", which is administered by the Danish EPA (Environmental Protection Agency). In 1994 a total of 224 pesticidal substances (= 984 products) were on the market. Since 1987 a total of 216 substances (= 1,232 products) have been newly evaluated. To date more than 82 agents have been withdrawn from the Danish market. At the start of 1995 some substances had yet to be evaluated (*Moe, 1995*). In May 1994 the Danish parliament passed a law to the effect that any product containing any of seven named substances could no longer be sold or used. The most recent ban affects phenoxycarboxylic acid derivatives. High mobility and a high level of persistence in soil are regarded as particularly critical characteristics.

Use of pesticides

In 1992 a total of 3,429 t of herbicides, 1,678 t of fungicides, 241 t of insecticides, 196 t of growth regulators, 65 t of nematicides, and 9 t of other plant protection agents were sold in Denmark (figures given in terms of active substance) (*Brouwer et al., 1994*).

In 1987 the Danish Ministry for the Environment and Energy established targets for reduction in use of pesticides. These included a 25% reduction in agricultural use of pesticides by 1990 and a further 25% reduction by 1997. Similarly, the frequency of pesticide use was meant to fall by half from 2.67 to 1.34 applications per year. Between 1985 and 1993 the amount used did in fact fall by 40%, though this was due to increasing use of pesticides that are effective in lower amounts (*Moe, 1995*), whereas the frequency of use showed no significant change during this period.

In order to achieve further reductions in amounts used and frequency of application, taxes on pesticides were drastically increased in 1995 from a general figure of 3% up to 27% for insecticides and soil fumigants and 13% for other pesticides (e.g. herbicides).

Occurrence of pesticides in groundwater and drinking water

As 98–100% of drinking water in Denmark is obtained from groundwater (*Moe, 1995*), the pesticide monitoring programme concentrates on groundwater (see above). The individual pesticides included in the national monitoring programme were found at up to 4% of the measurement sites studied (*Fig. 2.10*).

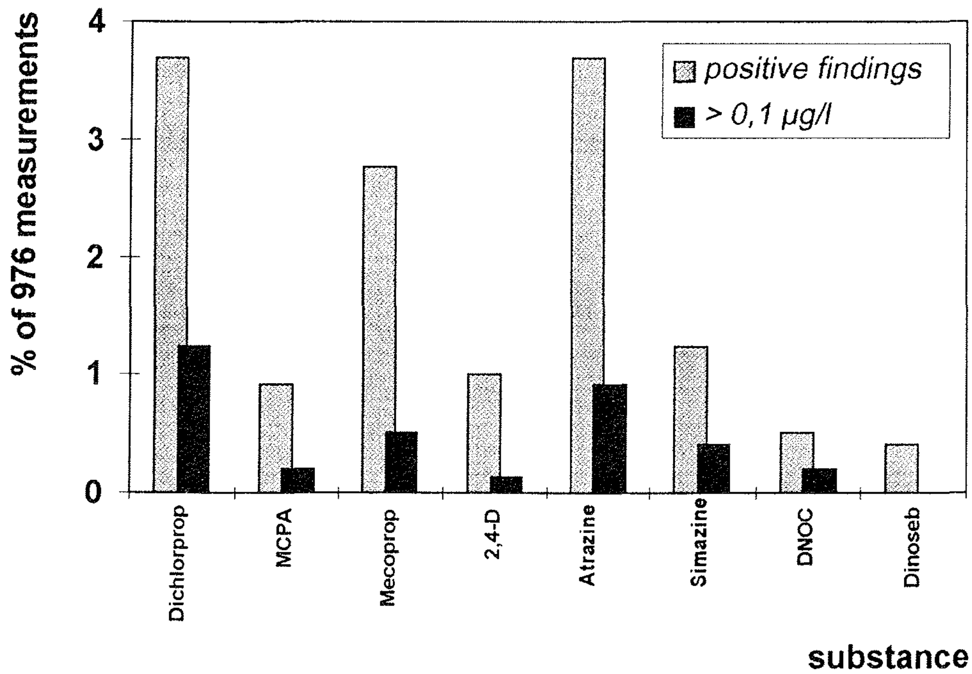


Fig. 2.10: Summary of findings of national monitoring programme for pesticides in groundwater (Miljø - og Energiministeriet, 1996)

The substances most commonly found were atrazine, dichlorprop, and mecoprop (found at 3.7%, 3.7% and 2.8% of measurement sites respectively). Concentrations above the limit value of 0.1 µg/l for drinking water were far less common (1.2%, 0.9%, and 0.5% of measurement sites respectively).

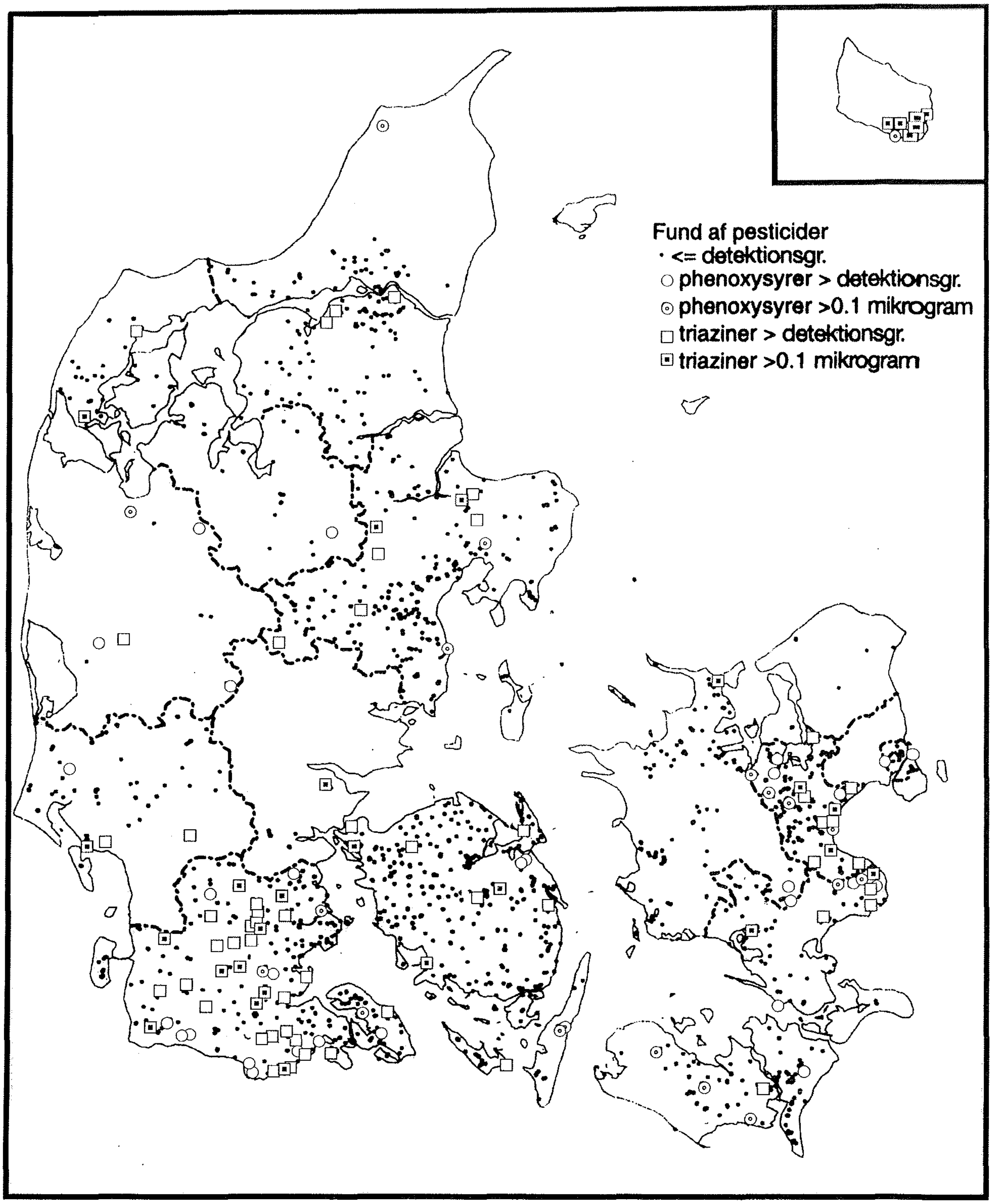


Fig. 2.11: Regional distribution of positive findings of triazine and phenoxy-carboxylic acid derivatives in groundwater in Denmark. (Miljø - og Energiministeriet, 1996)

Table 2.3: Frequencies of pesticide detections in groundwater (data from extended studies by the Ministry for the Environment and Energy)

Substance	No. of sites / wells tested	No. of positive findings	No. of findings > 0.1 µg/l	% of positive findings	% of findings < > 0.1 µg/l
Dichlorobenzamide, 2,6-	290	109	51	37.59	17.59
Atrazine, hydroxy-	63	20	10	31.75	15.87
Atrazine, desisopropyl-	552	113	29	20.47	5.25
Bentazon	552	89	4	16.12	0.72
Atrazine, desethyl-	551	84	26	15.25	4.72
Atrazine	586	47	7	8.02	1.19
Metamitron	369	22	0	5.96	0.00
Simazine	523	31	2	5.93	0.38
Pendimethalin	83	4	0	4.82	0.00
Dichlorprop	483	13	0	2.69	0.00
DNOC	483	13	0	2.69	0.00
Mecoprop	483	11	0	2.28	0.00
Isoproturon	447	9	2	2.01	0.45
MCPA	484	9	1	1.86	0.21
Dinoseb	524	9	4	1.72	0.76
Cyanazine	447	7	2	1.57	0.45
Hexazinone	523	8	3	1.53	0.57
Diuron	81	1	0	1.23	0.00
Terbuthylazine	488	6	0	1.23	0.00
Dichlorbenil	189	2	0	1.06	0.00
Metazachlor	326	3	0	0.92	0.00
D 2,4-	483	4	0	0.83	0.00
Dimethoate	409	2	0	0.49	0.00
Alachlor	326	0	0	0.00	0.00
Bromoxynil	83	0	0	0.00	0.00
Carbofuran	409	0	0	0.00	0.00
Chloridazon	43	0	0	0.00	0.00
Chlormethylphenol	43	0	0	0.00	0.00
CPP, 4-	30	0	0	0.00	0.00
DCPP, 2,6-	30	0	0	0.00	0.00
Dicamba	83	0	0	0.00	0.00
Dichlorophenol 2,4-	43	0	0	0.00	0.00
Fenpropimorph	43	0	0	0.00	0.00
Fluazifop-butyl	43	0	0	0.00	0.00
Ioxynil	83	0	0	0.00	0.00
Linuron	38	0	0	0.00	0.00
Methabenzthiazuron	43	0	0	0.00	0.00
Metribuzin	43	0	0	0.00	0.00
Phenmedipham	43	0	0	0.00	0.00
Pirimicarb	83	0	0	0.00	0.00
Pochloraz	43	0	0	0.00	0.00
Propazine	30	0	0	0.00	0.00
Propiconazole	83	0	0	0.00	0.00
Propyzamide	83	0	0	0.00	0.00
Triadimenol	83	0	0	0.00	0.00

The map (*Fig. 2.11*) shows the regional distribution of positive findings of triazine and phenoxycarboxylic acid derivatives in groundwater (with the exception of the county of Vejle where comparable data were not available at the time when the map was created. The supply of monitoring data from the counties of Viborg and Frederiksborg was low in comparison with other counties). The high frequency of positive findings in Bornholm are not representative since they are due to pesticide use at a certain known place. Two areas, namely South Jutland and Zealand, are clearly seen to have a particularly high frequency of positive findings. Ignoring differences between individual pesticides, it is seen that in the period 1989–1994 pesticides were found at 10% of measurement sites. At 3% of measurement sites the concentration of at least one pesticide was above the limit value for drinking water. The regional authorities and various individual research projects have not always limited the scope of their investigations to the eight pesticides included in the national monitoring programme; rather, up to 46 different agents have been considered in some cases. A summary of which pesticides were detected most commonly, and which not at all, in these studies, which were gathered together by the Danish Ministry for the Environment and Energy, is given in *Table 2.3* (*Miljø - og Energiministeriet, 1996*). One point that emerges clearly is that the pesticides included in the national monitoring programme, and in particular the metabolites of atrazine, are among those most commonly found in groundwater. Nevertheless, other substances such as 2,6-dichlorobenzamide, bentazone, metamitron, pendimethalin, and isoproturon are also commonly found.

Study results in South Jutland and Vejle (*Tab. 2.4*) suggest that limitation of the national monitoring programme to eight pesticides leads to underestimation groundwater pollution. Thus, the groundwater study performed by the South Jutland authority, which considered 18 pesticides and two metabolites, detected one or more pesticides in 75% of the wells monitored. Had it confined itself to the eight pesticides in the national monitoring programme it would have found positive results in only 15% of wells. A similar result was obtained by the Vejle authority, which considered 12 pesticides and four metabolites: 40% of measurement sites showed contamination with pesticides, whereas the eight pesticides included in the national monitoring programme were found in only 3% of samples. The South Jutland study also showed that groundwater near the surface (above 5–6 m) was highly polluted with pesticides (*Miljø - og Energiministeriet, 1996*).

Table 2.4: Summary of results from regional pesticide studies based on untreated-water wells and groundwater measurement sites (scope: the eight pesticides included in the national groundwater monitoring programme) (Miljø - og Energiministeriet, 1996)

Authority	No. of measurement sites and wells studied	No. of measurement sites with positive findings	% of measurement sites with positive findings	No. of measurement sites with PPP > 0.1 µg/l	% of measurement sites with PPP > 0.1 µg/l
Københavns og Frederiksberg komm.	75	21	28	6	8
København	270	63	23	6	2.2
Frederiksborg	146	2	1.4	0	0
Roskilde	261	33	13	6	2.3
Vestsjælland	244	11	4.5	10	4.1
Storstrøm	263	35	13	12	4.6
Bornholm	23	3	13	1	4.3
Fyn	560	30	5	7	1.3
Sønderjylland	495	82	16	22	4.4
Ribe	217	22	10	3	1.4
Vejle	246	15	6	17	6.9
Ringkøbing	143	7	5	5	3.5
Århus	510	19	4	4	0.8
Viborg	86	4	5		0
Nordjylland	399	19	5	6	1.5
Total	3700	351	9.6	88	2.4

Occurrence of pesticides in surface water

Between 1989 and 1991 the National Environmental Research Institute (NERI) performed studies on contamination of surface water with pesticides in three selected areas of Lolland, South Jutland, and Zealand (*Mogensen & Spliid, 1995*). Soil water, drainage water, and surface water were regularly tested for a selection of eleven pesticides (atrazine, simazine, MCPA, mecoprop, dichlorprop, 2,4-D, dinoseb, DNOC, bromoxynil, ioxynil, isoproturon), the amounts of which used were known. The number of positive findings and the pesticide levels were generally highest in the flowing water of the intensively exploited argilliferous catchment area of Lolland (particularly frequently found, and at high concentrations of 0.5 to 7.3 µg/l, were MCPA, 2,4-D, mecoprop, dichlorprop, bromoxynil, and ioxynil). The less intensively exploited sandy catchment area in South Jutland was found to be less polluted, the levels of pesticides here being higher in soil water than in flowing waters. Phenoxy herbicides were used most commonly, and were most frequently found, in South Jutland and on Lolland. The high levels of pesticides found in flowing waters as compared with drainage water and soil water suggest that contamination of surface water with pesticides may occur not just as a result of transport with groundwater, but also as a result of wind drift, runoff, and cleaning of application devices.

Reactions of authorities to contamination of water with pesticides

The presence of pesticide levels in excess of the limit values for drinking water can lead to temporary or permanent shutdown of the groundwater well concerned. Measures to purify untreated water are also undertaken in some cases. In all cases the health authorities are notified in order to determine whether there is a public health risk.

In addition, frequent detection of certain pesticides in groundwater and drinking water can lead to banning of the substances concerned (see section on registration of pesticides).

Principal areas of research

Up to now the national monitoring programme has investigated the presence in groundwater of eight selected pesticides. In addition to this there have been a number of extensive national and regional studies. Over the next few years the national monitoring programme is to be extended, one possible area of research being the biochemical metabolism of pesticides in the groundwater (*verbal communication from Walter Brüsch, Danmarks og Grønlands Geologiske Undersøgelse*).

2.4 Germany

Geographical situation

In terms of its soil types, morphology, geological characteristics, and climate, Germany can be divided into four major landscapes: the north German lowland, the central German highlands, the terraced landscape of the southwest, and the foothills of the Alps in the south. Annual precipitation is 500 to 700 mm in the north German lowland, 700 to 1500 mm in the central German highlands, and up to more than 2000 mm in the Alps.

Around 35% of the land surface is cultivated and 14% is used for grazing. Some 30% of the land surface is covered by forest, most of which is managed. Differences in land use correspond to differences in landscape. Prominent in northern Germany are grain cultivation (especially wheat and barley), fodder crops (e.g. maize), and, in certain regions, crops such as rape, potatoes, and sugar beet. Prominent in southern Germany are viniculture and fruitgrowing, while hops and sugar beet are intensively cultivated in some areas.

In Germany as a whole some 75% of drinking water is obtained from groundwater. The remainder is obtained directly or indirectly (as bank filtrate, water from dams in rivers, lakes, and valleys) from surface water (*Mull & Nordmeyer, 1994*).

Source of data

Responsibility for monitoring groundwater and surface water lies with the Federal States, while that for monitoring drinking water lies with local water suppliers, who forward their data to District Health Offices. It must be assumed that an enormous wealth of data is available. Nevertheless, the data as a whole have yet to be analyzed. The reports issued by the Federal States, for their part, contain only minor and incidental references to findings of pesticides in groundwater. An overview of pesticide levels in groundwater in Germany will be possible only when a large number of water quality reports have been brought together and analyzed.

The situation with regard to the presence of pesticides in surface water is somewhat clearer, as the Federal States publish regular reports on the quality of surface water. Joint reports on water quality in the large rivers (in particular the Rhine and the Elbe) are issued by the *Federal States* concerned. There also exists a wealth of detailed individual studies on the presence of pesticides in surface water. However, these have also yet to be brought together and analyzed as a whole.

With the exception of the Greenpeace report “Pesticides in Groundwater 1995”, which includes the results of a survey of District Health Offices, there are no up-to-date synoptic publications on the presence of pesticides in the raw water used by the water supply companies.

The *Federal States* and the water supply institutions supply statistical data on findings of pesticides in drinking water, groundwater, well-water, and surface water to the *Umweltbundesamt* (*UBA*) (Federal Office for the Environment). These include information on how many tests for pesticides in water were performed, which individual substances were tested for, how often these were detected, and how often the concentrations of these exceeded the limit value specified in the Drinking Water Ordinance. The essential content of these reports related to groundwater was kindly communicated to us by *Wolter* (Federal Office for the Environment). A list of available data on the occurrence of pesticides in German surface waters has recently been published by The Federal Office for the Environment *(Umweltbundesamt, 1996*). These data are also not aggregated and have to be investigated in further detail. The data comprise only mean concentrations in river water, the 90 % value and the maximum at a large number of stations along Germany´s major river systems.

Overall, the amount of information currently available on the presence of pesticides in groundwater in Germany is unsatisfactory. This situation may change with the publication — planned for 1997 — of the report of the *Länderarbeitsgemeinschaft Wasser* (LAWA) (Federal States Working Group on Water) on the presence of pesticides in groundwater.

Registration of pesticides

Responsibility for the registration of pesticides lies with the Federal Biological Institute in cooperation with the Federal Health Office and the Federal Office for the Environment. The registration procedure involves testing of the behaviour of the pesticide in the soil (degradation, mobility) and assessment of ecotoxicity on the basis of the NOEC (no-observed-effect concentration). It includes a number of steps involving laboratory studies, field studies, and computer models. Depending on the harmfulness and the probability of water-relevant effects of the substance, registration may be granted, in some cases with stipulations or limitations on use, or the application may be refused. In 1995 a total of 259 different pesticides (= 979 products) were on the market in Germany (*Fördergemeinschaft Integrierter Pflanzenbau, 1996*) (Society for the Promotion of

Integrated Plant Cultivation). Some 65% of registered pesticides are subject to stipulations and limitations on use (*Irmer et al., 1993*).

Registration may be revoked or limitations on use imposed if the pesticide concerned is subsequently found to have harmful effects on the environment. The most recent case of this is the prohibition of the use of diuron as a herbicide in the vicinity of railway tracks, a practice that was shown to lead to pollution of groundwater.

Detailed descriptions of the registration procedure and lists of the laws governing pesticides and water are given in *Mull & Nordmeyer (1994)* and in *Roth (1996)*.

Use of pesticides

According to the Federal Biological Institute, 14,834 t of herbicides, 7,698 t of fungicides, 4.006 t of insecticides, and 1,559 t of other pesticides (e.g. rodenticides) were sold in Germany in 1994. Sales of the pesticides registered by the Federal Biological Institute generally showed a slight decrease between 1988 and 1994. Only in 1991 could an increase be observed, as a result of the reunification of Germany.

Schmidt & Holzmann (1995) and *Schmidt (1996)* cite the following reasons for the decrease in the amount of pesticides used:

- Increasing application of the principles of integrated plant protection
- Tighter economic conditions (e.g. falling producer's prices, especially for grains)
- Development of new pesticides, particularly herbicides, with significantly higher efficacy (e.g. sulfonylurea derivatives)
- Development of devices for more effective application of pesticides

Minor fluctuations in amounts sold can also be due to year-to-year variation in climatic conditions. It is interesting to note that according to the *Industrieverband Agrar e.V (IVA, 1996)* (Federation of the Agricultural Industry) the amount of pesticides sold in Germany in 1995 rose by 18%, thus almost reaching the 1992 figure. Though this was partially due to a weather-related increase in the use of pesticides, in particular fungicides, it was also related to a fall in the ratio of set-aside land from 12% to 10%.

Pesticides are also used for non-agricultural purposes. In 1990, for example, some 200 to 300 t of herbicides were used in the vicinity of railway tracks and on roadsides, while household and garden use accounted for a further 717 t (*Umweltbundesamt, 1994b; IVA, 1995*). Though it is well known that incorrect use even of these amounts can cause considerable problems, the amounts concerned are minor compared to those used in agriculture.

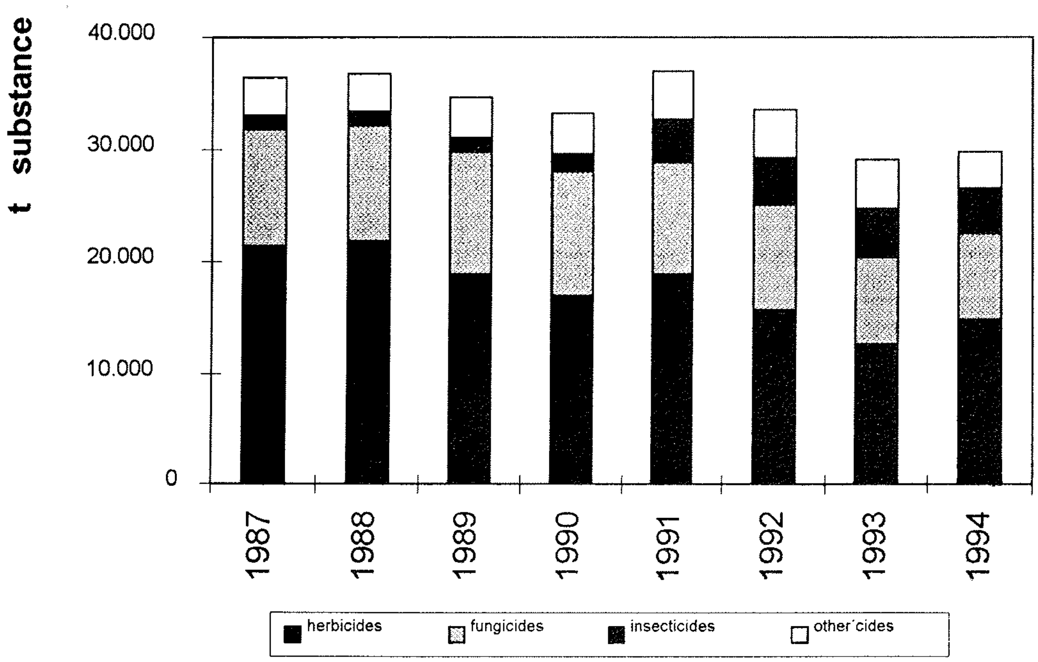


Fig. 2.12: Amounts of pesticides sold in Germany (data from Schmidt, 1996)

Occurrence of pesticides in water

The most important statistical data on the presence of pesticides in groundwater throughout Germany are those held by the Federal Office for the Environment (*UBA*) and those published in the report by Greenpeace. The *UBA*'s statistical data are to be published in the future. In order not to anticipate this publication, only a few basic facts can be reported here.

The *UBA*'s statistics relate to 25 substances and metabolites: atrazine, desethyl-atrazine, desisopropylatrazine, simazine, lindane, terbuthylazine, propazine, bromacil, 1,2-dichloropropane, chlorotoluron, isoproturon, ametryn, bentazone, metolachlor, mecoprop, methabenzthiazuron, diuron, dikegulac, metazachlor, dichlorprop, hexazinone, MCPA, diacetone-L-sorbose, dimethoate, and 2,4-D. The data collected annually by the *UBA* on the presence of pesticides in the environment come from some 10,000 analyses of surface water and groundwater. Not all analyses include all the pesticides listed above: some pesticides are subject of fewer than 100 analyses, whereas others are almost always measured.

As a generalization it can be stated that atrazine, desethylatrazine, simazine, terbuthylazine, chlortoluron, isoproturon, and diuron are found relatively frequently (> 10% of analyses) in groundwater and surface water. Terbuthylazine, chlortoluron, isoproturon, and diuron were found mostly in surface water, whereas simazine, atrazine, and desethylazine were found mostly in groundwater samples.

Nevertheless, as the findings that underlie them were not uniformly distributed throughout Germany, these data should not be used as a basis for generalizations regarding Germany as a whole *(pers. com. R. Wolter, UBA).*

A very suitable example of groundwater reports are these published by the State of Baden-Württemberg (*Landesanstalt für Umweltschutz Baden-Württemberg, 1996).* In these reports the pesticide findings are correlated with landuse (*table 2.5*). These data indicate clearly that occurrence of pesticides in water is not only caused by agriculture but also by housing and industrial settlements (e.g. bromacil, hexazinon, diuron).

Table 2.5: Pesticide findings in the groundwater of areas with different land use in the State of Baden-Württemberg (data from Landesanstalt für Umweltschutz Baden-Württemberg, 1996)

Substance	Total area (rd. 2200 wells)		Agriculture area (661 wells)		Industrial area (473 wells)		Housing area (448 wells)	
	% of positive findings	% of findings >0,1 µg/L	% of positive findings	% of findings >0,1 µg/L	% of positive findings	% of findings >0,1 µg/L	% of positive findings	% of findings >0,1 µg/L
Atrazine	28,2	4,7	29,7	7,9	29,2	4,7	28	3,4
Simazine	8	0,6	5,7	0,5	8,3	0,4	14,3	1,1
Terbutylazine	1,1	0,3	1,4	0,5	1,9	1,1	0,7	0
Desethylatrazine	34,6	8,7	38,1	13,2	32,8	6,8	28,6	8,3
Bromacil	4,7	3,0	1,5	0,2	7	5,9	7,4	4,5
Hexazinon	5,7	2,6	1,5	0,2	6,8	3,6	11,2	5,1
Diuron	2,4	0,9	0,9	0,2	3,4	1,7	4,0	1,6
Chlortoluron	0,5	0,1	0,2	0,2	1,3	0,2	0,9	0,2
Isoproturon	0,7	0,3	1,5	0,9	0,6	0,2	0,4	0
Linuron	0,4	0,1	0	0	1,3	0,4	0,2	0
Methabenz-thiazuron	0,3	0,1	0,2	0	0,6	0,2	0	0

In Baden-Württemberg the use of atrazine has been restricted since 1988, and banned since 1991. In spite of these measures there is no significant decrease of atrazine and desethylatrazine in the groundwater observable (figure 2.13). If anything, there has been a slight increase of desethylatrazine.

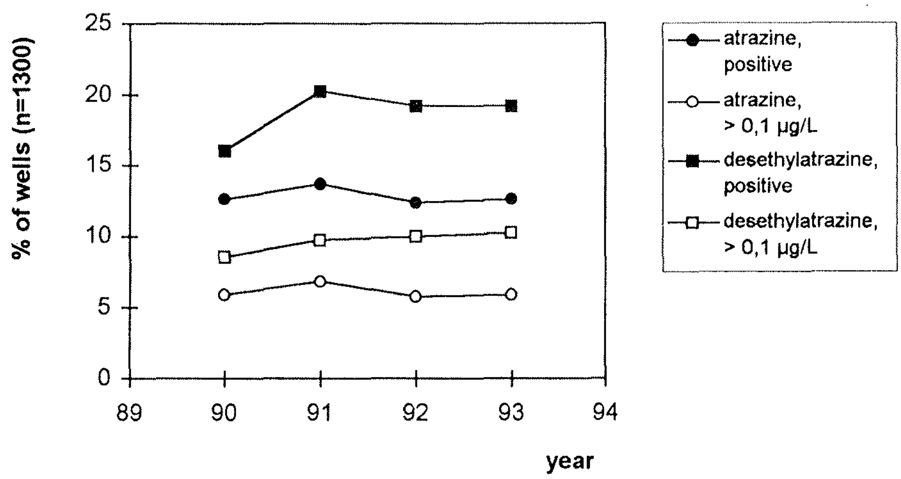


Fig. 2.13: Atrazine and desethylatrazine findings in Baden-Württemberg (data from Landesanstalt für Umweltschutz Baden-Württemberg, 1996)

Raw water and drinking water

The survey conducted by Greenpeace *(1995)* on the presence of pesticides in raw water used for producing drinking water (period: 1989–1994) drew a response from 424 of the more than 500 District Health Offices approached. It was found that the number of pesticides tested for in raw water varies greatly between Health Offices: some performed no analyses at all, whereas the Federal State of Hesse tested for 60 different substances.

Like other studies, this survey found that sites that test for a larger number of substances are more likely to detect at least one pesticide. Of all the substances whose presence in raw water was tested for, atrazine/desethylatrazine was found most commonly (12.5%), followed by simazine (5.1%) (*Table 2.6*). The proportion of analyses in which pesticide concentrations in excess of the limit value for drinking water were found was considerably smaller, e.g. only 2.9% even in the case of atrazine/desethylatrazine and 0.4% in that of simazine. Other pesticides were found with considerably less frequency. The third most common finding was "Others", a group comprising all pesticides tested for but not explicitly named.

Bearing in mind that atrazine has been prohibited since 1991, having previously been applied — against current good farming practice — in large quantities, these data do not provide evidence of any extensive current pollution of drinking water catchment areas with any individual substance that could be regarded as especially critical. It must nevertheless be borne in mind that not all District Health Offices responded to the Greenpeace survey.

In its report, Greenpeace *(1995)* also analyzed the positive findings of pesticides in terms of their geographical distribution. Unfortunately, the graphical presentation of the results of pesticide detection used in this analysis is so unfavourable that it is scarcely possible to derive any valid conclusions from the results. Nevertheless this study includes useful raw data as summarized in *table 2.6.*

Table 2.6: Summary of results of a survey of all District Health Offices on the presence of pesticides in raw water used by drinking water supply companies (data from Greenpeace, 1995)

Substance	No. of analyses	No. of positive findings	% of positive findings	No. of findings > 0.1 µg/l	% of findings > 0.1 µg/l
Atrazine / desethyl-atrazine	27,466	3,435	12.51	784	2.85
Simazine	26,050	1,335	5.12	93	0.36
Metazachlor	14,269	471	3.30	2	0.01
Metolachlor	11,812	387	3.28	0	0.00
Terbuthylazine	16,272	530	3.26	4	0.02
Bentazone	8,524	211	2.48	8	0.09
Bromacil	8,454	155	1.83	65	0.77
Lindane	8,015	133	1.66	1	0.01
Chlorotoluron	9,229	149	1.61	8	0.09
2,4-D	7,851	118	1.50	28	0.36
Isoproturon	10,932	161	1.47	4	0.04
1,2-dichloropropane	4,636	67	1.45	11	0.24
Diuron	8,710	119	1.37	25	0.29
Mecoprop-P	9,217	122	1.32	5	0.05
MCPA	8,138	88	1.08	1	0.01
Dimethoate	4,398	35	0.80	0	0.00
Dikegulac *	2,905	20	0.69	11	0.38
Parathion	5,923	38	0.64	0	0.00
Methabenzthiazon	7,446	40	0.54	1	0.01
Glyphosate	2,172	10	0.46	2	0.09
Others	22,477	874	3.89	141	0.63

* *possible sources: Vit. C product and use as regulator*

A study performed a few years ago found essentially the same pesticides to be relatively common contaminants of drinking water (*Zullei-Seibert, 1990*). This study analyzed the results of a 1990 survey of 780 water supply companies on the presence of pesticides in raw water and drinking water. At that time the pesticides and metabolites whose concentrations were most commonly found to exceed the limit value for drinking water were atrazine, desethylatrazine, chlorotoluron, dichlobenil, and 1,2-dichloropropane.

These data can be compared to monitoring data of the State of Baden-Württemberg *(Grundwasserdatenbank Wasserversorgung, 1996)*. The report contains analytical results from some 600 raw water extraction wells. Pesticide related information is only documented for atrazine, desethylatrazine, desisopropylatrazine, simazine, terbuthylazine, metolachlor, metazachlor, desethylterbuthylazine and propazine. Atrazine and desethylatrazine were found most frequently (20 % to 25 % of the wells) but rarely exceeded the drinking water standard (atrazine in 1 % and desethylatrazine in 4 % of the cases). There were also some findings of simazine (4 % findings, < 1 % in excess of the drinking water standard). The other pesticides were of minor interest.

Surface water

The nationwide report of the Federal Office for the Environment on pesticides in surface water contains data on 39 pesticides and metabolites (ametryn, atrazine, azinphos-ethyl, azinphos-methyl, bentazone, bromacil, chloridazon, chlortoluron, 2.4-dichlorphenoxy acetic acid, 1.2-dichlorpropane, dichlorprop, dichlorvos, dimethoat, diuron, a-endosulfan, b-endosulfan, fenitrothion, fenthion, α-HCH, β-HCH, δ-HCH, γ-HCH, hexazinon, isoproturon, linuron, malathion, MCPA, mecoprop, metazachlor, methabenzthiazuron, metolachlor, methabenzthiazuron, metolachlor, parathion-methyl, parathion-ethyl, prometryn, propazin, simazine, terbuthylazin, triazophos, trifluralin). The data are based on measurements carried out between 1982 and 1993.

The underlined substances were only seldomly detected in rivers. Atrazine, diuron and simazine are abundant in concentrations generally less than 0.1 µg/l. The annual maxima reached 0.1 to 1.0 µg/l. Chlortoluron is a widespread substance with mean concentrations below 0.1 µg/l, the maximum values varying between 1.0 - 2.0 µg/l. These higher values occurred in the late eighties, and decreased significantly in the early nineties. Dichlorprop was found above all in the rivers Nidda and Rhine. The annual maximum values were just slightly above the drinking water standard (0.1 - 0.3 µg/l). Dimethoat has been detected in the rivers Rhine and Elbe. The maximum values in the river Elbe reached 20 µg/l. In the early nineties the concentration dropped to 1 µg/l. The HCH-isomers are detected very frequently. The reason is a very low detection limit of chlorinated hydrocarbons. The content rarely exceeds 0.1 µg/l. Traces of isoproturon and mecoprop are very common in German rivers. Particularly the rivers Nidda, Main and Rhine have contents above 0.1 µg/l in certain sections. Terbuthylazine, metazachlor and metolachlor are only detected in a small section of the Rhine between the cities Mainz and Worms, where values above 0.1 µg/l are common.

There is a characteristic occurrence of pesticides in the river Elbe. The concentration of the pesticides parathion-methyl and prometryne decreased significantly after German reunification (1991).

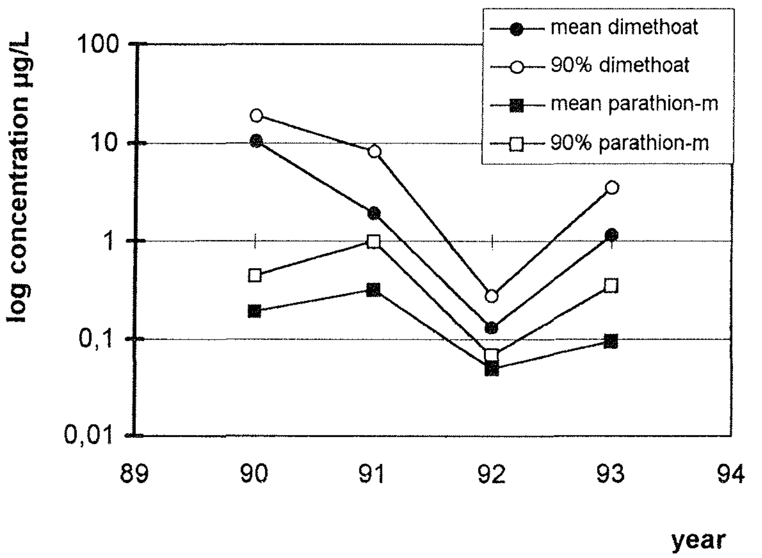


Fig. 2.14: *Pesticide concentration in the river Elbe between 1990 and 1993 (data from the Federal Office for the Environment, 1996, station Schnackenburg)*

According to report by the *Arbeitsgemeinschaft der Rhein- und Maaswasserwerke* (*RIWA, 1996*) (Association of Rhine and Meuse Waterworks), pesticides are among the problem substances present in the surface water of the Rhine and Meuse. This assessment was made because a large proportion of Dutch drinking water is obtained from the bank filtrate of these rivers. At its measuring station at Lobith (The Netherlands), *RIWA* tests the Rhine for the presence of a large number of pesticides (47 pesticides, including metabolites). In 1994 there was no case in which the mean level of any of the substances considered exceeded the limit value for drinking water. Levels of phenoxycarboxylic acid derivatives, urea derivatives, organophosphorus and sulphur compounds, and triazine derivatives exceeded the respective analytical detection limit on isolated occasions. It is noteworthy that isoproturon and atrazine levels in the Rhine occasionally exceeded the limit value for drinking water. Dinitrophenols and Nmethylcarbamates were not found at all. The concentration of isoproturon in the Rhine was found to vary greatly over time.

The water quality report of the State of Bremen for the year 1995 contains monitoring results of two smaller rivers (Blumenthaler Aue, Beckedorfer Becke) between 1992 and 1994. Of 111 water samplings, 78 were positive for atrazine and in six of these cases the concentration was above 0.1 µg/l. The fact that the frequency of positive results was higher shortly after the main application time suggests that atrazine-containing pesticides were still being used (*Freie Hansestadt Bremen, 1995*). It is also clear from the report that higher pesticide levels in the two rivers are generally related to precipitation and pesticide application times.

A comparative study of the Rems (Baden-Württemberg), Nidda (Hesse), and Ruhr (North Rhine-Westphalia) that took account of differences in land utilization and settlement showed markedly different levels of pesticide residues in these three rivers (*Seel et al., 1995*). The Nidda proved to be the most polluted in terms both of the frequency of positive findings and of the concentrations found. The greatest input into this river was apparently from the municipal sewage treatment works (entry of spray residues and runoff from contaminated paved surfaces via rainwater channels). The frequent finding of the total herbicide diuron in the Ruhr likewise suggests non-agricultural input via sewage treatment works and rainwater run-off. In general there appeared to be rapid superficial input of pesticides (from surface run-off, erosion, and sewage channels) into these rivers, commonly in association with precipitation.

From these three examples it can be seen that surface water, and hence both superficial run-off and groundwater, is always subject to input of pesticides. Superficial run-off of rainwater is of great importance in this regard. The pesticides do not only come from agriculture, but also from pesticide use in urban catchment areas (industry, gardens, etc.).

Reactions of authorities to contamination of water with pesticides

Official reactions to contamination of water with pesticides vary greatly and depend upon local circumstances. In general, action is required only when the limit values specified in the Drinking Water Directive are exceeded. Various measures are prescribed for such cases (*Heinz et al., 1995*):

- Closure of individual wells or of the entire water supply plant
- Mixture of polluted with clean water
- Switch to other or newly bored wells
- Purification (e.g. by means of charcoal filters).

Additional measures that can also be used preventively are:

- Designation and extension of water protection areas
- Acquisition of land in the catchment area of the well
- Change to less intensive cultivation in return for compensatory payments

Finally, the detection of various pesticides in water, especially groundwater, has led to changes in registration. Use of certain pesticides (dichloropropane, atrazine, and bromacil) has even been prohibited totally.

Research areas

The research areas are the same as those for the other countries already described.

2.5 France

Geographical Situation

France is the largest country in western Europe. Three main areas dominate its geographical mosaic: the low-lying and coastal areas, the semi-mountainous regions (Massif central, Vosges, Ardennes) and the mountain ranges (Pyrenees, Alps, Jura). Roughly speaking, the climatic zones also divide into three. The proximity to the sea of the flat areas in the west and north gives them a moderate maritime climate. Further inland, the temperature differences between summer and winter increase, and rainfall lessens. In the southeast, along the Mediterranean coast and in its hinterland, the climate is one of mild winters and hot, dry summers.

About a quarter of France's surface area is covered by forests, and another 60% are devoted to agriculture. Regional geographical differences affect the focus of local agriculture. Low-lying areas are strong on field crops. Examples include the Paris basin, France's corn belt, and the large-scale sugar beet areas of Nord-Pas de Calais and Picardy. Farmers in the semi-mountainous and mountain regions concentrate on livestock and fodder. Fruit and vegetable farming is largely irrigation-based.

Source of data

The main source of monitoring data is the 1996 study by the Ministries of the Environment and of Agriculture, Fisheries and Food (ME/MAFF). The results summarised here come from investigations in a number of different regions. The monitoring programme was led by local and/or regional agriculture and health authorities. The programme was based on a list of pesticides drawn up by an interministrial working group (agriculture, health and environment). The information below is drawn from the Brittany study, which contains a detailed description of the monitoring strategy. A detailed study of pesticides occurring in groundwater in the central region of France was published by *GREPPES (1995).* The results of this two-years groundwater monitoring programme are interpreted in detail in its report. A comprehensive summary is presented here. The additional data available on triazine residues (atrazine plus metabolites, simazine) also mainly apply to groundwater *(Grigier, 1995)*. These data are from precisely described individual recording sites.

Registration of pesticides

About 400 substances have French product licences, one of the largest numbers in any EU Member State. Less than one quarter of these pesticides have been the subject of monitoring programmes *(Zullei-Seibert, 1996).*

Use of pesticides

In 1991, 100,000 tonnes of pesticides were used in France. Fungicides accounted for 58% of this total, and herbicides for 35%. The remaining 7% were composed of insecticides and other pesticides. In 1995, less than 90,000 tonnes of pesticides were applied. With one seventh of the total EU application volume, French farmers are among the largest pesticide consumers *(Brouwer et al., 1994)*. Italy and the Netherlands, however, use more pesticides per unit area *(Metayer, unpublished data)*. Usage of the triazines atrazine and simazine roughly halved between 1985 and 1992 *(Grigier, 1995)*.

Brittany is one of the most intensively farmed areas for the processing industry. About 25% of the arable area is devoted to maize for animal feed. Herbicide use in 1991 was approximately as follows: 43% atrazine, 29% dinoterb, 7.5% bentazone, 7.5% pariad, 6.5 % alachlor and 6.5 % others *(DRAF)*. Only about 1% of herbicides is used for purposes other than agriculture or forestry, mainly for roads and pavements. In Brittany, the main pesticides used for this application are aminotriazole, or amitrole (25.5%), diuron (18.4%), simazine (17.7%) and atrazine (11.4%) *(Ministère de l'Environment & Ministère de l'Agriculture, de la Pèche et de l'Alimentation 1996)*.

In the central basin region of France about 5600 tons of pesticides per year (data from 1992 and 1993) were used for agricultural purposes on about 1,750,000 ha intensively farmed land (*GREPPES, 1995*). Less than one percent (44,464 kg) is applied by other users, like local authorities and the railways. The most important pesticide group are the fungicides with 66 %, which are primarily sprayed in vineyards, followed by the herbicides (28 %) and the insecticides (5%).

Occurrence of pesticides in water

Its geology (impermeable hard rock) makes Brittany a sensitive area. Substances entering surface water reach the sea within a matter of days. 40% of drinking water supplies come from reservoirs. The Brittany study results thus refer only to surface water.

In the central basin region of France groundwater is more important for drinking water supply. A variety of 45 different catchment areas was monitored in order to obtain a survey of typical hydrogeological and agricultural situations.

Surface water

1990 saw the start of investigations in five Breton rivers (Arguenon, Aven, Oust, Seiche and Vilaine). These revealed traces of lindane, atrazine, simazine and carbofurane. In three rivers, carbofurane only appeared in certain samples, whereas the remaining substances were present throughout. 92% of samples showed atrazine levels above 0.1 µg/l. Half the probes contained more than 2 µg/l. 80% of samples exceeded the combined limit value of 0.5 µg/l.

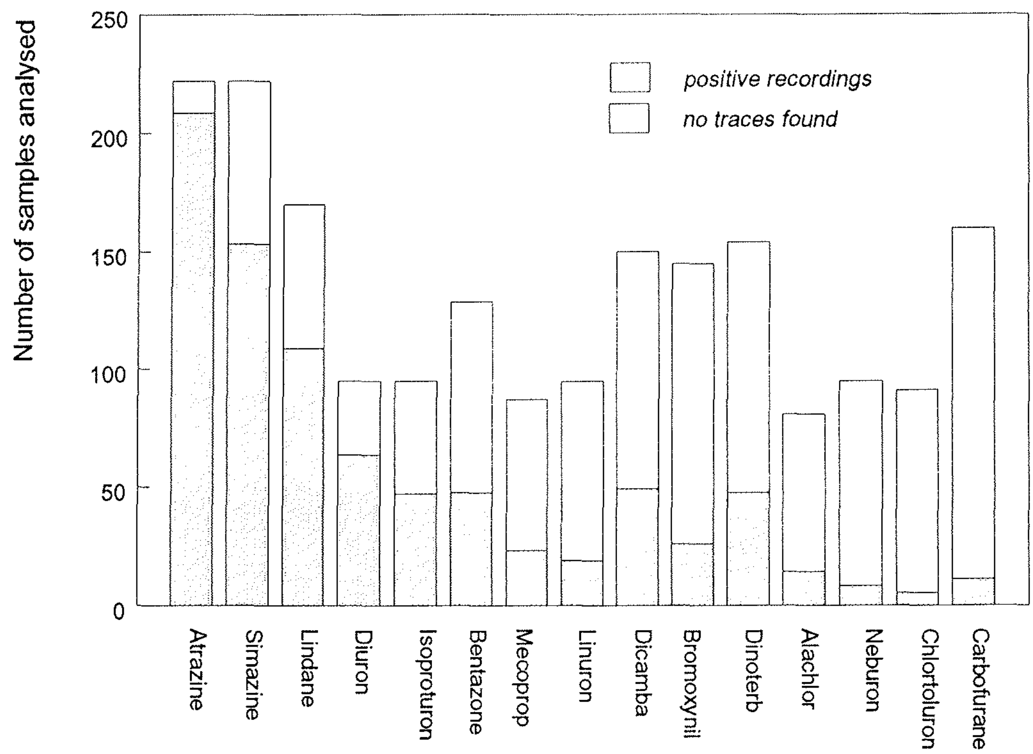


Fig. 2.15 Pesticide measurements in five Breton rivers, 1990 to 1995 (Data from Ministere de l´Environment & Ministère de l´Agriculture, de la Pèche et de l`Alimentation 1996)

In 1991, analysts extended the scope of their investigations to cover 55 substances and metabolites. 20 of these were detected. *Figure 2.15* shows the proportion of positive probes to total sampling for the 15 most important substances between 1990 and 1995.

The data provide a good overview of the occurrence of pesticides in water in Brittany. Analysis shows that residues are not only caused by substances in agricultural use (e.g. atrazine, bentazone and alachlor). Pesticides used for other purposes (e.g. simazine, diuron) also play a role, despite their relatively small share of total application volumes. There was a noticeable correlation between run-off and high concentrations in river water. In the areas monitored, the triazines atrazine and simazine caused the greatest amounts of residues, followed by lindane. Phenylureas head the list of the remaining substances found.

Groundwater

About 60 % of French drinking water comes from groundwater, for which there is no national monitoring programme.

The groundwater systems react completely differently to surface water. Whereas in surface water the pesticides are detected soon after their application in the field, the groundwater system reacts much more slowly. This is because water residence time in the subsurface from rainfall to groundwater extraction is in the order of decades and for deep groundwater even of hundreds and thousands of years. This means that in most cases the pesticides in groundwater today were applied a very long time ago. Depending on the age of the groundwater, the spectrum of pesticides will vary. These hydrological differences have to be borne in mind, except in the cases of substances reaching groundwater via preferential flow pathways.

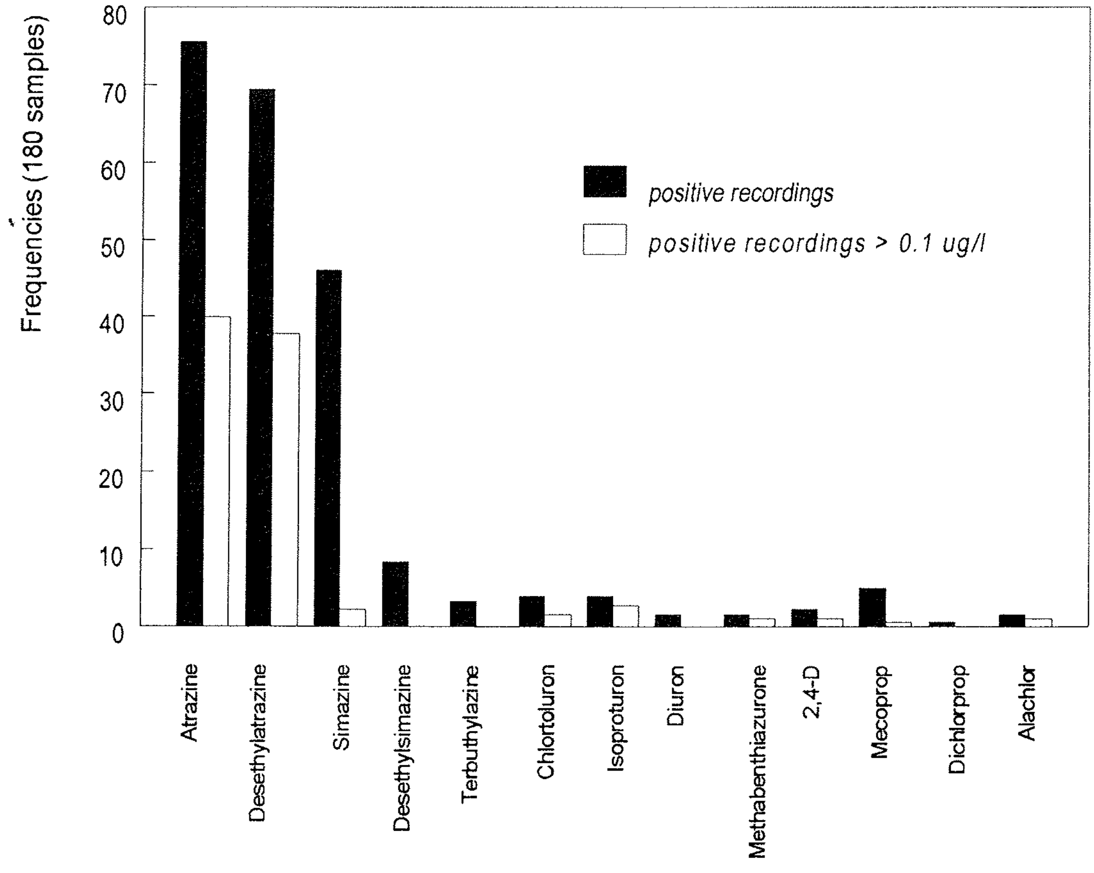


Fig. 2.16: Major pesticides: frequencies of positive recordings and recordings exceeding the drinking water limit in the groundwater of the central basin region (data from GREPPES, 1995).

A regional groundwater monitoring programme for the central basin region was conducted in 1992 and 1993. 45 groundwater captures were sampled twice a year. The report from *GREPPES (1995*) provides very detailed insights into the data base. The results are correlated to the regional hydrogeology and agriculture. The data presented as frequencies of positive probes (> 0.1 µg/l) (*Figure 2.16)* indicate that the triazines and their metabolites are the pesticides most frequently found in groundwater, followed by the phenylurea derivates and the phenoxycarboxylic acids. Atrazine as well as desethylatrazine are frequently non-compliant with the drinking water limit.

Atrazine and desethylatrazine were detected at concentrations of up to 1 and 1.1 µg/l respectively. These levels were exceeded by isoproturon (2 µg/l), whereas the other maximum concentrations were significantly lower. In only three out of 45 captures were no pesticide residues detected. In 14 captures the residues were below the standard of 0.1 µg/l. 28 had one or more positive findings above the drinking water limit.

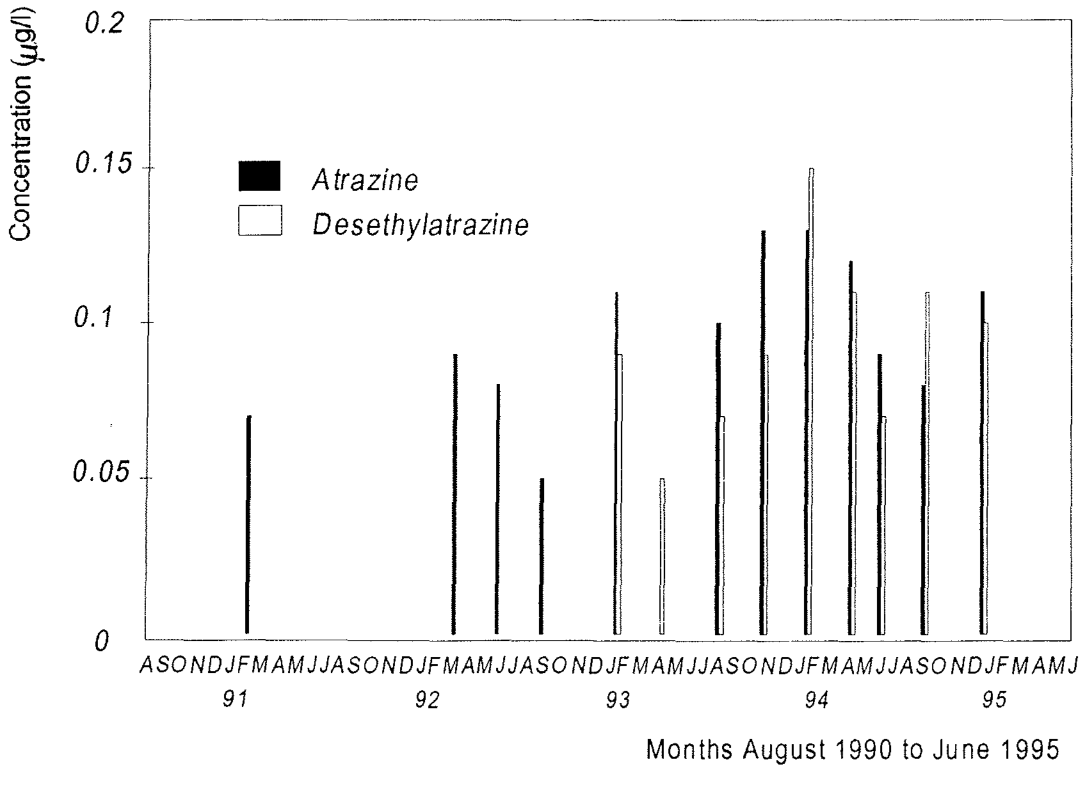


Fig. 2.17: Development of atrazine and desethylatrazine content in groundwater over a period of five years at a typical groundwater measuring site (Example from Grigier, 1995).

Grigier (1995) has reported in detail on the regional occurrence of atrazine, desethylatrazine and simazine in ground- and surface water. He also comes to the conclusion that groundwater in France's largest natural reservoirs, the sediment basins, is contaminated by triazines throughout. Concentrations of these substances are close to the drinking water limit value. At such low levels, analytical error can be expected to be about 20%. *Figure 2.17* shows one example from Grigier´s data pool. It presents a time series of samples over a period of five years. The measuring site in Drome includes alluvial terrace sediment described as a well permeable coarse sand. When occurring in groundwater, atrazine is typically accompanied by metabolites. Desethylatrazine is present here at levels comparable to its parent compound.

Reactions of authorities to contamination of water with pesticides

Pesticide-testing in France starts with enzymatic methods. Positive probes are then checked chromatographically. The form and intensity of pesticide checks is designed to match the size of population drawing on a particular water supply.

Van Haasteren & van den Berg (1993) recommend the following approach to water pollution:

- At atrazine levels over 2 µg/l and simazine concentrations above 17 µg/l, water should be declared "unfit for use as a source of drinking water."
- Consumers should be informed if the limit value of 0.1 µg/l is exceeded.
- This should then be followed by intensified checks,
- a search for the source of contamination, and
- instigation of a clean-up programme.

The stepwise transition of single case analysis as described above fits into the concept of applying the drinking water limit as a real test value. So in France, some pesticide applications are reduced regionally to avoid further significant water pollution.

3. Conclusions and outlook

The final chapter of this study offers a summary assessment of the findings in the individual countries featured above. The data have to be evaluated according to the monitoring strategies and the interpretation of monitoring results. Regional aspects in the countries have also to be considered. Some general statements about the "pesticide pollution problem" are made with reference to our data. Finally, possible future approaches to minimizing pesticide residues in water are considered.

3.1 Summary assessment of pesticide residues in water

The data presented in this study were extracted from official reports. In most cases the monitoring results are evaluated using the 0.1 µg/l drinking water standard value. Toxicological aspects are not discussed, and so conclusions on the real danger of the pesticide residues in water cannot be deduced here.

An overall judgement of the present situation focuses on the following questions:

- How reliable are the different data presented for individual countries, given the monitoring strategies and data interpretation in the reports?
- To what extent are pesticide residues found in surface water in the different countries, and which major processes govern the occurrence of pesticide residues in surface water?
- To what extent do pesticides occur in groundwater, how does this correlate to regional agriculture and geography, and why?
- Which problems have to be discussed in relation to pesticide residues in raw water for drinking water supplies exceeding the drinking water standard of 0.1 µg/l?

Reliability of data

The data presented here were taken from very different data bases. Differences in data quality prompt the question of reliability. No evaluation of analytical is possible, because the analytical methods are not evaluated statistically. In most of the summarising reports, a short description of the analytical procedure is incorporated and in some cases the corresponding detection limits are given. These detection limits indicate quite different technical facilities. Whereas in Denmark, analytical methods seem to be highly developed, in some other countries, e.g. Spain, pesticide monitoring is hanpered by technical problems. For this reason, the data available for Spain are unreliable (*pers. com. Prof. Candela, Barcelona*) and were not interpreted here. Investigation of pesticide residues in water requires reliable sampling methods as well as accurate analytical methods and reliable confirmation techniques. Above all it is necessary to quantify analytical errors and give standard deviations for the measured concentrations. Options for checking the reliability of analytical data are presented and discussed by *Häfner (1994).*

Monitoring strategies differ considerably between EU countries. In Denmark, for example, there is a national monitoring programm which covers numerous measuring points all over the country. In France regional studies focused on representative sampling points. Assessment of a monitoring strategy requires knowledge of ist geographical scope and the precise type of water studied. A huge data base including all types of water exists for the UK and the Netherlands, but the most heterogeneous data pool exists in Germany. In order to obtain reliable and comparable information about the development of water quality in general and with regard to pesticide residues, harmonised monitoring targets and concepts are required for the EU countries. Considerable know-how in this field already exists in Europe, which should be applied for this purpose.

A further problem occurring during data analysis from different sources is that the results are summarised in different ways. Official reports often contain statistical overviews of residue data with no indication of regional distribution or developments over time. The extent of findings is not stated clearly and it cannot be deduced whether water is really endangered. In the final reports from France, pesticide data are presented in a complex form. The choice of pesticides measured is explained in detail for the agricultural and non-agricultural usages. The sampling results are given for each site and time. Regional data are presented in distribution patterns, and the main features are summarised and evaluated afterwards. In our opinion, the data base for two regions in France is really reliable (except for analytical errors, which are not mentioned), and can serve as a good example.

Surface water

Nearly all of the pesticide measurements from surface, ground- or raw water are evaluated on the basis of the 0.1 µg/l limit value for drinking water, presenting the measurements above and below this value. Sometimes maximum concentration values are also given, mostly without any additional statistics. The data presented above show that pesticide residues in surface water occur commonly in Great Britain, the Netherlands, France and Germany and, to a lesser degree, also in Denmark.

There is a large spectrum of traceable substances: the number rises in line with the scope of the monitoring programme. There is an extremely close correlation between the very frequent use of a substance and its occurrence in water. The same is true of high application amounts. Even when only a small share of a product's sales are non-agricultural, use as a blanket herbicide means high doses (atrazine up to 20 kg/ha), which are reflected in prominent occurrence in water. Two groups of substances are therefore found in drainage waterways: those used with preference by local farmers, and those applied at high amounts. This is, however, not the case with fungicides, which are used in large numbers for example in the Netherlands and France. Two explanations for this seem plausible: 1. The tests only covered a limited number of fungicides, and 2. Application methods during the vegetation period inhibit passage into water. A correlation has also been demonstrated between substance concentrations and water transport volumes. This suggests an increase in water entry following heavy rainfall. Examination of the substances predominantly involved reveals a similar spectrum in Great Britain, the Netherlands, France (Brittany) and Germany. In surface water, the most frequently occurring pesticides by number are triazine, phenylurea and phenoxycarbolic acid herbicides. This suggests at first sight that substances' properties have a major influence on their occurrence in water. Closer investigation of surface water data, however, leads to a different conclusion. The herbicide groups mentioned all have considerable shares of the maize, long-term crops, cereals and blanket weedkiller markets. Not only the properties of the substance itself are responsible for residues in water but also widespread use and high intensity of application. Thus it can be deduced that a ban on single substances does not avoid further occurrence of pesticides in surface water.

Most readings for surface water are considerably above the 0.1 µg/l limit values. This is a useful valve for evaluating raw water. The question arises whether this value is valid for making a risk assessment for surface water in general. In some countries other values are applied for surface water (the Netherlands, United Kingdom). These vary depending on the substances` ecotoxicological impact. There is still a lot of scientific work to be done to develop reasonable limits for surface water which is not used for drinking water supply. It has to be stated that the use of pesticides in water catchments always results in the occurrence of the pesticides in the water, because the surface water system is highly vulnerable and reacts very fast. On the other hand the "memory effect" is relatively low so that a reduction of pesticide application at once results in decreasing concentration levels in the water.

Groundwater

Groundwater presents a somewhat different picture. The concentrations are lower, and normally exceed the limit value of 0.1 µg/l considerably less often (e.g. Denmark). The spectrum of substances found is also much more limited. On the other hand, an increase in analysis tends to generate more findings; notably fewer substances have been analysed in groundwater.

Atrazine and its metabolites still are the most abundant pesticides in groundwater. This is because overall, the groundwater system reacts much more slowly to outward circumstances than does surface water. The first determining factor is the top soil layer. The Dutch monitoring results show a close relationship between positive findings and the distance of the groundwater surface from the treated field. In the French groundwater study pronounced pesticide occurrence in groundwater was limited to free vulnerable aquifers. Thus the hydrogeological situation is one of the most important regional characteristics. Mid-term, the problem remains of contamination from substances no longer on the market or subject to restrictions. The problem of "inherited pollution" is illustrated by the rising atrazine levels seen in groundwater (in contrast to surface water) between 1992 and 1995. In addition, groundwater shows noticeable concentrations of atrazine's polar metabolites, which play a much smaller role in surface water. Farmers used atrazine over many years at high volumes, which is likely to have left behind a soil pool. The age of groundwater determines its impact as well. So a less pronounced application, e.g. according to Good Agricultural Practise, will lead to a decrease of concentration levels in several years. In the meantime, other substances could play a more important role, e.g. the urea derivates.

Other sporadic cases of pollution probably come from non-agricultural use (e.g. railways) or inappropriate disposal. These sources lead to direct impact and relatively high concentrations. The very low levels of a whole series of pesticides are likely to stem from "preferential flow" processes. This way pesticides might reach groundwater in a very short time with relatively high concentrations, which are diluted by mixing processes with the groundwater.

It can be said in summary that the groundwater system is affected by a range of factors and processes. Pesticides´ characteristics, as well as climatic and geological features play a stronger role than in the case of surface water. The time scale of impact as well as of possible decrease in residues in most cases extends over decades. For a detailed report on the processes involved, see the German-language report by *Matthess et al., 1995.*

Drinking water supply

The relevance to drinking water supply of the pollution scenario described above depends on the water category used. A very good overview of the water volumes of interest to European countries in this context is given by *Zullei-Seibert (1996).*

Of the countries studied in this report, the Netherlands face the greatest pesticide related problems. This is the result of a whole number of factors in combination. The Dutch farm intensively, using Europe's heaviest pesticide volumes per unit area. A very large percentage of Netherlands drinking water comes from surface water. A lot of the groundwater is close to the surface and therefore relatively heavily polluted. If the conventional form of water use is to continue, new preventive measures and drinking water processing techniques are required. The authorities must develop their own yardsticks, as will soon be fully the case in the Netherlands.

Countries which can use a large percentage of groundwater as unprocessed water (Denmark, Germany) face considerably fewer problem with their drinking water supplies. Nonetheless, it is frequently precisely these countries which employ stricter methods like product bans or refusal to renew registration, combined with compulsory well-closures. Product bans do not affect pollution short-term, because the groundwater system reacts relatively slowly. Long-term, mere substitution of one substance for another probably only shifts the problem, unless accompanied by other aspects of Good Agricultural Practice. In *Walker et al., 1995*, Seiler has neatly shown how use of atrazine at lower application volumes reduces residues in the water. However, use of another pesticide like terbuthylazine (its substitute in Germany), at similar volumes to those employed for atrazine before the ban, would lead to a similarly high impact. This example clearly demonstrates that a substance's properties are of only secondary importance for pesticide occurrence. The decisive factors are the volume and intensity of application.

Given this, it seems necessary to define levels at which pesticide occurrence in water has to be tolerated. In Denmark and Germany, about two percent of the groundwater samples investigated were non-compliant with the drinking water limit. This value is relatively low compared to the Netherlands (taking into account that the data base is not that reliable) or the French central basin region. Problems for drinking water supply can arise mainly for the small distributors, because the facilities for water treatment are expensive. Violation of the drinking water standard should not lead to the closure of waterworks, but to detailed assessment of the specific situation and appropriate information to water consumers.

3.2 Recommendations for the future

Preventive measures

The most important long-term method for reducing pesticide water pollution is the reduction and improvement of their use.

"Political measures" like the Danish pesticide tax aim to reduce application amounts.

Good Agricultural Practice now includes a number of further measures to the same end. GAP usage recommendations are based on the principles of integrated farming. For example: Pesticides should only be used when pests are present at above a given level, and application volumes should be kept to a minimum. Farmers should also take local soil conditions into account. A major contribution to surface water quality is abstention from the treatment of riverbanks. The most important question is site-specific farming. Very exposed sites should not be used extensively, fertilizers and pesticides should not be applied. Another important aspect is precision dosing. Appropriate technology helps to reduce diffuse contamination, e.g. via wind drift. In combination with measures like crop rotation and agricultural de-intensification on exposed sites, this can lead to a considerable reduction in water pollution. Correct disposal of spray residues is also essential.

Expert systems and other models now enable forecasting of a whole range of scenarios. Optimum application volumes can be calculated, as can the necessary size of pesticide-free zones. The example of bentazone shows that such forecasts can now support prediction of a particular substance's threat to water. These models can thus be used both for registration purposes and for designing pesticide monitoring programmes.

The pesticide industry has for some time been developing a highly active substance type which can be applied at considerably lower volumes (multiples of 10 g/ha). First results for sulfonylurea herbicides suggest that this is a promising way to reduce usage. Another practical purpose is the reduction of biologically inactive isomers or analogues in the trade product.

Monitoring strategies

The available data refer to an ample number of monitoring strategies. A particularly carefully targeted example is the Brittany study. Before establishing the spectrum of substances to be monitored, the programme's organisers conducted a detailed survey of pesticide use in the region. Monitoring should ideally include testing for all pesticides conceivably present. Actual findings depend on the substance spectrum analysed. However, the effort involved is enormous, so that it is prudent to limit the region for investigation. Solid conclusions on nationwide pollution by particular pesticides require a central monitoring programme for a set spectrum of chemicals. Search for a broad spectrum makes such a project very expensive, but still provides reliable data. The timing of sampling activities also plays an important role, at least in the case of surface water. When examining maximum passage into water, it is perfectly legitimate to measure levels soon after application, if possible following heavy rain. In such cases, it should always be stressed that the findings are short-term values. The most productive approach is that of sampling over time. Material transport provides a clearer picture of overall water pollution than does a specific concentration measurement. On the other hand, short-term peaks can be of eminent importance in relation to use as unprocessed water. No major short-term changes are to be expected in groundwater. Samples can be taken at considerably longer intervals.

A central problem is the interpretation and evaluation of the data. Data should not be over-summarised, for example when dealing with findings in excess of standard values. It is necessary to reveal correlations between findings and regional aspects as well as usage. An interesting alternative to conventional monitoring practice would be an assessment on the basis of "negative" probes. This might reveal alternative substances probably otherwise not detectable at the same application intensity. "Good Monitoring Practise" should be developed with experts from different fields, like agriculture, hydrogeology, ecology, water economy, industry and toxicology.

Research requirements

Cases of water pollution led to a rapid increase in related research. A review of the recent literature shows the considerable body of knowledge now available on the subject of crop protection products and water. There are countless individual studies of substances' behaviour in water and soil. Field case-studies have also been published. The public pesticide debate has thus accelerated some positive developments. There remain numerous major gaps in our knowledge and understanding of the behaviour of pesticides and their metabolites in the environment, and their impact on the ecological system.

Topics of relevant research include:

- transport and degradation behaviour of metabolites
- the role of bound residues
- the mobility of humic substance-pesticide associates (carrier function of humic substances)
- groundwater age and pesticide occurrence

Nonetheless, present knowledge allows the development of appropriate practical measures. Happily, the various groups involved within each EU Member State are already in discussion with each other.

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APPENDIX: Legal background

United Kingdom

Use of pesticides in the UK is governed by a number of laws, in particular Part III of the 1985 Food and Environment Protection Act (FEPA) and the 1986 Control of Pesticide Regulations (COPR). The legal stipulations governing control of water pollution and protection of water supplies are laid down in the 1991 Water Resources Act and are applicable to all inland and coastal waters and to groundwater. This Act establishes the National Rivers Authority (NRA) as the responsible body for ensuring adherence to the various regulations governing water protection and prevention of water pollution in England and Wales. By contrast, compliance with EU quality requirements for drinking water is the responsibility of the water supply companies.

The Netherlands

Pesticide regulation began early in the Netherlands, with the 1962 Pesticides Act. This was followed by further legislation aimed at limiting environmental pollution (Surface Water Pollution Act 1969, Drinking Water Decree 1984, Soil Protection Act 1986 and Chemical Substances Act 1987). The Pesticide Act only permits use of plant protection products (PPP) which pose no risk to drinking water. The Drinking Water Decree corresponds to the EEC Directive. The Dutch aim is for all drinking water sources to meet the requirements on PPP content.

A "maximum risk tolerance level" has been set for a number of PPP. This "Maximaal Toelaatbar Risiconiveau" (MTR) is designed to protect surface water. Sub-MTR PPP-levels cause no harm to 95% of species present. The MTRs are subject to constant revision in the light of ongoing toxicological research. In the case of those PPP lacking an MTR, the National Institute for Inland Water Management and Waste Water Treatment (RIZA) applies "indicative test values", so-called i-MTRs. All these tolerance levels are based on the available toxicological data. They therefore vary between PPP. For example: the MTR for the organophosphate mevinphos is only 0.00016 µg/l, whereas the phenoxycarbolic acid MCPA is permissible at levels up to 250 µg/l. This represents a difference of more than 10^6.

Denmark

The registration of plant protection products (PPPs) is governed by the 1984 "Act on Chemical Substances and Products".

Water protection is governed by a number of laws. The 1989 "Environmental Protection Act" prohibits all use of liquids or solids that could result in groundwater pollution. In order to further improve groundwater protection, local authorities are also empowered to designate water protection zones.

The regulations governing the quality of drinking water, which are laid down in the 1980 "Statutory Order on Quality Demands for Surface Water Inteded for Drinking Water" and the 1988 "Statutory Order on Water Quality and Inspection of Water Supply Plants", are based on the EU directive and thus specify a limit value of 0.1 µg/l for individual PPPs and 0.5 µg/l for total PPPs.

Germany

The central law governing the use of plant protection products (PPPs) is the 1986 Plant Protection Law. This makes the Federal Biological Institute responsible for the registration of PPPs. These are registered only if they have no harmful effects on humans or the environment. The 1992 Plant Protection Use Ordinance specifies which PPPs may be used only with restrictions, or not at all, and which PPPs may not be used within water protection areas.

The legal possibility of designating water protection areas is created by the 1986 Water Management Law and is used mostly to protect public water supplies. The Water Management Law also empowers the German Federal States to draw up management plans for surface water and groundwater. These may contain target levels of environmentally relevant substances — including PPPs — in water. The International Commission for the Protection of the Rhine (*IKSR*) and the Federal/*Land* joint working group on "Dangerous substances – quality targets for surface water" (BLAK-QZ) have now published the first target levels for plant protection agents (in the case of the *IKSR*, for 18 pesticides); these relate to different objects to be protected (*IKSR, 1992; Markard, 1992*). In the case of some PPPs the target levels specified for the protection of the "aquatic environment" (in many cases 0.001 µg/l) are considerably lower than the limit values stipulated in the Drinking Water Ordinance.

The EC Drinking Water Directive (80/778/EEC), which has been incorporated into German national law (1986 Drinking Water Ordinance), specifies limit values for concentrations of plant protection agents in drinking water, namely 0.1 µg/l for individual agents and 0.5 µg/l for the total concentration of all agents. The Drinking Water Ordinance permits deviations from these values for limited periods provided that any risk to human health is excluded and drinking water cannot be supplied by any other means.

France

PPP registration in France is governed by the 1943 Pesticides Act. The procedures follow the EC Directives and European Council's "Pesticides" brochure (7th edition). Drinking water regulations appear in § L19 et seq. of the 1989 Health Code. In addition to the EU limit values for drinking water (0.1 µg/l for individual substances and 0.5 µg/l for the overall total of pesticides and metabolites), France has set special limits for aldrin and dieldrin (0.03 µg/l) and for hexachlorbenzol (0.01 µg/l). A 1964 Regulation and a 1989 Decree lay down protection measures for the drinking water catchment areas.

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