

*TNO-report*

R 91/219

**CALCULATION OF THE ATMOSPHERIC  
DEPOSITION OF 29 CONTAMINANTS TO  
THE RHINE CATCHMENT AREA**

**Authors : Drs. A.C. Baart  
Ir. H.S.M.A. Diederer**

**Date : 29 October 1991**

**Order no. : 21447**

**Sponsor : IWAD (Interministerial  
Working group for  
Atmospheric Deposition)**

**With contributions from:  
L.Th. de Leu, Ing. C. Veldt**

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## SUMMARY

In this study the atmospheric deposition of 29 contaminants on the Rhine catchment area and on the Dutch part of this area have been calculated. The contaminants consist of heavy metals, chlorinated hydrocarbons, benzene, PAH, PCB, pesticides and nitrogen. Additionally the atmospheric deposition of six pesticides and nickel on the Netherlands is calculated; nickel is included as an erratum to Warmenhoven (1989a).

The atmospheric inputs have been calculated on basis of European emissions by means of a long range transport model with homogeneous meteorology and deposition characteristics over the whole area of study. The model calculated deposition fields over the receptor area, total deposition to the Rhine catchment area, to the Dutch part of the Rhine catchment area and to the Netherlands, and relative contributions of surrounding countries to the atmospheric deposition.

Atmospheric emissions from all European countries have been taken into account. The values taken, are based on recent research or on information on industrial and agricultural activity within the relevant countries. The reference year is 1985. A distinction has been made between emissions from the former West and East-Germany. Where possible, data provided in the Kd group of the IKSR, have been used.

The validity of the model results is not equal for the different substances. The calculated depositions of heavy metals are reasonably realistic. The results for the chlorinated hydrocarbons, PAH, PCB, benzene and lindane show a lower degree of reliability due to uncertainties in the emissions and the deposition parameters used. The emissions of pesticides are based on rough estimates and the uncertainty in the atmospheric behaviour of this group of compounds is large. Results, therefore, should be used with caution. Some of the contaminants are relatively stable in the atmosphere and large scale background concentrations are known to exist. Contributions to the deposition from background concentrations have not been taken into account. The calculated deposition of these contaminants will therefore be an underestimation of the actual deposition.

Uncertainties in the results caused by model assumptions and the use of a homogeneous meteorology are small compared to those caused by uncertainties in emissions and atmospheric behaviour of the compounds.

The total deposition of individual compounds on the Rhine catchment area varies from some tons per year to several thousands of tons per year. For all contaminants over eighty percent of the deposition on the Rhine catchment area results from emissions of the Rhine states and their surrounding countries. Contributions from emissions of countries farther away (Spain, Greece, Scandinavian countries, Eastern European countries) are small.

Major contributions to the total deposition are made by West German emissions, especially of those compounds related to industrial activity, and French emissions (mainly pesticides)\*. This result can be attributed to the coincidence of the geographical location of a major part of the Rhine catchment area within West-Germany and to large agricultural activities in the North of France combined with the prevailing meteorologic situation in that area.

The total deposition of individual compounds on the Dutch part of the Rhine catchment area varies from several tens of kilos to some hundred tons per year. On this part of the Rhine catchment area the total deposition is mainly caused by emissions from the Netherlands, Belgium and Luxembourg, France and West Germany.

The deposition on the Netherlands of the six pesticides results mainly from French and Dutch emissions. The deposition of nickel on the Netherlands is caused mainly by emissions from Belgium and Luxembourg and the Netherlands.

The total deposition directly on water surfaces in the total Rhine catchment area is compared with an estimation of the direct input into the river Rhine by industrial and communal sources. For several compounds atmospheric deposition dominates or contributes significantly to the total input of contaminants into the river Rhine.

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\* Information, which has become available after this study was performed, indicate lower French and West-German emissions. See Chapter 4.3 and Appendix A7.

## 1. INTRODUCTION

### 1.1 Background

In 1990 the Interministerial Workinggroup for Atmospheric Deposition (IWAD) requested TNO to make a study of the pollution of the Rhine catchment area by atmospheric deposition of twenty-nine priority contaminants. This study is a sequel to previous studies on the pollution of the North Sea, the Dutch Wadden Sea and the Netherlands (Warmenhoven, 1989, 1989a). To the previously studied 23 priority contaminants, six new compounds have been added. The compounds are given in Table 1. The input of contaminants by atmospheric deposition has been calculated on the basis of European emissions, the input of nitrogen was taken from studies of EMEP and RIVM (Iversen, T. et al. 1990; Derwent, R.G. et al. 1989, Schneider et al., 1991).

*Table 1 List of contaminants .*

Cadmium	Benzene
Chromium	PAH (six of Borneff)
Copper	PCB
Lead	Atrazine
Mercury	1,3-Dichloropropene
Nickel	Endosulfan
Zinc	Fentin compounds
1,2-Dichloroethane	Lindane
1,1,1,-Trichloroethane	Parathion
Chloroform	Azinphos-methyl*
Carbontetrachloride	Bentazone*
Trichloroethene	Dichlorvos*
Tetrachloroethene	Pentachlorophenol*
Nitrogen	Simazine*
	Trifluralin*

\* Compounds of which additionally the deposition on the Netherlands have been calculated.

The objectives of this study were:

- to calculate the total deposition to the Rhine catchment area and to the Dutch part of the area;
- to calculate the relative contribution of the surrounding countries on the total deposition;
- to calculate the total deposition of the six additional contaminants to the Netherlands;
- and the relative contribution of the surrounding countries to this deposition.

The part of this study concerning the deposition of the six additional compounds to the Netherlands can be regarded as supplementary to the previous study of deposition on the Netherlands (Warmenhoven, 1989a). The calculation of the deposition of nickel on the Netherlands is included as an erratum to Warmenhoven (1989a).

The results of this study should provide information which is useful for drawing priorities in the abatement of atmospheric deposition and in the assessment of the importance of atmospheric deposition on the water quality.

## 1.2 Methodology

In principle it is possible to estimate the total depositions on basis of concentration measurements, representative for the complete receptor area and the period studied. For the compounds studied here, these concentration measurement were not available.

Therefore the deposition has been calculated on basis of the emissions to the atmosphere of the compounds. To calculate the deposition of a compound from its emission data, Krell & Roeckner (1988) and Graßl et al. (1989) concluded that it is necessary to use a dispersion model to calculate the total atmospheric input into a large receptor area. This is also necessary if the contributions of different countries are to be estimated. The results of deposition calculations of some heavy metals with a model developed by van Jaarsveld (1986) at the Dutch National Institute of Public Health and Environmental Hygiene are comparable to the result of more complex models. The model has been used in previous studies of deposition into the North Sea and the Netherlands (Warmenhoven, 1989). The model calculates the total deposition on receptor regions on basis of emissions of all relevant sources in Europe. The model does not calculate the atmospheric deposition caused by background concentrations of a compound. In case of low deposition velocities and little reactivity of a compound, which result in long residence times, a background concentration might occur.

For compounds with large background concentrations (e.g. chlorinated hydrocarbons) the total deposition calculated by the OPS model, will be an underestimation of the actual total deposition because of not including sources from outside Europe and because of not including the European contribution to the background concentration.

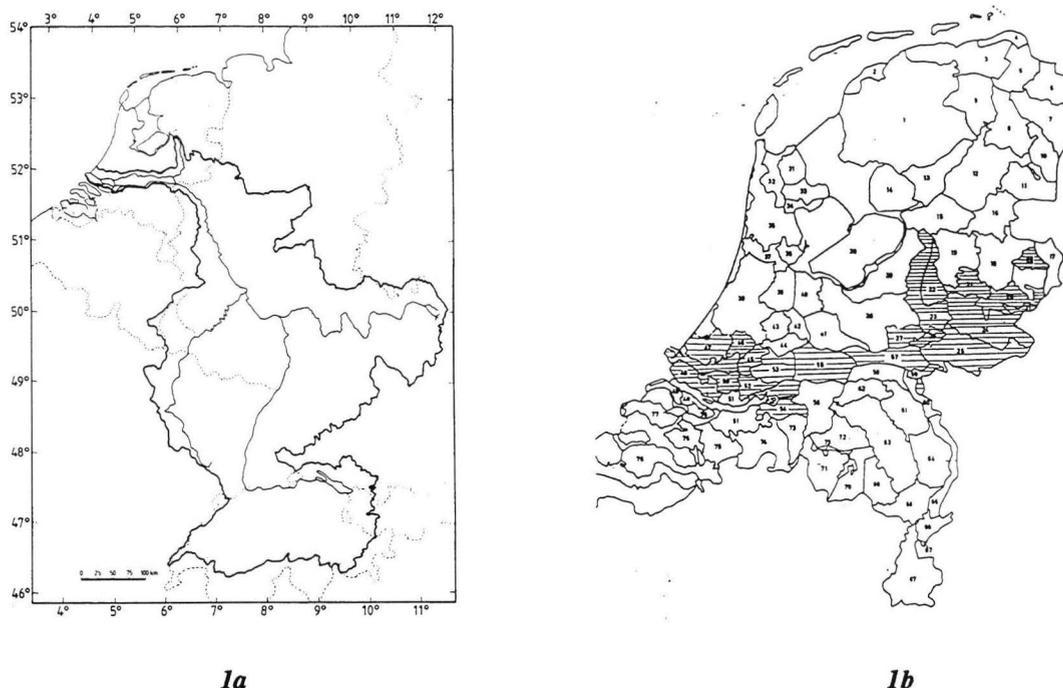
The receptor areas in this study are the total Rhine catchment area, the Dutch part of the Rhine catchment area and the Netherlands (for six compounds only). The part of this study dealing with the deposition on the Netherlands of six compounds can be regarded as supplementary to the previous study on deposition on the Netherlands (Warmenhoven, 1989).

The Rhine catchment area is considered to be that part of Europe on which deposition of contaminants might either directly or indirectly influence the water quality of the river Rhine.

In Switzerland the hydrologic Rhine catchment area has been used.

Downstream in the Dutch section of the Rhine catchment area, the IJsselmeer and the area of the effluent rivers of the Rhine are not included in the receptor area for calculations in this report. However because the information on the deposition on the area of the effluent rivers might be of specific interest, result of the deposition calculations on the larger area, influenced by the Rhine and its effluent rivers, are given in Appendix G.

The receptor areas are shown in figure 1.



**Figure 1** Receptor areas: *1a* Total Rhine catchment area  
*1b* The Netherlands and Dutch part of the Rhine catchment area

As the model calculates the deposition on basis of emissions followed by transportation and deposition of the contaminants, uncertainties in the emissions or in the atmospheric behaviour of the compounds have a direct influence on the calculated deposition.

Most of the contaminants studies in this project are relatively stable in the atmosphere; therefore a large source area had to be taken into account. We have used emissions from the whole of Europe. For some countries and some pollutants there were explicit data on emissions but generally the annual emissions from all countries had to be estimated on the basis of industrial and agricultural activities within countries. Chapter two and three give a description of the methods used to estimate the emissions and an indication of the uncertainty of the estimates; the emission inventory is discussed in detail in Appendix A. The physical and chemical properties of the compounds regarding their behaviour in the atmosphere are known for several compounds, otherwise they have been estimated on basis of the compound structure. Chapter three gives a description of the uncertainty in the used physical and chemical properties. The properties used in the model are specified in Appendix B.

## 2. MODEL DESCRIPTION

### 2.1 The emission grid

Because of the stability of some of the components studied in this project it was necessary to take into account emissions from almost the whole of Europe. In principle it would be possible to use whole countries as big source areas in a model; however, to get a realistic view of the contributions of different countries to the deposition to the Rhine catchment area it is necessary to use a more detailed emission grid for the countries in or close to the Rhine catchment area. In the PHOXA (Photochemical Oxidant and Acid Deposition Model Application) area (47.5°N to 60°N and 10°W to 24°E; (PHOXA, 1989), grid with a spatial resolution of 0.5° latitude and 1° longitude (ca. 55x55 km) was used. The same spatial distribution of emissions was used in the remaining parts of France, Switzerland and Austria. Outside this area a more coarse grid was used. The emission area is showed in Figure 3. For this study all European countries were taken into account (for the Soviet Union only the area west of 38°E, with the population of 103.10<sup>6</sup> inhabitants).

For most of the pollutants there was no information on the spatial distribution of the emissions within the country. To get a general idea of this we assumed that the bulk of the emissions of the metals, chlorinated hydrocarbons and aromatic compounds were linked to areas with a high population density. Therefore these emissions could be distributed in accordance with the distribution of the population within the country. In a similar manner the emissions of the pesticides were distributed in accordance with the distribution of arable land and permanent crops. The population distribution and the land use information was obtained from the PHOXA database (PHOXA, 1989). For the area south of 47.5°N in France, Switzerland and Austria information on the distribution of the population was taken from Bosatlas (1988), the distribution of arable land was taken to be evenly distributed over the grids. If specific point sources were known, they were placed at their actual locations. The emission grid was used as input to the dispersion and deposition model to calculate the deposition on the receptor grid.

### 2.2 Receptor grid

The receptor area is shown in Chapter 1 Figure 1.

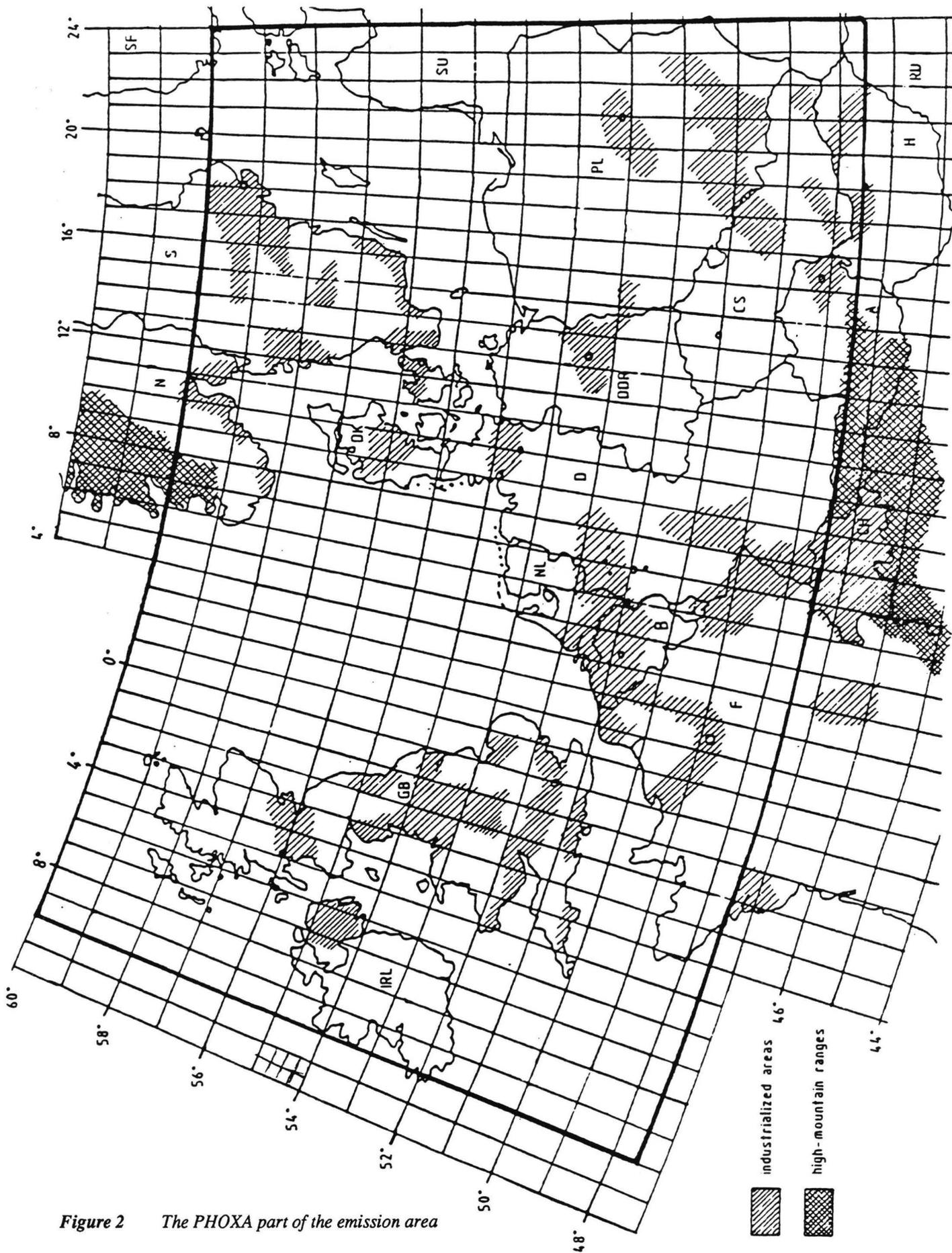


Figure 2 The PHOXA part of the emission area



The resolution of the receptor grid was the same as that of the fine emission grid:  $0.5^\circ$  latitude and  $1^\circ$  longitude. The receptor grid is shifted relative to the emission grid by  $0.25^\circ$  latitude and  $0.5^\circ$  longitude.

The total Rhine catchment receptor region has an area of  $170848 \text{ km}^2$ . The Dutch part of the Rhine catchment region has an area of  $6534 \text{ km}^2$ .

For deposition on the Netherlands a specification is given for deposition on dry surface, inland waters, coastal waters and the IJsselmeer. A further specification of the deposition on different provinces and different categories of land use is made.

## 2.3 Dispersion and Deposition model

### Dispersion model

The model used to calculate the concentration at each receptor grid due to the emissions is based on a long range transport model. This means that the dispersion from a source is assumed to follow the prevailing wind direction and wind speed within a sector of  $30^\circ$  in the horizontal plane. The vertical dispersion is limited by the earth surface and the top of the mixing layer. Due to wet and dry deposition and chemical reactions atmospheric concentrations decrease during transport; this process is also taken into account in the model. To calculate a mean concentration on the basis of these assumptions the relevant meteorological data are ordered in classes. After calculation of the concentration for each meteorological class the mean concentration is calculated in accordance with the frequency of occurrence of each class.

The model uses twelve wind direction classes and six stability classes which describe the vertical mixing height. Three of the stability classes are used to describe the prevailing situation of neutral stability with three classes of different mixing height which enables us to calculate the dispersion from high sources more accurately. High sources may emit above the mixing layer when the mixing height is low, which means that ground level concentrations nearby are not influenced by these sources under these situations. The statistics of wind speed and direction, stability and other relevant parameters were obtained from Dutch measurements between 1977 and 1988. There are three different meteorological statistics in the model: one describing local situations for dispersion calculations on a local scale, one for source receptor distances up to 100 km and one for long-range transport.

The dispersion/deposition model calculates the deposition flux in  $\text{kg}\cdot\text{km}^{-2}\cdot\text{y}^{-1}$  to each receptor grid cell due to each source grid cell. The total sum of these deposition fluxes

result in a distribution of the deposition flux over the receptor area. The contributions of the surrounding countries to these fluxes are added separately to be able to calculate the relative contributions of these countries.

### Dry deposition

The dry deposition of pollutants to the surface is described within the model with a deposition flux independent of the height:

$$F = V_g(z).C(z) \quad (1)$$

where  $V_g(z)$  is the deposition velocity in  $m.s^{-1}$  and  $C(z)$  the concentration in  $\mu g.m^{-3}$ , both at a height  $z$ . The deposition velocity of gases is a function of three resistances: the aerodynamic resistance  $r_a$ , the laminar boundary layer resistance  $r_b$  and the surface resistance  $r_c$ . In the model  $r_a$  and  $r_b$  are functions of windspeed, stability and surface roughness and independent of the pollutant. They are incorporated in the meteorological statistics. The surface resistance depends only on the properties of the pollutant and the surface and is an input parameter for the model. If the  $r_c$  of a pollutant is not known one may use the deposition velocity as input, thereby taking  $r_a$  and  $r_b$  as constants. For aerosols the dependence of the deposition velocity upon the size is taken into account by splitting the total amount of aerosol up in size classes with different deposition velocities for each class.

### Wet deposition

The model uses a relatively simple parameterization for describing the wet deposition process. The washout and rainout is therefore modelled by means of an effective scavenging coefficient  $\Lambda_r$  (in  $h^{-1}$ ):

$$\Lambda_r = W.R/H \quad (2)$$

where  $W$ , the scavenging ratio, is the ratio between the concentration in rain water and the concentration in the air,  $R$  the rain intensity (in  $m.h^{-1}$ ) and  $H$  the mixing height (in  $m$ ). To derive a mean wet deposition velocity from the scavenging ratio taking into account the incontinuity of the occurrence of rain it is assumed that wet and dry periods follow a Poisson distribution along the source receptor trajectory:

$$\bar{\Lambda} = (P/T_w) \cdot (1 - \exp(-\Lambda_r \cdot T_w)) \quad (3)$$

where  $P$  is the probability of rain,  $T_w$  the mean length of a period of rain (in h). The parameters  $P$ ,  $T_w$ ,  $R$  and  $H$  are also a part of the meteorological statistics which means that the wet deposition is dependent upon the wind direction. The scavenging ratio depends on pollutant properties.

### Chemical reactions

Chemical reactivity of pollutants is considered to be a linear depletion term:

$$K = a + b \cdot R \quad (4)$$

Where  $K$  is the overall reaction constant (in percentage per hour),  $a$  is the first-order reaction constant,  $b$  is a reaction constant dependent on the global radiation and  $R$  is the global radiation which is a part of meteorological data. For the pollutants in this study reaction with the OH radical is the most important chemical removal process. The  $K$  is estimated on basis of a yearly averaged OH radical concentration and the reaction rate of the pollutant with the OH radical.

Pollutants which occur in the aerosol phase are considered to be stable.

### 3. INPUT DATA

#### 3.1 Emissions

In this study deposition of pollutants is calculated on basis of European emissions. Uncertainties in the emissions have a direct influence on the uncertainty of the calculated depositions. For some countries and some pollutants explicit data on emissions were known, however most emissions had to be estimated.

The emission of a substance into the atmosphere is generally an unwanted result of some activity, which may be the production, the use or the destruction of it or of other substances. The quantity released is then strongly related to the extent of that activity, and can be estimated from it by multiplying with a so-called *emission factor*.

Consequently, this factor is defined as the mass of the pollutant emitted (per unit of time) per unit of activity (per unit of time). The activity may be the quantity produced, or applied, or combusted in a certain time. The emission factor is usually expressed in  $\text{kg}\cdot\text{ton}^{-1}$ .

Emission factors of a given substance may differ strongly with different polluting activities. Even for similar activities they may differ, depending on working conditions. Therefore emission factors presented in literature are averages, based on a number of estimates which may be large, but sometimes also may be small. In the latter case the accuracy and reliability of the emission factors of some compounds is low, and emissions estimated from such factors are then only rough estimates.

The emission of a certain pollutant in a certain region ( $0,5^\circ$  latitude and  $1^\circ$  longitude, in the fine emission grid) is estimated by multiplying all relevant activities in that region with the corresponding emission factors and then adding up. If specific point sources were known, they have been included as located emission sources. However, as most of the polluting activity are only known per country, emissions have been only estimated on that scale.

In those cases the geographical distribution of emissions has been related to population densities or land use. This assumption will only cause errors if the actual emissions are not linked to these distributions (e.g. if the emissions are caused by only a few point sources). In general, however, the emissions from industrial and collective sources are well correlated with the population distribution and the emissions of pesticides are obviously linked to agricultural activities.

A distinction has been made in the emissions from the former FRG and GDR. The difference in economic development and emission of pollutants clearly supports a differential approach.

The emission estimations were taken from previous studies on deposition on the North Sea and the Netherlands. They have been corrected if new information or insights were available, adaptations however are small except in the case of benzene and PAH.

In the next paragraphs the methods of estimating the emissions and the uncertainties of the estimates are discussed. The specific emission data are given in Appendix A.

## **Metals**

The emissions of metals in Europe have been subject to extensive research (Pacyna, 1983, 1984, 1989; Van Jaarsveld, 1986).

Pacyna estimated national emissions on the basis of an assessment of all metal-emitting processes, consumption and composition of raw materials and differences in manufacturing techniques between European countries.

Van Jaarsveld updated some emission estimated of Pacyna for some Western European countries, these values have been used.

Some state authorities provided total annual emissions (Netherlands: all metals except Hg, Switzerland: cadmium, mercury, lead, zinc), which have been used.

The extensive research in the last decade of the emissions of trace metals and the relative consensus on the emissions makes the emission values fairly reliable. The yearly averaged emissions per country can be considered accurated within a factor 2 to 3.

## **Chlorinated hydrocarbons**

Chlorinated hydrocarbons are emitted into the atmosphere from various point and area sources related to their production and use. With the exception of 1,1,1-trichloroethane they have been subject of detailed study, including emission estimation for Western-European countries for the production of Criteria Documents (Slooff et al., 1984, 1987). These documents therefore were considered as the basic material for this study. Since the reference year is 1981 and the required reference year for IWAD is 1985 the study was restricted to an investigation into the necessity and the possibility of updating and adding recent knowledge. Other sources than the Criteria Document are a study on the occurrence of some chlorinated solvents in the environment (CEFIC, 1985, 1986) and some national estimates: Austria (Forschungszentrum Seibersdorf, 1989), Denmark (Ministry of the Environment, 1989), France (CITEPA, 1988), the Netherlands (Baars, 1989; VROM, 1989) and Norway (State Pollution Control Authority, 1989). From United Nations

statistics (UN World Trade Annual, 1985) import data were additionally used for those countries that have no production and no or negligible export. For some other countries a rough mass balance could be made (production + import - export; UN statistics). Also, as a result of emission inventorying for the PHOXA project, attempts were made to more or less pattern emissions from COMECON countries.

Contributions from diffuse sources and point sources have been added up per country. The emissions are based on country data. For the Netherlands, the data given by VROM have been chosen.

The emission values provided by the state authorities may be considered accurate.

Emission estimations of chlorinated hydrocarbons, if not provided by state authorities, are fairly reliable for Western-European countries, probably within a factor 2 to 3. The data for the Eastern European countries is mainly based on default values, estimated on a general comparison between Western and European countries. Therefore they should be considered as order of magnitude values.

Further details on the methods of estimation and the reliability of individual chlorinated hydrocarbon emissions are given in Appendix A.

## **Benzene**

Pollution of the atmosphere by benzene is caused by a large number of source types. Important sources of benzene emission into the atmosphere are:

- traffic (use of gasoline and diesel oil as fuels);
- refineries (production of gasoline);
- production of benzene and benzene derivatives;
- coke factories;
- domestic space heating by combustion of coal, lignite and oil.

Estimations of the emitted amounts have been reported by two groups of authors at about the same time (Slooff et al., 1987; Huygen C., H.J. Huldy, J. Hulshoff, P.F.J. van der Most, C. Veldt, 1987). The total emissions in nine West-European countries as estimated in these studies differ only 3 %. The emission estimates for refineries and coke factories by Huygen et al. were updated by Veldt (Veldt, 1991) on basis of studies of Schaff (1989), Sexton et al. (1983) and Edwards (1986).

The emissions from refineries and coke factories have been included as point-sources. Also production figures and fuel consumption used by Huygen (base year 1981 and 1984) were

updated to 1985 values by Veldt (Veldt, 1991) on basis of OECD/IEA Energy Statistics and UN statistics.

The Swiss delegation in der Untergruppe Kd der IKSr provided emission values for Switzerland. These have been used.

The major uncertainty in these emission estimations are the used emission factors for domestic space heating. High estimates were used, emissions by this source might therefore be overestimated. Due to the fact that in Western European countries benzene emissions are caused for a major part by the use of fuel for transportation, the emissions can be considered quite reliable for Western European countries. For Eastern European countries the uncertainty of the emission estimation is somewhat larger, but emission values are probably accurate within a factor 3.

## **Polycyclic aromatic hydrocarbons**

Polycyclic aromatic hydrocarbons (PAH) are compounds consisting of two or more fused aromatic carbon five or six rings. Many of them are regarded as, or suspected to be carcinogenic or mutagenic. Most of the PAH which are formed and emitted are the result of combustion processes and are directly released into the air. Although a vast number of PAH have been identified, emission data frequently regard only 20 of them, whereas information on other PAH is found only incidentally.

Six selected PAH, the so-called six of Borneff, have been chosen for this study. Their selection is based partly on their carcinogenicity, and partly on the method available for their analysis (Borneff and Kunte, 1969). These PAH are: fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene. It has to be mentioned that together with these PAH usually also other PAH are found to be emitted, and that the six of Borneff only form a minor part (at most 30%) of the total PAH emitted.

In a recent literature study on the emission of PAH to the atmosphere (Duiser and Veldt, 1989) emission factors are given for various processes.

It has been assumed in this study that the emission profile (the ratio in which the different PAH are emitted) is the same for a given type of process in any country in Europe.

PAH are a large group of compounds of which some compounds occur only in the gas phase, others only in the aerosol phase. As the fate of PAH in the atmosphere is dependant on the phase-state (gas or aerosol) of the PAH, the six of Borneff PAH in this study have been divided in volatile PAH and non-volatile PAH.

The PAH emissions from wood preservation, and open burning of biomass, have not been taken into account because of lack of available data concerning these processes, making reasonable estimation impossible. The PAH emissions used in this study therefore are probably an underestimation of the actual emissions.

It should be noticed that the emission factors presented, result from data which are either sparse or show a large spread. Therefore values are not very accurate, sometimes they indicate order of magnitude only.

### **Polychlorinated biphenyls**

Polychlorinated biphenyls (PCB) are derivatives of biphenyl in which one or more hydrogen atoms have been substituted by chlorine atoms. Of the 209 congeners which theoretically exist, more than 60 substances with different physical and chemical properties can now be identified. Commercial products are mixtures of them in which the chlorine content is between 21 and 68 %.

Although PCB were already introduced into commerce in 1929 they were regarded as an environmental contaminant only in the late sixties after some accidents. Since then the number of studies on dispersion and effects has increased strongly. The hazardous properties of PCB are widely recognized now. Estimates of emissions have been made on basis of a literature study on the emissions of PCB which has been made recently by Duiser and Veldt (1989). As important sources of PCB have been mentioned:

- dumps and landfills,
- leaks and disposal of industrial fluids,
- vaporization from plasticized products,
- vaporization during open burning of disposed scrap and materials in dump.

Of these, only vaporization is regarded as a source of emission into the atmosphere. The authors propose to relate these emissions to population densities. The thus estimated emission flux density may represent the order of magnitude of present emissions, except those caused by incidental leakages and illegal activities.

### **Pesticides**

Pesticides enter the atmosphere mainly by emission during and/or after their application to soil and crop. The emission in the atmosphere above a certain region is the product of:

- The area of the region;
- The applied quantities per unit of area and per unit of time in that region;
- The emission factor.

The product of the latter two factors is the emission flux density (the emission per unit of area per unit of time). This parameter has been used to characterize the emissions in a certain region (country) and will be expressed in  $\text{kg.km}^{-2}.\text{y}^{-1}$ . It is obtained from the application density of the pesticide by multiplying it with an emission factor the value of which depends on the rate of evaporation from the crop or from the soil.

The application density is defined here as the amount used per unit of area used for agriculture (or, for some pesticides, the area of the the specific culture where they are used for). This area of agriculture is assumed to be equal to the area of arable land and permanent crops. Then the emission flux is the product of the application density, the fraction of arable land and permanent crops in the region, and the emission factor. Fractions of arable land and permanent crops per country (quoted from the FAO) are given in Appendix A. Pesticide application data in agriculture for the Netherlands have been collected by Berends (1988) and by VROM (1989).

When annual consumption data were available (FAO, 1987; Duiser and Veldt, 1989; provided by state authorities) these values have been used.

If only consumption of a group of pesticides was known, consumption has been estimated on the estimated fraction of the specific pesticide in the total group. However for many countries and pesticides little or no information on consumption was available.

In those cases the application densities were estimated on basis on the Netherlands consumption data and applications.

Emissions of pesticides with a wide agricultural application (bentazone, simazine, atrazine, endosulfan, parathion) were related to the total area of agriculture, emissions of those with a more specific application, like on potatoes, maize, wheat, barley or apples (1,3-dichloropropene, fentin, azinphosmethyl, trifluralin) were related to the area of that specific culture. Of the insecticides PCP and dichlorvos, of which a large part of the application lies in non-agricultural applications, default emissions have been related to number of inhabitants.

Emission factors for several pollutants from industrial and combustion processes have been estimated since many years, and can now be found in handbooks. Unfortunately the emission factors of pesticides, which relate predominantly to their application in agriculture, are considerably less well-established. The emission factor, which is the fraction of

the applied pesticide that is emitted, depends largely on the type of application (whether it is sprayed onto the crop or injected in the soil), and, except for fumigants with a high vapour pressure, in a lesser extent on the physical properties of the pesticide. Further it depends on the type of soil and its humidity and temperature, or on the type of foliage, and on air temperature and wind velocity.

The fraction of the pesticide which is deposited on the crop (which fraction is the most subject to emission by evaporation) depends largely on the spraying conditions. It appears to be often about a quarter to half of the total amount sprayed. Experiments on volatilization of pesticides have been made by several authors. From their data it follows that 60-90% of the pesticide intercepted by the crop has been evaporated during the first month after application. From these results together it would follow that roughly a third of the total quantity applied has been evaporated after that time. However, there is still lack of knowledge on this subject, e.g. about the influence of the vapour pressure on the vaporization rate. In this study we used the emission factors, suggested by the contractor on basis of the compounds vapour pressure and way of application, which have values between 0.1 and 0.5 kg.kg<sup>-1</sup>.

The way of estimating the national consumptions and the uncertainty in the emission factors, probably introduce considerable errors in the emission data. The emission data should therefore be used as tentative estimations only.

Some new information on the use of pesticides has become available after this study was written, this data and its implications are discussed in Chapter 4.3 and Appendix A.

An overview of the estimation methods of emissions of the different countries and pesticides is given in Appendix A.

### **3.2 Physical and chemical properties**

Once emitted the compounds undergo transportation during which they are subject to deposition (wet and dry) and degradation (either photolytic or chemical).

The physical and chemical properties of a compound determine the way and extent to which the pollutants are transported.

Compounds, which have high-deposition velocities or which are unstable in the atmosphere, will only be transported over a short distance. If the compounds have a low deposition velocity and if they are stable in the atmosphere, the range of transport can be very long and world-wide background concentrations of these compounds may exist.

Of major importance to both deposition and chemical behaviour in the atmosphere is the physical state of the compound: gaseous or as aerosol.

It has been shown that compounds with vapour pressures higher than  $10^{-7}$  atm. occur exclusively in the gas phase while compounds with vapour pressures less than  $10^{-11}$  are exclusively aerosol bound. In this study we considered all compounds with vapour pressures higher than  $10^{-9}$  atm. gases, and all other compounds aerosols.

Deposition velocities are fairly accurately known for aerosols, and for a few gases. For most gaseous compounds in this study no deposition velocities were known. Liss and Slater (1974) have developed a model, for estimating a compounds deposition velocity and washout-ratio on basis of its Henry constant and diffusion coefficients in air and water. If not known, diffusion coefficients have been estimated according to the method of Hayduk and Laudie and the method of Fuller, Schettler and Giddings (Lyman W.J., W.F. Reehl, D.H. Rosenblatt, 1982).

Using estimations of physical data to calculate another physical property clearly implies a large uncertainty in the resulting physical quantity. The range of the deposition velocities of organic chemicals is usually confined to two orders of magnitude. Scavenging ratios might differ several orders of magnitude. Estimated deposition velocities on basis of a compound's physical properties are probably correct within one order of magnitude.

Although the estimated deposition velocities of the gaseous compounds, refer to deposition on water, Tucker and Preston (1984) conclude that this method can also be used to estimate dry deposition velocities above land. The scavenging ratio was estimated to be equal to the inverse value of the dimensionless Henry constant (Tucker and Preston, 1984; Slinn et al., 1987). This method does not take into account the potential revolatilization of gases from the surface. Therefore the calculated deposition velocities might be too high for the very volatile gases.

Reaction with the OH radical is the main degradation route for the gaseous compounds in this study. Degradation rates were calculated on the basis of reaction rate constants for reactions with the OH radical and the mean OH concentration. Photolysis is only of minor importance or not known and has been neglected. Degradation of compounds in aerosol phase is generally much slower and are of little importance on the time scale of transportation. Therefore compounds in aerosol phase are considered to be stable.

The way that the uncertainty of the atmospheric behaviour of the compounds will influence the results is dependent on the properties itself.

When the emissions are uniformly distributed, the compound is relatively stable and the deposition velocity is relatively large, the total deposition on a large area will not be that

much influenced by uncertainties in the physical properties (like residence/transport time) of the compound.

With an increase of the residence time the relative contributions from sources further away will increase and those of sources nearby will decrease. The total deposition will then be nearly linear dependant on the deposition velocity. For compounds which are relatively unstable in the atmosphere, the uncertainty in the chemical properties has a more direct influence on the total deposition.

A longer residence time in the atmosphere will then result in a lower total deposition due to the degradation of the compound during its transport.

The uncertainties in the atmospheric behaviour of the individual compounds will more directly influence the uncertainties in the relative contributions of individual countries to the deposition than in the total deposition on the receptor area.

Uncertainties in the physical and chemical properties of the individual compounds will be discussed briefly below. Data which has been used as input for the model calculations are given in Appendix B.

## **Metals**

Except mercury, all metals have been shown to occur only in the aerosol phase.

The data on deposition velocities, scavenging ratios and reactivities are relatively well founded for the heavy metals. For mercury recent research pointed out that the actual deposition velocity might probably be lower than the one used in this study. Data were taken from Van Jaarsveld (1990).

## **Chlorinated hydrocarbons**

In the atmosphere, these compounds only exist in the gas phase. The reactivity of the compounds is very well studied and reliable (Van Aalst, 1983). The deposition velocities have been calculated according to Liss and Slater (1974). The Henry's constants are relatively well established; the diffusion coefficients, necessary for the deposition velocity calculations, have been estimated. Resulting deposition velocities are fairly reliable estimates.

## **Benzene**

Data regarding reactivity, deposition velocity and scavenging ratio is well known. Data were taken from Van Jaarsveld (1990).

## **PAH**

The PAH in this study regard the six of Borneff. Based on occurrence in the atmosphere and physical properties a distinction has been made between more volatile gaseous PAH and non-volatile aerosol bound PAH.

The volatile PAH (fluoranthene and half of the benzofluoranthenes) are considered to occur in the gas phase only; the deposition velocity and reactivity are based on those of fluoranthene (Atkinson, 1990; Duyzer, 1989). Non-volatile PAH (half of the benzofluoranthenes, benzo(a)pyrene, benzo[g,h,i]pyrene, indeno(1,2,3-c,d)pyrene) are considered to be in the aerosol phase. Aerosol phase PAH have been shown to occur relatively stable under atmospheric conditions. Within the time scale of transportation in this study, reactivity is taken to be zero.

The extrapolation of physical properties of one compound to all congeners clearly is an oversimplification of reality. The main uncertainty, however, regards the deposition velocity and scavenging ratio of the volatile PAH. This value is probably accurate within a factor 3.

## **PCB**

PCBs are derivatives of biphenyl in which one or more hydrogen atoms have been substituted by chlorine atoms.

Theoretically 209 congeners exist. In this study PCB are treated as a group of compounds with identical physical and chemical behaviour. PCB occur mainly in the gas phase and are very stable. The main uncertainty is the deposition velocity and scavenging ratios.

The deposition velocity of PCB-52 has recently been subject to a laboratory study by Baart et al. (1991) and is applied to the total group of PCB. Clearly extrapolating the deposition velocity of one congener to all PCB congeners needs some qualification. The deposition velocity and scavenging ratio should be considered an order of magnitude estimation.

## Pesticides

Information on physical and chemical behaviour of pesticides in the atmosphere is very scarce.

Henry's constants have been calculated from their vapour pressures and solubilities (Worthing, 1983). Diffusion coefficients and deposition velocities have been estimated. On basis of vapour pressures compounds were treated as gas or aerosol bound.

Degradation rates were estimated on basis of compound structure and analogy with similar compounds. The degradation rates of lindane and trifluralin were taken from literature, but are based on one study only and should be used with care.

Major uncertainties remain on all properties: deposition velocities, scavenging ratios and degradation rates. They should be regarded as order of magnitude estimations only.

## 4. RESULTS AND DISCUSSION

### 4.1 Reliability of the results

#### 4.1.1 General

There are no other studies on the deposition to the Rhine catchment area to compare the results of this study with.

The results previous calculations of the deposition on the North Sea (Warmenhoven, 1989) showed good agreement with several other model calculations of Krell et al. (1988), van Jaarsveld (1986), Graßl et al. (1989) concerning the deposition of some heavy metals.

In order to validate the method we additionally calculated the mean concentration of the some pollutants over the Netherlands. These were compared to concentrations measured in the Netherlands as far as these were available. Although some of the measured concentrations were incidental measurements and not necessarily representative of the mean concentration, most of the model results seem to agree relatively well with the measurements. However a large deviation was found for those compounds of which a global background concentrations is known to exist (chloroform, carbontetrachloride) (see table 2).

*Table 2 Mean yearly concentrations over the Netherlands calculated by the model compared with measurements. All data in  $\mu\text{g}\cdot\text{m}^{-3}$ .*

	Calculated	Observed	Source
cadmium	$0.9 \cdot 10^{-3}$	$0.7 \cdot 10^{-3}$	RIVM 1988
lead	0.1	$0.6 \cdot 10^{-1}$	RIVM 1988
mercury	$0.3 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	PEO 1985
zinc	$0.6 \cdot 10^{-1}$	$0.6 \cdot 10^{-1}$	RIVM 1988
carbon tetrachloride	$0.2 \cdot 10^{-1}$	0.8	PEO 1985
chloroform	$0.7 \cdot 10^{-2}$	0.2	VROM 1985
dichloroethane	$0.8 \cdot 10^{-1}$	0.16	PEO 1985
tetrachloroethene	0.5	0.7	PEO 1985
trichloroethene	0.5	0.5	PEO 1985
benzene	1.1	3.0	RIVM 1987
PAH	$0.5 \cdot 10^{-2}$	$0.1 \cdot 10^{-1}$	Slooff et al. 1988
PCB	$0.2 \cdot 10^{-2}$	$0.1 \cdot 10^{-2}$	VROM 1986
lindane	$0.8 \cdot 10^{-3}$	$0.4 \cdot 10^{-3}$	Slooff e.a 1987

As described in chapter two and three the results stem from model calculations, with input of meteorological data, emission data and pollutant properties. Uncertainties in these input data will result in uncertainties in the results.

#### **4.1.2 Input data**

##### **Meteorological data**

The meteorological data like statistics of wind speed and direction, stability and other relevant parameters were obtained from Dutch measurements between 1977 and 1988. Application of this data to the whole of Europe clearly introduces some errors. However, in general, the data used are in line with the situation in a large part of the Rhine catchment area and its surrounding countries.

The use of this meteorological data will affect mainly the relative contributions to the total depositions from areas further away from the Rhine catchment area. The contributions of these countries to the total deposition on the Rhine catchment area are generally less than 20% of the total deposition. The uncertainty resulting from the use of the meteorological data will generally be of minor importance compared with the influence of uncertainties in emission data and compound properties.

Only in the case that the emissions and physical properties are relatively well known (as for heavy metals), uncertainty caused by meteorological data might contribute to the uncertainty in the final results.

##### **Emission data**

Emissions are the most important input data because uncertainties in emissions will have a direct influence on the results. Uncertainties in emission data differ for different pollutants and countries.

The emission data of the Rhine catchment area and surrounding countries is generally more reliable than those from Eastern European countries.

##### **Pollutant properties**

The uncertainty caused by the pollutant properties on the total deposition is also of importance. Especially the uncertainty in the relative contributions of the countries to the total deposition and the deposition on smaller parts of the Rhine catchment area will be influenced by the pollutants physical and chemical properties.

The influence of the uncertainty in these properties on the final results is dependent on the absolute values of these properties.

When the degradation rate of a compound in the atmosphere is small, uncertainty in the precise value will hardly influence the calculated total deposition.

Also when the deposition velocity and/or scavenging ratio are large, uncertainties herein will only minorly influence the total deposition. However when the deposition velocity is slow, the total deposition will become nearly linear dependant of the deposition velocity.

Although some properties of most of the compounds have been studied, major uncertainties exist on the deposition velocities of most compounds and on both physical and chemical properties of the pesticides.

## 4.2 Results

The results of the calculations from the OPS-model of the total atmospheric deposition of 29 priority pollutants on the Rhine catchment area and on the Dutch part of this area are presented in table 3. Relative contributions of surrounding countries to the deposition are given in Appendix C.

Supplementary to the study of deposition on the Netherlands (Warmenhoven, 1989), the total atmospheric deposition of six compounds on the Netherlands and the Dutch Wadden Sea, coastal waters and IJsselmeer are given in Table 4. The value of the total atmospheric deposition of nickel is included as an erratum to Warmenhoven, 1989. Iso deposition plots are given in Appendix E.

The relative contributions of the surrounding countries to this deposition are given in Appendix E. The total deposition in the Netherlands has been further specified to deposition on different provinces and different categories of land uses, results are given in Appendix F

In Appendix D iso deposition plots on the Rhine catchment area are given for 29 compounds. They show the geographical distribution of deposition flux densities in kg/ha/yr. Data on the deposition of nitrogen was taken from studies of EMEP and RIVM.

**Table 3** Total deposition to the Rhine catchment area and the Dutch part of the Rhine catchment area (reference year 1985).

Compound	Deposition on	
	Rhine catchment area ton/y	Dutch part of the Rhine catchment area ton/y
Cadmium	22	0.8
Chromium	100	3.6
Copper	120	6.3
Lead	1900	104.5
Mercury	18	6.3
Nickel	130	5.6
Zinc	1500	54.7
1,2-dichloroethane	63	4.3
1,1,1-trichloroethane	730	30.4
Carbontetrachloride	4.3	0.2
Chloroform	12	0.6
Trichloroethene	280	10.4
Tetrachloroethene	110	4.5
Benzene	520	23.7
PAH	36	5.6
PCB	28	1.4
Atrazine	170	5.3
Azinphos-methyl	1.5	0.1
Bentazone	57	1.8
Dichloropropene	79	4.4
Dichlorvos	7.3	0.4
Endosulfan	12	0.3
Fentin	77	4.4
Lindane	42	1.2
Parathion	50	1.4
Pentachlorophenol	260	7.0
Simazine	10	0.3
Trifluralin	3.6	0.1
Total nitrogen (ton N/y)	$3.4 \cdot 10^5$	$30.6 \cdot 10^3$

**Table 4** Deposition on the Netherlands.

Compound	Deposition on the Netherlands on			
	Dry land ton/y	Coastal waters ton/y	Waddensea ton/y	IJsselmeer ton/y
Azinphos-methyl	0.26	0.05	0.01	0.01
Bentazone	8.7	2.0	0.5	0.4
Dichlorvos	1.9	0.3	0.1	0.1
Pentachlorophenol	34	7.3	1.5	1.4
Simazine	1.5	0.4	0.1	0.1
Trifluralin	0.3	0.05	0.01	0.01
Nickel	26	5.0	1.3	1.2

### 4.3 Discussion

In general over 80% of the total deposition on the Rhine catchment area is caused by emissions from Rhine-states and surrounding countries, West-Germany and France being the major contributors.

The calculated total deposition is therefore very sensitive to the uncertainty in emission data of West-Germany and France. Uncertainties in the emissions of other countries will influence the results to a much lesser extent.

The major part of the Rhine catchment area shows significant overlap with West Germany, and completely covers the highly industrialised and polluted Ruhr area.

This combined with a high degree of industrialisation in West Germany, the West German emissions are expected to dominate the deposition of compounds related to industrial activities. The West German emissions are indeed the major contributor to the deposition of 21 of the 29 compounds (benzene, cadmium, chromium, diclorvos, dichloropropene, endosulfan, fentin, copper, mercury, lead, nickel, PAH, PCB, bifluralin, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloromethane, chloroform, trichloroethene, tetrachloroethene, zinc).

The large agricultural activities in the north of France combined with prevailing western winds result in a relatively large contribution to the deposition on the Rhine catchment area of compounds related to agricultural activities. French emissions are the major contributor to the deposition of 7 of the 29 compounds: all are pesticides (atrazine, azinphos-methyl, bentazone, lindane, parathion, pentachlorophenol and simazine)\*.

The total deposition of the individual compounds on the Rhine catchment area ranges from several some tons per year to over threehundred kilo tonnes per year.

#### Metals

Both the emissions and the physical and chemical properties were extensively studied. Model assumptions and meteorological data might influence the calculated deposition especially in the south of the Rhine catchment area. Overall results however are very reliable.

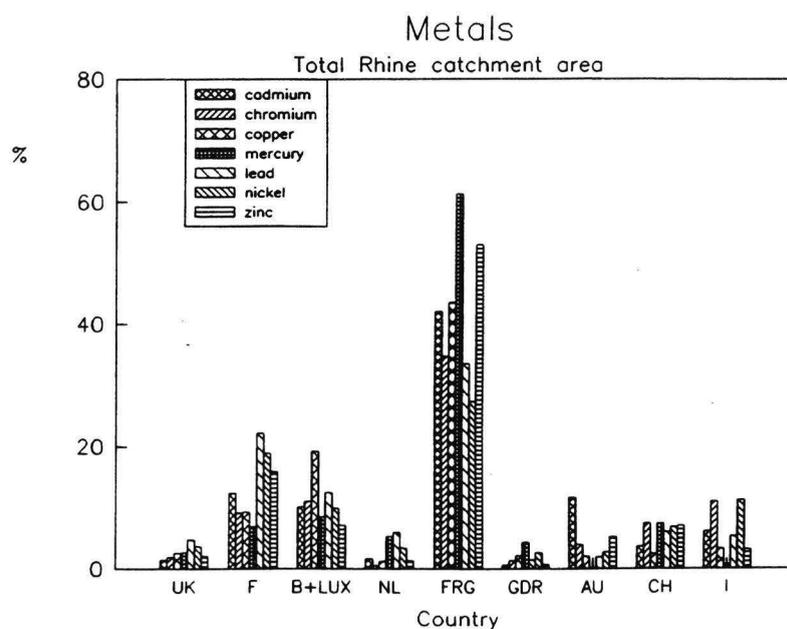
The total deposition on the Rhine catchment area ranges from 18 ton mercury to 1900 ton lead per year.

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\* See footnote on page 39

Deposition of heavy metals result for 80% to 97% from emissions in Rhine states and surrounding countries.

The major relative contribution to deposition of heavy metals in the Rhine catchment area is made by West German emissions: 27% to 61% (see figure 3).



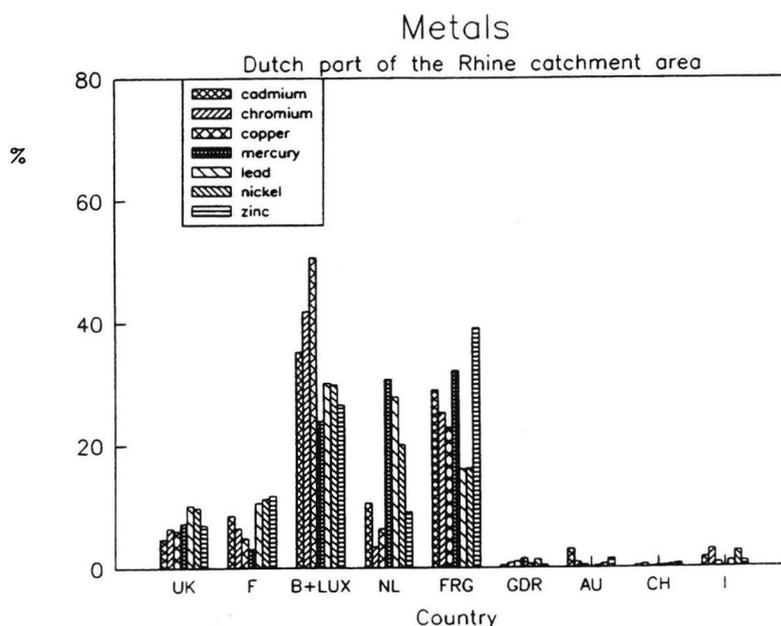
**Figure 3** Relative contribution of the surrounding countries to the deposition of metals to the Rhine catchment area.

The relative contributions of West-Germany to the deposition of cadmium, copper, mercury and zinc are at least twice as large as those of the second most important contributor. For copper, mercury and zinc West Germany also has the largest emissions. The emissions of lead and nickel from France are larger than those of West Germany resulting in relative contribution of France more in the same order of magnitude.

The fact that deposition on the Rhine catchment area is less influenced by countries further away is clearly illustrated here: Italian emissions of chromium, lead and nickel are 50% to 400% larger than the emissions of France or West Germany, however the relative contribution of Italian emissions do not exceed 12%.

## Dutch area

Due to low Dutch heavy metal emissions deposition on the Dutch part of the Rhine catchment area is mainly caused by contributions from surrounding countries. Especially the contributions of Belgium/Luxembourg and West Germany are significant. Together they are responsible for 44-75% of the deposition. For cadmium, chromium, copper and zinc the Dutch contribution to deposition on its own area is less than 11%. Only for mercury, lead and nickel the Dutch emissions contribute significantly (from 20 to 30%) to the deposition on its own area. Small contributions, in the order of 10%, are made by French and UK emissions (see figure 4).



**Figure 4** Relative contribution of the surrounding countries to the deposition on the Dutch part of the Rhine catchment area.

## Chlorinated hydrocarbons

It is important to note that the calculated deposition is based on European emissions of these compounds.

However, for 1,2-dichloroethane, chloroform and tetrachloromethane large background concentrations exist, due to their low deposition velocities and relative stability in the

atmosphere. The measured concentrations of some of these compounds are up to 50 times the concentrations calculated from the European emissions. This may partly be due to an underestimation of the emissions or an over estimation of the deposition velocities, and partly to the occurrence of a background concentration. For tetrachloromethane the background concentration can be estimated on basis of its residence time and an estimation of emissions in the Northern hemisphere to be around six times the concentration calculated from European emissions alone. Deposition of these compounds will be dominated by the contribution from background concentrations. However, in the model calculations the background concentration has not been taken into account. Also the contribution from European emissions to the background concentration is not taken into account. The calculated deposition of carbontetrachloride and chloroform will be an underestimation of up to two orders of magnitude of the actual deposition.

In the discussion of the abatement of atmospheric deposition it should therefore be noted that an European emission reduction would influence the actual total deposition also through a lowering of the background concentration as through the reduction of the concentration, directly caused by European sources.

The reactivity and Henry's constants are well known for chlorinated hydrocarbons. Uncertainty remains on the deposition velocities, which are estimated to be relatively low. There is some uncertainty in the emission data, however this concerns mainly emissions for Eastern European countries. The emissions in these countries are of minor importance to the deposition on the Rhine catchment area.

The emissions of 1,2-dichloroethane are localised at specific sites. The geographical distributions of the emissions of the other chlorinated hydrocarbons is correlated to population density, supplemented with emissions from localised point sources (for chloroform and carbontetrachloride) and may be considered an accurate representation of the actual distribution of emissions.

The influence of the localised point sources can be seen in the iso deposition plots (Figure D8, D10 and D11, Appendix D). The point sources are located in the centre of the areas with a steep deposition flux gradient.

The results (both total deposition and relative contributions) can be considered relatively reliable, but apply only to direct atmospheric deposition caused by European emissions.

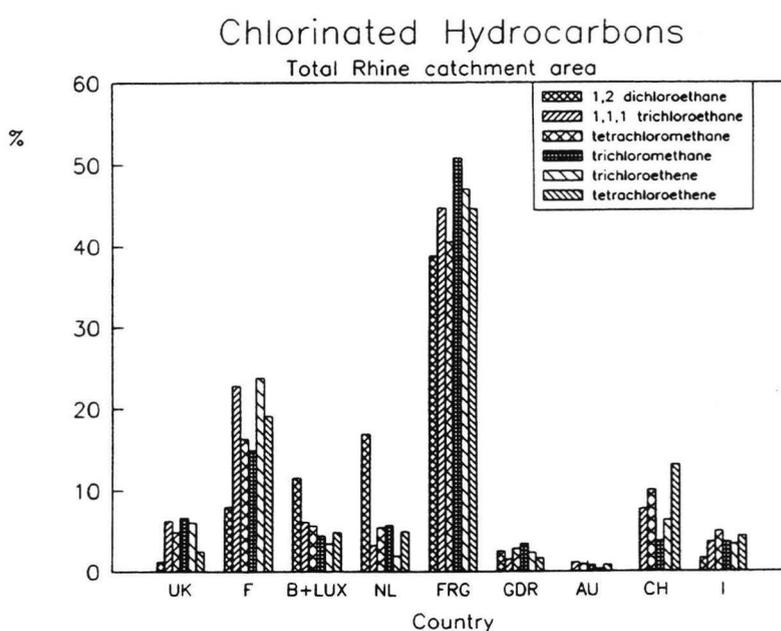
Of the total deposition on the Rhine catchment area, 80 to 95% is caused by emission in Rhine states and surrounding countries.

The total deposition ranges from 4.3 ton for tetrachloromethane to 730 ton per year for 1,1,1-trichloroethane.

The deposition is clearly dominated by West German emissions, which are responsible for 40-50% of the deposition. The contribution to the deposition made by French emissions lies in the range of ten to twenty percent.

For 1,2-dichloroethane, the relative high Dutch emissions are responsible for 17% of the total deposition.

Contribution in the order of ten percent are made by Swiss emissions of 1,1,1-trichloroethane, tetrachloromethane and tetrachloroethene and the emission of 1,2-dichloroethane from Belgium/Luxembourg (see figure 5).

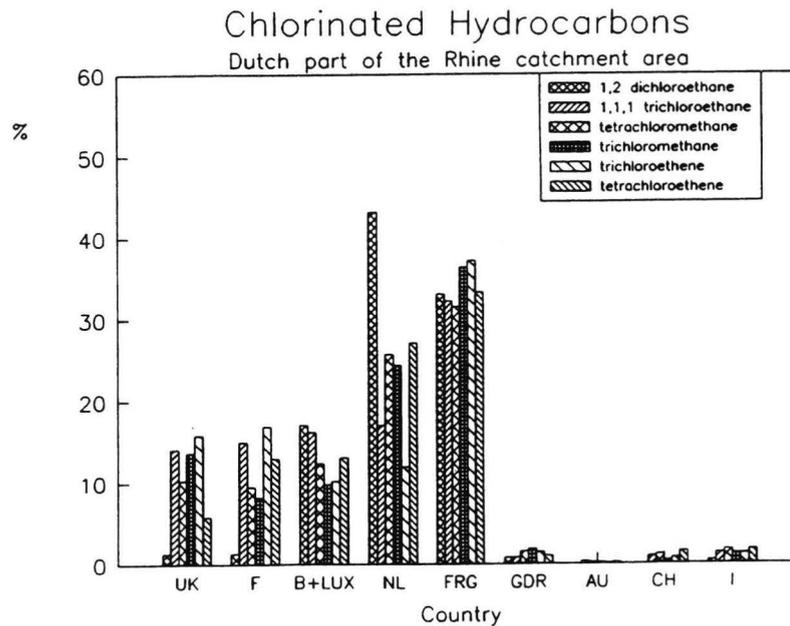


*Figure 5 Chlorinated hydrocarbons. Relative contributions of the surrounding countries to the deposition on the Rhine catchment area.*

### Dutch area

Of 1,2-dichloroethane, the deposition on the Dutch area is caused for more than 40% by Dutch emissions, followed by the contribution of the FRG of about 30%.

Concerning the other chlorinated hydrocarbons, the emissions of the FRG are responsible for thirty to forty percent of the deposition on the Dutch area, while Dutch emissions typically contribute twenty percent and the emissions from the UK, France and Belgium/Luxembourg each contribute about ten to fifteen percent to the total deposition (see figure 6).



**Figure 6** Chlorinated hydrocarbons. Relative contributions of the surrounding countries to the deposition on the Dutch part of the Rhine catchment area.

## Benzene

The physical and chemical properties of benzene are well known.

Due to the stability and low deposition velocity of benzene a possible important background concentration may exist. As the deposition resulting from the background concentration is not taken into account, the deposition calculated in this study is an underestimation of the actual deposition.

The emissions have been reasonably well estimated for the Rhine states and their surrounding countries. Uncertainty in the emissions mainly are concerned with emissions from domestic space heating. However even high emission estimates show this source to be of minor importance to the emission for the Western European countries. The emissions of the Rhine states and their surrounding countries are therefore reasonably well estimated. As the uncertainty of the emissions in Eastern Europe is of minor importance to the deposition of benzene on the area of study, the result can be considered fairly reliable.

The geographical distribution of the emissions is correlated to population density for diffuse sources (traffic), known point sources (refineries) have been included on their actual positions.

The total deposition on the Rhine catchment area amounts to 520 ton per year. Ninety percent of the deposition on the Rhine catchment area is caused by emissions from the Rhine states and surrounding countries, mainly from West German (40%) and French (21%) emissions. Contributions from the other surrounding countries do not exceed the ten percent (see Figure 7).

### **Dutch area**

Although the Dutch emissions are of little significance to the deposition on the total Rhine catchment area, they are, together with West German emissions, mainly responsible for the deposition on the Dutch area (each for about thirty percent).

Further contributions are made by UK, French and Belgium/Luxembourg emissions, in the order of ten percent each (see figure 8).

### **PAH**

The PAH studied here are the six of Borneff: fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene.

Both the emissions and deposition values refer to these six compounds, not to total PAH.

Some emission data was available for 16 other PAH besides the six of Borneff. In those cases the six of Borneff amounted to about 30% of the total of 22 PAH. The deposition of the six of Borneff will therefore at least be an underestimation of the deposition of total PAH by a factor 3. The emission estimates have not taken all emitting processes into account, as some of them are very hard to quantify. Emissions and resulting depositions should be considered as lower limits to the order of magnitude of the deposition.

The six of Borneff have been divided in this study in two separate groups: volatile (gaseous) PAH (fluoranthene and 50% of the benzo(b+k)fluoranthenes) and non-volatile (aerosol) PAH (50% of benzo(b+k)fluoranthenes, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene).

Aerosol bound PAH are relatively stable in the atmosphere while gaseous PAH react readily with the OH radical. It should be noted that, although they are not taken into account in this study, the products of the atmospheric reaction of gaseous PAH are at least as much a risk to public health as PAH itself. Due to the reaction of gaseous PAH the fraction of

gaseous and aerosol PAH changes during transportation from gas : aerosol = 3:2 at the source to gas : aerosol = 1:3 at the deposition area.

The geographical distribution of the emission has been correlated to population densities, supplemented with located specific point sources (Aluminium production plants and coke production plants). The geographical distribution is thought to well represent reality.

West German emissions contribute for a major part to the total deposition (about 40%), followed by a contribution of about 25% by French emissions. Emissions of other countries do not exceed 10% (see figure 7).

#### **Dutch area**

West German emissions cause nearly 50% of the deposition on the Dutch part of the Rhine catchment area.

Dutch, Belgium/Luxembourg and French PAH emissions are each responsible for about 10 to 15% of the PAH deposition on the Dutch part of the Rhine catchment area.

#### **PCB**

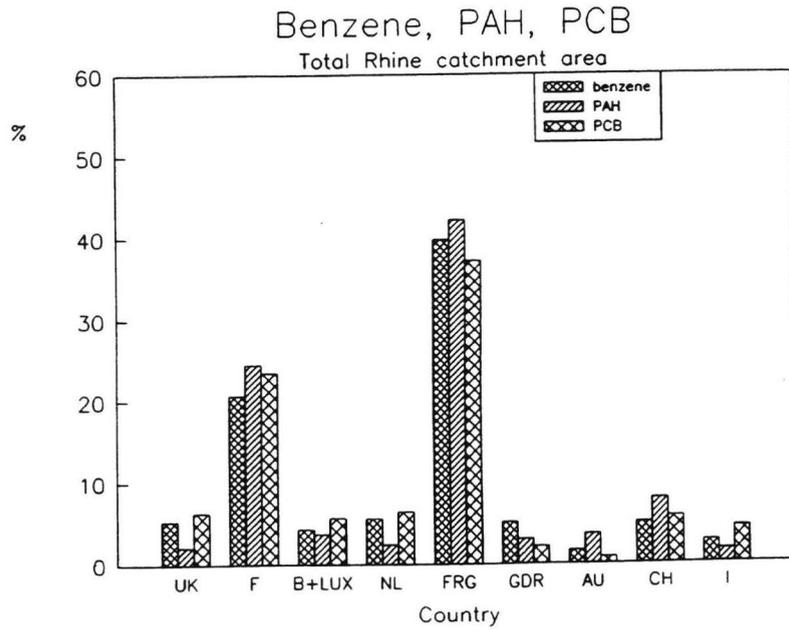
PCBs are a large group of compounds which are treated in this study as one with identical deposition properties, taken from those of PCB-52. Emission data relate to the total group of PCB: values may represent the order of magnitude of the emissions but do not take into account incidental leakages and illegal activities.

The emission and geographical distribution has been related to the population density, no distinction has been made in the emissions per inhabitant between different countries. The resulting depositions should be considered as order of magnitude estimates. Deposition on the Rhine catchment area stems mainly from emissions in the Rhine states and surrounding countries (>90%) and amounts to 28 ton/year. The largest contribution to the deposition are made by West German (37%) and French (24%) emissions.

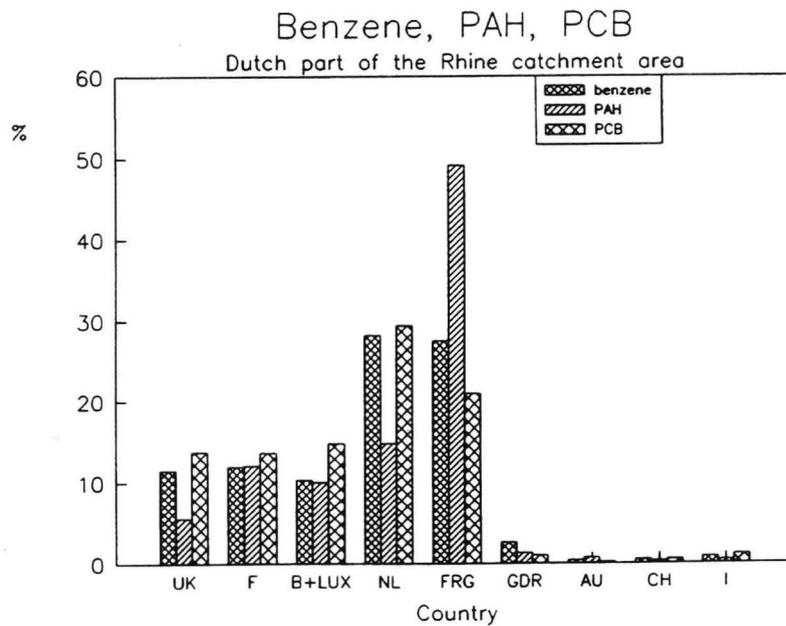
Contributions from other countries do not exceed the 7% level (see figure 7).

#### **Dutch area**

Although Dutch emissions do not contribute significantly to the deposition on the total Rhine catchment area, they are the main contributor (30% of the total deposition) to the deposition on the Dutch part of the area of study (1.3 ton/year), followed by a contribution from West German emissions of about 20% and contributions from Belgium, UK and France (about 14% each) (see figure 8).



**Figure 7** Benzene PAH and PCB. Relative contributions of the surrounding countries to the total deposition on the Rhine catchment area.



**Figure 8** Benzene, PAH and PCB. Relative contributions of the surrounding countries to the total deposition on the Dutch part of the Rhine catchment area.

## Pesticides

Although pesticides are widely used, their emission to the atmosphere and behaviour in there are not well studied. Consequently, various assumptions have been made to make these deposition calculations possible.

First of all, on the atmospheric behaviour of these compounds is very scarce, most data used in this study was estimated on basis of the compound structure and is probably reliable within order of magnitude only.

Secondly, although all the pesticides are brought into the environment, the fraction of the amount used which is emitted to the air is dependent on a large number of factors which might differ in various areas and during the year. Temperature, soil composition, humidity, way of application etc., all influence the actual emission.

The use of the compound is also often not known for countries other than the Netherlands (and Denmark). Use in other European countries is often extrapolated from the applications and consumption in the Netherlands. Especially the accuracy of emission estimates for France and West Germany, who have large agricultural areas in or near the Rhine catchment area, are important. In general it can be assumed that application and use in France and West Germany will be comparable to the Dutch use. When known, major differences between use in the Netherlands and other countries (parathion, PCP) have been taken into account.

The geographic location of the pesticides emissions to the agricultural areas is obviously a reasonable one for compounds with in general applicability in agriculture (lindane, atrazine, endosulfan, simazine, bentazone, parathion). However it might not be correct for pesticides which are mainly used on a specific culture (maize and potatoes) which need not be divided evenly over the agricultural areas (fentin, dichloropropene, azinphos-methyl, trifluralin).

As dichlorvos and pentachlorophenol have a large domestic application, geographical distribution of the emissions is related to the population distribution.

The nature of the use of pesticides is such that they are often used during only a part of the year. Emission of the pesticide will occur mainly during and in the first weeks after the application. The meteorological conditions in that time can be very different from the yearly averaged meteorological conditions used in this study.

Results of these deposition calculations should therefore be considered as tentative estimations only.

The deposition results for about 90% from Rhine states and surrounding countries.

The results for the pesticides atrazine, bentazone, endosulfan, lindane, parathion and simazine, of which the emissions have been estimated by using a default value related to the total agriculture area, (see Figure 9) show a constant picture of the relative contributions.

The large area of agriculture in France, combined with prevailing western winds, cause French emissions to be responsible for a major part (about 40%) of the deposition of these pesticides, followed by emissions from West Germany (about 30%)\* .

The results for the other pesticides are more varied (see Figure 10). Large potato cultures in West Germany, the Netherlands and East Germany cause the deposition of the potato culture related pesticides (fentin and 1,3-dichloropropene) to stem mainly from emission of these countries.

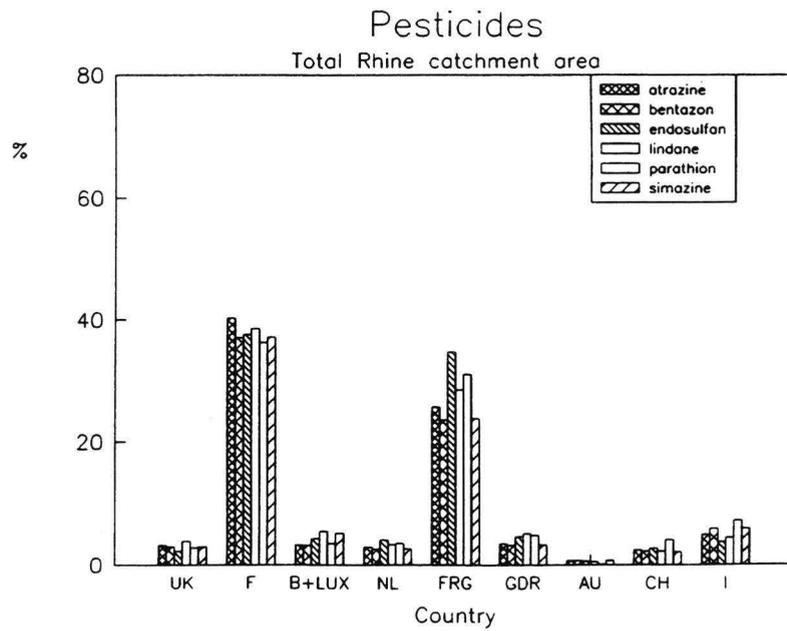
The short atmospheric lifetime of trifluralin results in a relatively low total deposition. As long range transport of this compound is very limited, deposition is caused by emission close to or in the receptor area. A large relative contribution is therefore made by West German emissions.

The use of PCP in France is known to be much higher (at least a factor fifteen) than in the surrounding countries, where the use is prohibited or very low. French emission are therefore mainly responsible for the deposition on the Rhine catchment area.

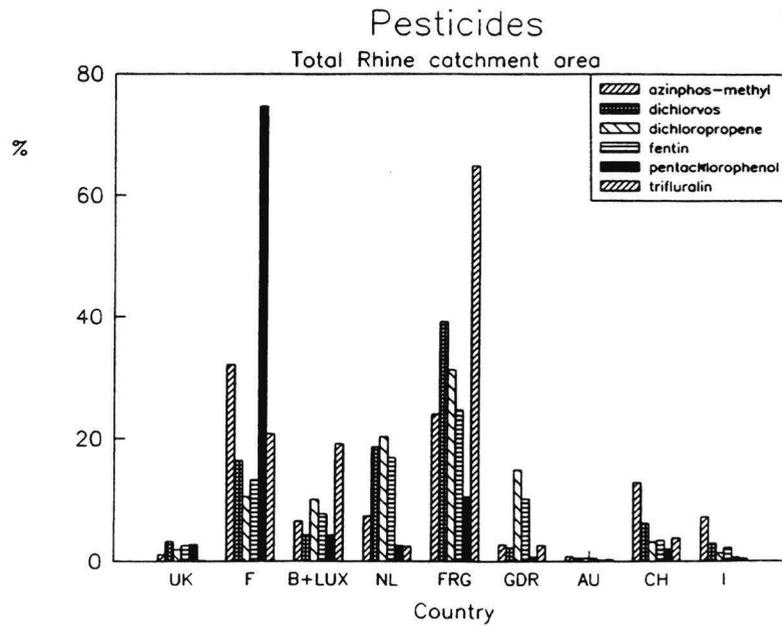
The relatively large use of dichlorvos in the Netherlands (caused by application in greenhouses) makes the Dutch emissions a relative important contributor to the total deposition (20%), preceded however by West German emissions.

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\* After this study was performed, new information has become available on the use of pesticides in the Rhine catchment area, which is discussed briefly in Appendix A7. This information indicates a lower contribution of France for the pesticides bentazone, endosulfan, parathion and azinphos-methyl. The relative contribution of France for the pesticides atrazine and simazine might be an underestimation as is the case for the West-German contribution to the deposition of azinphos-methyl. The Dutch contribution to the deposition of parathion, simazine and endosulfan might be underestimated. The total deposition of simazine and atrazine might be underestimated, the deposition of parathion, bentazone, fentin, trifluralin and endosulfan might be overestimated by at most a factor two.



**Figure 9** Pesticides, related to the total area of agriculture. Relative contributions of the surrounding countries to the total deposition on the Rhine catchment area.



**Figure 10** Pesticides, related to specific cultures. Relative contributions of the surrounding countries to the total deposition on the Rhine catchment area.

## Dutch area

Deposition on the Dutch part of the receptor area of pesticides, related to the total agricultural area, is caused mainly by French emissions followed by emission from the Netherlands itself.

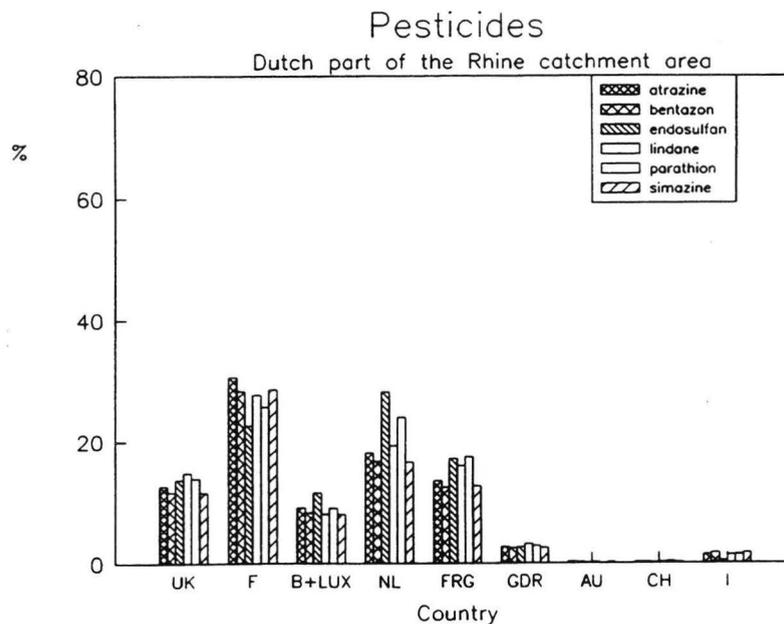
Dutch emissions are the main contributor (60-70%) to deposition for the pesticides, applied potato cultures (fentin and 1,3-dichloropropene) and for dichlorvos which has a large application in Dutch greenhouses.

Also the depositions of trifluralin is, due to its short atmospheric lifetime, caused for a major part by Dutch (40%) and West German (32%) emissions (see figures 11 and 12).

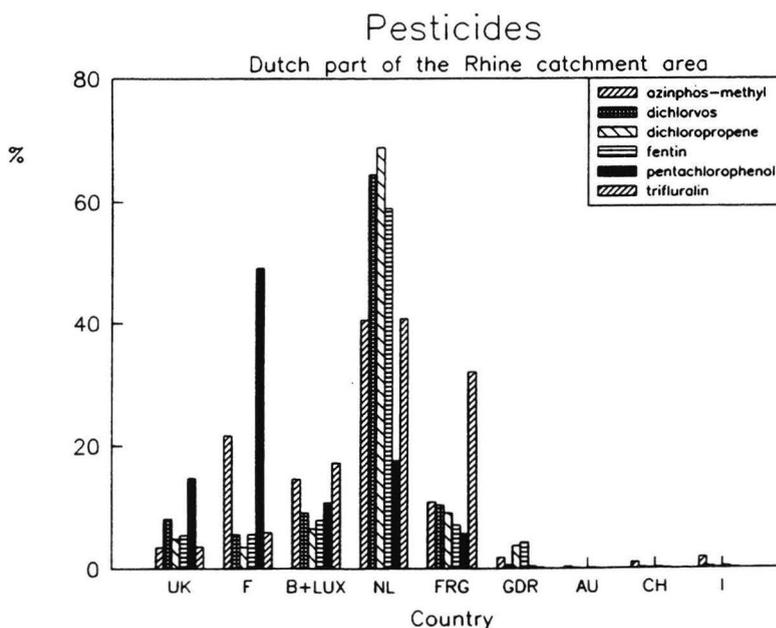
## The Netherlands

The deposition of bentzone, pentachlorophenol and simazine on the Netherlands is dominated by contributions from French emissions (30-50%). The deposition of azinphos-methyl, dichlorvos and trifluralin is caused mainly by Dutch emissions of these compounds (35-60%).

The contributions from emissions from the UK, Belgium and Luxembourg and West-Germany lie in the range of 10%. Contributions from other countries do not contribute significantly to the deposition on the Netherlands.



**Figure 11** Pesticides, related to the total area of agriculture. Relative contributions of the surrounding countries to the total deposition on the Dutch part of the Rhine catchment area.



**Figure 12** Pesticides, related to specific cultures. Relative contributions of the surrounding countries to the total deposition of the Dutch part of the Rhine catchment area.

## Nitrogen compounds

The OPS-model is developed for dispersion calculations of compounds that are chemically stable or are destroyed by photolysis or reaction with hydroxyl radicals resulting in first order chemical decay processes. Nitrogen compounds, especially the oxidized nitrogen compounds like NO and NO<sub>2</sub> and their reaction products, have a complex chemical behaviour which could not be incorporated in the OPS model. To achieve an assessment of the deposition of nitrogen compounds on the Rhine catchment area, results of model calculations by ECE-EMEP and RIVM have been taken from literature.

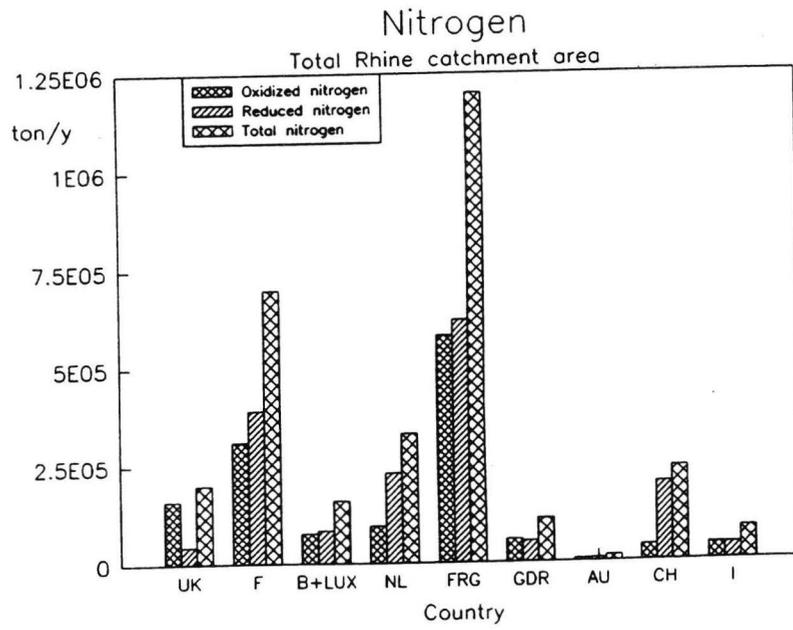
In a recent study calculations are made for atmospheric nitrogen budgets for Europe with the use of the EMEP model (Iversen et al., 1990). The calculations are carried out for the year 1988. In their study, for the whole European area, the deposition of reduced (NH<sub>x</sub>) and oxidized (NO<sub>y</sub>) nitrogen in a 150 km by 150 km grid was calculated. The total deposition and the contribution of individual countries were given.

In this study the deposition on the Rhine catchment area has been calculated by integrating the deposition on the individual EMEP grids and grid sections located in the Rhine catchment area. In table 3 the depositions of total nitrogen as well as the deposition of reduced and oxidized nitrogen is given. In figure 13 the relative contributions of the surrounding countries to the deposition are given. From the total nitrogen deposition of  $3.4 \cdot 10^5$  ton N/y on the Rhine catchment area,  $1.84 \cdot 10^5$  ton N/y is in the form of reduced nitrogen and

1.58  $10^5$  ton N/y is in the form of oxidized nitrogen. The sources of oxidized nitrogen (e.g. electricity production, traffic, industrial and domestic heating) have about the same geographical distribution as the overall industrial activity. Therefore the contribution of the individual countries is comparable with that of industrially emitted compounds like benzene. The reduced nitrogen is emitted in the form of ammonia by manure from live stock, mainly cattle. The deposition of nitrogen consist of about equal amounts of reduced nitrogen and oxidized nitrogen. In the contribution of countries with high ammonia emissions like the Netherlands and Switzerland the reduced form is dominant. In that of the United Kingdom the oxidized form is dominant.

The EMEP grid is too coarse to estimate the deposition of nitrogen compounds on the Dutch section of the Rhine catchment area. In the framework of the Dutch Priority Program on Acidification, RIVM calculated the deposition of nitrogen in the Netherlands (Schneider et al., 1991). The calculations were made with the TREND model. In an intercomparison study it was concluded that the EMEP model results in about a factor two lower values of the nitrogen deposition in the Netherlands than the values calculated by the TREND model. The values of the TREND model are more in agreement with observed values (Derwent et al., 1989).

The deposition of reduced nitrogen, oxidized nitrogen and the sum of both are given in table 3 and figure 13. The results are calculated by integrating the deposition on the individual so called PAWN-districts in the Dutch section of the Rhine catchment area. The geographically defined deposition densities calculated with the TREND model are taken from (Schneider et al., 1991). The nitrogen deposition of  $30.6 \cdot 10^3$  ton N/y on the Dutch section of the Rhine catchment area is mainly in the form of reduced nitrogen (68%).



**Figure 13** Relative contributions of the surrounding countries to the total nitrogen deposition on the Rhine catchment area.

## 5. NON-ATMOSPHERIC INPUTS

As the river Rhine flows through a very densely populated area (around 42 million inhabitants in the Rhine catchment area), with a very high degree of industrialisation, direct inputs of contaminants from these sources will significantly influence the water quality of the Rhine.

An estimation of the direct inputs of several contaminants in the Rhine has been made in IKSR (1989). In the IKSR study, the input into the river Rhine was estimated on basis of the inputs from industrial, communal and diffuse sources. The estimations of the input were provided by State authorities. The direct input from diffuse sources also include a rough estimation of the input through deposition.

As this study has provided more detailed and reliable data on the atmospheric deposition we have compared the atmospheric deposition with the direct input into the Rhine caused by industrial and communal sources (see Table 5).

To get an indication of the relative contribution of atmospheric deposition to the total loading of the Rhine, we have compared the estimated direct inputs from industrial and communal sources (IKSR, 1989) with the atmospheric deposition directly on water. In the estimation of the direct input in the Rhine, the run off from agricultural use of some compounds has not been included.

There was no specific data available on the total water surface area of the Rhine catchment area and its geographical distribution.

According to an estimation of the RIZA (RIZA, 1991) around 3.3% of the total Rhine catchment area consists of water. Deposition on these water surfaces is thought to directly influence the Rhine water quality.

A detailed study of the substance flows in relation to the disposal of waste water in the Netherlands (Baars, H.P. 1989) has shown that the amount of deposited contaminants which eventually will reach the Rhine is about twice the input caused by direct deposition into the Rhine.

This fraction however is dependent on the amount of paved surfaces, discharges from rainwater sewers, overflow from sewers to the water course and the amount and types of sewage treatment plants. As this information was not available for the Rhine catchment area, we have not taken this indirect atmospheric deposition into account. This will result in an underestimation of the input through atmospheric deposition of at least a factor two or more.

We compared the estimated direct input from industrial and communal sources with the direct deposition on water surfaces (estimated to be 3.3% of the total area). The results are given in table 5.

**Table 5** Comparison of atmospheric deposition to direct input by industrial and communal sources into the river Rhine.

Compound	Deposition on 3.3% of the Rhine catchment area ton/year	Direct input into the Rhine by industrial and communal sources ton/year
Atrazine	5.6	n.a. <sup>1)</sup>
Azinphos-methyl	0.05	n.a.
Bentazone	1.9	n.a.
Benzene	17.2	23.9
Cadmium	0.7	6.1
Chromium	3.3	519.1
Dichlorvos	0.2	n.a.
1,2-Dichloropropene	2.6	n.a.
Endosulfan	0.4	0.002
Fentin	2.5	n.a.
Copper	4.0	421.3
Mercury	0.6	1.9
Lindane	1.4	n.a.
Lead	62.7	241.0
Nickel	4.3	360.2
PAH	1.5	n.a.
Parathion	1.7	0.02
PCB	0.9	3.3
Pentachlorophenol	8.6	1.8
Simazine	0.3	n.a.
Trifluralin	0.1	n.a.
1,2-Dichloroethane	2.1	556.8
1,1,1-Trichloroethane	24.1	6.0
Tetrachloromethane	0.1	17.6
Chloroform	0.4	107.8
Trichloroethene	9.2	12.9
Tetrachloroethene	3.6	13.6
Zinc	49.5	2019.6
Total nitrogen (ton N/y)	$1.1 \cdot 10^4$	$3 \cdot 10^5$

1) n.a. = no data available

The pollutants can be divided in three categories:

- I atmospheric deposition dominates the input
- II atmospheric deposition might be important to the input
- III atmospheric deposition does not contribute significantly to the total input.

- Category I : endosulfan, parathion, pentachlorophenol, 1,1,1-trichloroethane
- Category II : benzene, cadmium, mercury, lead, PCB, trichloroethene, tetrachloroethene
- Category III : chromium, copper, nickel, 1,2-dichloroethane\*, tetrachloromethane\*, chloroform\*, zinc, nitrogen.

No comparison could be made for the following compounds:

the pesticides: atrazine, azinphos-methyl, bentazone, dichlorvos, 1,2-dichloropropene, fentin, lindane, simazine and trifluralin, and PAH.

For most pesticides no data was available on the direct input into the Rhine by industrial and communal sources. For those pesticides for which this data was available, atmospheric deposition is the dominating process in the contamination of the Rhine. In analogy with endosulfan, parathion and PCP, the other pesticides belong most likely in category I. Of the metals, chromium, copper, nickel and zinc are thought not to contribute significantly to the contamination of the Rhine through atmospheric deposition.

1,2-Dichloroethane, tetrachloromethane and chloroform are classified as category III compounds. This is due to not taking into account the contribution to the deposition from the background concentration nor the European contribution to the background concentration. Otherwise these compounds would probably be filed in category II or even category I.

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\* When not taking the atmospheric background concentration into account.

## 6. CONCLUSIONS

- The uncertainty of the results of the model calculations depends on the uncertainty in the input data: mainly on the emission data and the chemical and physical properties (i.e. the atmospheric behaviour) of the compounds. The validity of the results of the model calculations is therefore not equal for the different compounds. Model assumptions and uncertainty in the meteorological data will only be of importance to the uncertainty of the results if both emission and atmospheric behaviour of a compound is well known, which is the case for the metals studied here.

For the chlorinated hydrocarbons, benzene and PCB, the emissions are reasonably well known as are the degradation rates in the atmosphere. Large uncertainties remain with the deposition parameters. Uncertainty remains with the emissions of PAH, which are probably an underestimation and the atmospheric behaviour of PAH. Large uncertainties remain on all the input data for the pesticides. Very little data exists on both emissions as well as atmospheric behaviour of those compounds.

- The influence of uncertainties in the input data and model assumptions on the results will be larger when the receptor area is small. Therefore the uncertainty in the total deposition on the Rhine catchment area will be less than in the deposition on the Netherlands, which will be less than on the relatively small Dutch part of the Rhine catchment area.
- In the model calculations emissions from outside Europe are not taken into account. For some compounds, however, background concentrations are known to exist, especially for chloroform and tetrachloromethane and to a lesser extent for 1,2-dichloroethane, benzene, PAH and PCB. As in this study the deposition is calculated on basis of European emissions and neither a background concentration nor the European contribution to the background concentration is taken into account, the calculated deposition of these compounds will be an underestimation of the actual deposition.
- In general the countries of the Rhine catchment area and surrounding countries are responsible for over eighty percent of the deposition. The contributions from countries further away (Spain, Greece, the Scandinavian countries and Eastern European countries) is relatively small. This indicates that the uncertainty in the Eastern

European emissions will not bear much influence on the calculated deposition on the Rhine catchment area.

- The total deposition of individual compounds on the total Rhine catchment area varies from some tons per year to several thousands of tons per year.

West-German emissions are the major contributor to the deposition on the Rhine catchment area of those compounds which are related to industrial activity or population density.

French emissions are the major contributor to the deposition of seven pesticides, caused by a combination of high emissions\* and the large agricultural activities in the north of France combined with prevailing western winds in that area.

- The total deposition on the Dutch part of the Rhine catchment area varies from several tens of kilos to some hundred tons per year.

On the Dutch part of the Rhine catchment area the contribution from Dutch emissions to the deposition is much larger than on the total Rhine catchment area.

Dutch emissions here are in general one of the major contributors and for nine compounds even the major contributor to deposition on the Dutch area.

The emissions from Belgium and Luxembourg are a major contributor to the deposition of metals on the Dutch area.

- The relative contributions of the countries to the deposition of the compounds on the Netherlands are comparable with those to the deposition on the Dutch part of the Rhine catchment area.

- The total deposition directly on water surfaces in the Rhine catchment area has been compared to an estimation of the direct input into the river Rhine by industrial and communal sources.

The contribution to the contamination of the Rhine through indirect atmospheric deposition (like effluent water from unpaved and paved surfaces, discharges from rain water sewers, overflow from sewers to the water course etc.) has not been taken into account. The calculated contribution from atmospheric deposition to the contamination of the Rhine water is therefore an underestimation of the input of at least a factor two.

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\* Information which has become available after this study was performed, indicate lower French and West-German emissions, see §4.3 and Appendix A7.

For at least eleven compounds atmospheric deposition dominates or plays a significant role in the contamination of the Rhine.

For four compounds atmospheric deposition does not contribute significantly to the input of these contaminants to the Rhine. For ten compounds (mainly pesticides) no comparison could be made due lack of information on the direct input into the Rhine by industrial or communal sources.

## 7. RECOMMENDATIONS FOR FUTURE RESEARCH

It has become clear in this chapter that there are still many uncertainties concerning the estimates of atmospheric inputs to the Rhine catchment area.

In this paragraph we wish to list the most important subjects that should be studied to improve our estimates:

- The emission data for most of the pollutants are very uncertain especially those used for the pesticides. Setting up databases in an international cooperation on a European scale could solve this problem and would result in a better consensus about emission data.
- The deposition parameters of many pollutants are not well known. Only measurements of dry and wet deposition parameters will meet this lack. Meanwhile, it is recommended to develop better methods to estimate these parameters especially as to the influence of the surface (water or soil).
- A priority ranking for further research can be achieved by a sensitivity study of the uncertain parameters and their effects on the model results. The incorporation of a surface dependent deposition velocity can be investigated.
- Measurements of long term averaged concentration fields over the Rhine catchment area have to be added to validate model calculations.

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## APPENDIX A EMISSIONS OF SELECTED COMPOUNDS INTO THE ATMOSPHERE OVER EUROPE

### A1 Metals

Emission factors depend on combustion and process technology and operating conditions. This may explain the spread in these factors, e.g. for hard coal power plants in individual European countries, as reported by Pacyna. The average emission factors and the emissions in European countries estimated from the national consumptions with these factors presented by this author are listed in Tables A1 and A2, respectively. They refer to the year 1979.

*Table A1 Emission factors of some trace elements in g.ton<sup>-1</sup> (produced or incinerated) (Pacyna, 1984).*

Activity	Trace element					
	Cd	Cr	Cu	Ni	Pb	Zn
Hard coal power plants <sup>1)</sup>	5-20	82-334	61-278	94-381	53-216	77-311
Non-ferrous metal production						
(primary) copper-nickel	200		2500	9000	3090	845
zinc-cadmium	500		140		2540	15720
lead	5		72	85	6360	110
(secondary) copper	4		150		134	1610
lead	2.5				770	300
Steel production	0.1	40.5 <sup>3)</sup>	4.5	0.9	38.5	27
Sinter production	0.08					
Refuse incineration						
(municipal incinerators)	2.25	1.06	3.68	0.33	17.57	260.4
(sewage sludge incinerators) <sup>2)</sup>	11.8	9.7	58.3	1.0	138.9	104.2
Phosphate fertilizer production	1.8		5.1	5.1	0.42	15.2
Cement production	0.04	1.6			1.8	

1) in  $\mu\text{g.MJ}^{-1}$ ; different values for different countries

2) in  $\mu\text{g.ton}^{-1}$

3) for steel and alloy production

**Table A2** Emissions of some trace elements in European countries (tons.y<sup>-1</sup>)  
(Pacyna, 1984; Van Jaarsveld et al./PEO, 1986; VROM, 1989)

Country	Author 1)	Trace element						
		Cd	Cr	Cu	Hg <sup>3)</sup>	Ni	Pb	Zn
Albania	P	1.0	5	71	0.6	92	134	72
Austria	P	137	200	134	1.1	184	1933	4370
Belgium/Luxemb.	J	22	103	240	12.6	125	2376	1093
Bulgaria	P	67	181	288	8.6	291	2234	1722
Czechoslovakia	P	23	791	323	14.9	472	1726	635
Denmark	J	2.4	7.1	17	2	57	440	420
Finland	P	84	115	246	3	237	1621	2460
France	J	40	130	170	16.7	350	6200	3600
Germany, D.R.	J	6.2	52	122	23.7	151	1203	482
Germany, F.R.	J	78	260	460	41.3	290	5400	6900
Greece	P	4	77	55	1.5	273	1303	121
Hungary	P	8	198	509	2.9	162	888	280
Ireland	P	1	11	13	0.2	65	456	33
Italy	P	124	1055	385	10.8	1300	9365	4420
Netherlands, the	V	4.2	5	19	8.8	53	1390	236
Norway	P	39	40	56	1.3	66	803	1188
Poland	J	45	121	494	39.8	180	2650	2854
Portugal	P	3	27	29	2.6	97	525	39
Romania	P	13	619	228	16.1	338	1827	614
Spain	P	126	571	565	9.3	510	5534	3255
Sweden	P	16	195	237	7.3	323	2270	346
Switzerland <sup>4)</sup>	P	1	40	18	6	51	1680	640
United Kingdom	J	22	127	210	37.6	300	5900	2100
U.S.S.R. <sup>2)</sup>	P	421	3691	3375	52.3	6014	22644	10922
Yugoslavia	P	65	205	287	6.4	284	2423	2013

1) J: Van Jaarsveld et al./PEO; P: Pacyna; V: VROM

2) In the area of study

3) From Pacyna (1989)

4) Emissions of cadmium, mercury, lead and zinc are given by Swiss authorities.

For mercury the following emission factors have been presented referring to primary non-ferrous metal production:

Pb	: 3 g Hg/ton Pb
Zn	: 8 g Hg/ton Zn
Lignite combustion in electric power plants	: 10-42 $\mu$ g/MJ
Wood combustion	: 0.2 g Hg/ton wood
Chlor-alkali plants	: 5.2 g Hg/ton production capacity

More recent estimates by Pacyna (1985) led to lower values of the emissions. Because of that, and as the emission factors originally were higher than other literature data referring to the European community (Hutton, 1983), Van Jaarsveld et al. (1986) corrected Pacyna's original data (1983) for some European countries. Corresponding data with data for some other countries have been presented in a study of PEO in the same year (1986). For the Netherlands Pacyna's data have been replaced by values provided by the Dutch Ministry of Housing, Physical Planning and Environment (VROM, 1989).

Pacyna's data on the Swiss emission of cadmium, mercury, lead and zinc have been replaced by values provided by the Swiss delegation in the Kd-committee of the IKSR (Internationale Kommission zum Schutze des Rheins gegen Verunreinigungen).

## A2 CHLORINATED HYDROCARBONS

Estimated emissions presented per country are given in Table A3. For this purpose contributions from diffuse sources and point sources have been added up per country. The emissions are based on country data. For the Netherlands, the data given by VROM have been chosen.

### A2.1 Carbon tetrachloride (tetrachloromethane) (CCl<sub>4</sub>)

Generally no additional information was available to update the Criteria Document (emission 410 tons.y<sup>-1</sup> in 1981). In the STRAVERA project (Baars, H.P. 1989) an emission of 418 tons.y<sup>-1</sup> is given; the value presented by VROM is about half as large (200 tons.y<sup>-1</sup>). The main source in the Netherlands is the pharmaceutical industry and pesticides manufacturing. On a per capita basis the value of production of these branches in West European countries seems not to differ more than a factor of two compared to this country. The only exception is Switzerland because of its large pharmaceutical industry. Therefore CCl<sub>4</sub> emissions other than from its productions and from freon manufacturing were estimated with an overall figure of 12 g.cap<sup>-1</sup>.y<sup>-1</sup> and 30 g.cap<sup>-1</sup>.y<sup>-1</sup> for Switzerland. For Denmark this will be an overestimation as, according to the Danish authorities, the net import of carbon tetrachloride in 1987 amounted to only 4 tons. The consumption per inhabitant derived from this figure (0.8 g.cap<sup>-1</sup>.y<sup>-1</sup>) is much lower than the value assumed here.

### A2.2 Chloroform (CHCl<sub>3</sub>)

Except for the Netherlands, Norway, Switzerland and Denmark (letters from the authorities) no additional information was available for updating the results of the Criteria Document. In this document the emission in the Netherlands was estimated to be 218 tons.y<sup>-1</sup> in 1981 and was expected to be reduced to about 148 tons in 1985. VROM estimates it to be 70 tons.y<sup>-1</sup>. This last value was used for the Netherlands; for the other European countries the estimate was based on the Criteria Document, but the following choices of parameters for spatial distribution of emissions were adapted:

- Chlorination of potable water was used for a high estimation.
- Chlorination of swimming pools was arbitrarily used for a high estimation.

- Chlorination of cooling water was taken into account with 0.5 kg per 100 MW per day or 1.8 tons.GW<sup>-1</sup>.y<sup>-1</sup>. Distribution with installed thermal capacity.
- Chlorination of waste water effluents was not taken into account.
- Emissions from road transport were extrapolated with gasoline consumption data. For East European countries the fractions used in 2-stroke engines and trucks were assumed to emit one-third of reported emissions.
- Emissions from chemical industry were estimated to be 3 g.cap<sup>-1</sup>.y<sup>-1</sup>, to be multiplied with a factor that more or less takes into account the involvement of chemical industry in national economics: contribution of wood, paper and chemicals to total manufacturing value (Britannica Book of the Year, 1988). This factor varies between 0.1 and 0.8 (the Netherlands = 1). For Sweden and Finland these figures were halved, for East-European countries Alperowicz and Cox (1981) were consulted. Data on chloroform manufacturing and freon production are from the Criteria Document. These emissions have been added to the emissions from diffuse sources.

According to the Norwegian authority 6 tons of chloroform was sold in Norway in 1982, which corresponds with 1.5 g.cap<sup>-1</sup>.y<sup>-1</sup>. Consumption in Denmark will probably be lower, as in 1987 the reexport of chloroform was larger than the import (no chloroform manufacturing industry is known).

The data which have been presented in Tables A3 and A4 for these countries may therefore be overestimations.

### **A2.3 1,2-dichloroethane (CH<sub>2</sub>ClCH<sub>2</sub>Cl)**

The main use of this substance is for the production of vinyl chloride monomer which is used for PVC manufacturing. Emissions therefore are localized at production sites. Starting from the Criteria Document its data were updated and completed with COMECON data.

All available data on production capacity, production, import and export of dichloroethane (DCE) and vinyl chloride and on capacity and production of PVC per country were analysed for an estimation of 1985 DCE production per site. Sites were taken from Chemfacts and, for COMECON countries, from various sources, mainly from Alperowicz and Cox (1981). Capacities, production and trade data were taken from the UN statistics.

The emission factors used in the Criteria Document reportedly were taken from American publications: 10 kg.t<sup>-1</sup> (controlled) and 40 kg.t<sup>-1</sup> (uncontrolled). No reference was given.

In an EPA publication from 1978, factors (in  $\text{kg.ton}^{-1}$ ) are given for various levels of control that could be attained with incineration of vent gases. No control had been demonstrated at the time:

	<i>no control</i>	<i>99% control</i>
direct chlorination	2.4	0.03-0.04
oxychlorination	25-70	0.25-0.7
storage	0.6	

Recently, emission factors have been proposed in the framework of NAPAP in order to replace unknown by - at least - default values. For DCE factors are given as follows (Stockton et al., 1987):

oxychlorination : 12  $\text{kg.ton}^{-1}$  (based on a single VOC value)  
 direct chlorination : 0.65  $\text{kg.ton}^{-1}$  ( , , )  
 fugitive emissions : 82  $\text{tons.process unit}^{-1}.\text{y}^{-1}$

From the Emission Registration project a factor of  $0.3 \text{ kg.ton}^{-1}$  (oxychlorination) can be deduced. In 1985 its value was  $1.5 \text{ kg.ton}^{-1}$ .

Obviously it is difficult to propose factors straightforwardly from these data. For this study the following values are taken:

direct chlorination : 0.5  $\text{kg.ton}^{-1}$   
 oxychlorination : 1  $\text{kg.ton}^{-1}$   
 East European plants : 2  $\text{kg.ton}^{-1}$   
 fugitive emissions : 80  $\text{tons.process unit}^{-1}.\text{y}^{-1}$

As a representative size for a process  $200 \text{ ktons.y}^{-1}$  is taken (Slooff and Tangena, 1987). For the Netherlands, VROM estimates the emission to be  $1100 \text{ tons.y}^{-1}$ . This value has been used.

#### **A2.4 1,1,1-trichloroethane (CH<sub>3</sub>CCl<sub>3</sub>)**

For this solvent no Criteria Document has been produced. Therefore the study by CEFIC (1986) and some additional data sources were the basis of the emission estimation. Maximum values for the total emissions are 139 and 37 ktons for West and East Europe respectively. The emission estimation for Switzerland was given by: Der Schweizerische Delegation in der Untergruppe Kd der Internationale Kommission zum Schutze des Rheins gegen Verunreinigung. Since consumption estimates for West Europe reportedly are 155 ktons (sales, constant from 1979 through 1984) (CEFIC, 1985) and 150 ktons (Whim, 1984) it is assumed that the results of this study are realistic.

#### **A2.5 Tetrachloroethene (CCl<sub>2</sub>CCl<sub>2</sub>)**

With the available information West European national consumption data could be estimated. No attempt was made to estimate differences in accuracy between national data. For COMECON countries no quantitative information was available which made it necessary to adopt default values by comparison with the OECD-European pattern. For Czechoslovakia and the DDR a higher figure was used because of the higher economic activity of these countries. It should be emphasized however that this is only a rough estimate.

The use of tetrachloroethene is mainly in dry cleaning. The exception of the FRG - metal degreasing - may be out of date in view of the large difference between the 1981 and 1984 consumption data. The emission estimation for Switzerland was given by: Der Schweizerische Delegation in der Untergruppe Kd der Internationale Kommission zum Schutze des Rheins gegen Verunreinigung

A difference exists in the fraction of consumption released into the air. According to the Criteria Document this fraction is ca. 0.7; CEFIC (1986) mentions 0.6. Therefore to the maximum emissions are added estimated values which are 70 % of these, yielding 112 ktons and 53 ktons for West Europe and East Europe, respectively. The Criteria Document reports 177 ktons for West-Europe and CEFIC (1986) reports 90 ktons. The latter figure is only 6 % lower than the result of this study, taking into account the difference in the released fractions. For the Netherlands the value given by VROM.

## A2.6 Trichloroethene (CHCl<sub>3</sub>)

The emission estimation procedure of this substance is almost identical to that used for tetrachloroethene. The main applications of trichloroethene are in metal degreasing, dry cleaning and graphic arts. Therefore the input emission data are given in kg.cap<sup>-1</sup>.y<sup>-1</sup>, assuming a homogeneous spatial distribution of applications, proportional to population density.

The Criteria Document equals consumption and emission data and therefore the data, should be interpreted as maximum emissions. According to this table total emissions are 155 ktons for West-Europe and 72 ktons for East Europe (including Yugoslavia). The Criteria Document gives 219 ktons for West Europe (1981). CEFIC estimated emissions as 60 % of consumption and arrived at 96 ktons (1984), corresponding to a consumption of 148 ktons (without Spain and Poland). Whim (1984) quotes a CEFIC consumption estimate of 250 ktons (1980). The well-known downward trend in consumption is clearly illustrated, but the conflict remains about the fraction of consumption that is released. On the one hand there is the philosophy of consumption being identical to the make up of losses (no relation with recycling). On the other hand waste dumped or incinerated is taken into account. Since dumping (landfilling) is still more practiced than incineration and landfilling implies delayed release, the first option is considered to better reflect reality. However, real emissions actually may be somewhat lower than the maximum values. The emission estimation for Switzerland was given by: Der Schweizerische Delegation in der Untergruppe Kd der IKSr.

The value for the Netherlands taken here is 1940 tons.y<sup>-1</sup> (VROM) which is smaller than the emission according to the Criteria Document (2239 tons in 1982).

## A2.7 Results

The total emissions are shown in Tables A3. Data between parentheses are merely based on default values. The values given for the U.S.S.R refer to the area west of 38° EL (103. 10<sup>6</sup> inhabitants).

The data for trichloroethane, tetrachloroethene and trichloroethene are merely based on consumptions; for trichloroethane and trichloroethene the quantities emitted are assumed to be equal to these consumptions, whereas for tetrachloroethene the emissions are assumed to be 70 % of the consumptions.

Table A4 shows the emissions per inhabitant. Data between parentheses are default values. Note that the emissions of tetrachloromethane per inhabitant in the European countries

(except Switzerland) vary only slightly (between 12 and 18 g.y<sup>-1</sup>) because of the fact that for the dominating area sources in all countries the same default value has been taken.

**Table A3** Emissions of chlorinated hydrocarbons in European countries, in tons.y<sup>-1</sup>.

Country	Chlorinated hydrocarbons					
	Carbon tetra-chloride	Chloro-form	Di-chloro-ethane	Tri-chloro-ethane	Tetra-chloro-ethene	Tri-chloro-ethene
Albania	36	2	–	(300)	(450)	(600)
Austria	90	27	–	3400	2100	1000
Belgium/Luxemb.	180	47	850	5700	4100	3000
Bulgaria	110	21	500	(900)	(1400)	(1800)
Czechoslovakia	205	60	900	(3100)	(3100)	(4600)
Denmark	61	29	–	1000	500	2100
Finland	59	31	100	1000	600	1000
France	890	248	1400	32000	24500	32000
Germany, D.R.	230	92	450	(3400)	(3400)	(5100)
Germany, F.R.	920	402	2100	31000	28000	30000
Greece	120	30	–	900	900	2000
Hungary	130	20	600	(1100)	(1600)	(2200)
Ireland	43	13	–	–	900	600
Italy	850	213	1450	20000	22000	19000
Netherlands, the	200	70	1100	3380	4750	1940
Norway	49	13	350	1305	1200	800
Poland	440	90	600	(3700)	(5500)	(7400)
Portugal	120	18	150	1100	1400	2000
Romania	320	48	850	(2300)	(3400)	(4500)
Spain	570	110	600	4300	7000	13000
Sweden	100	37	350	4000	2800	10000
Switzerland	190	25	–	4500	7000	3400
United Kingdom	840	374	600	30000	11000	30000
U.S.S.R. <sup>1)</sup>	1240	270	1950	(10300)	(15500)	(20700)
Yugoslavia	280	43	400	(2300)	(3500)	(4600)

1) In the area of study.

**Table A4** Emissions per inhabitant of chlorinated hydrocarbons in European countries, in g.cap.<sup>-1</sup>.y<sup>-1</sup>

Country	Chlorinated hydrocarbon					
	Carbon <sup>2)</sup> tetra- chloride	Chloro- <sup>2)</sup> form	Di- <sup>2)</sup> chloro- ethane	Tri- chloro- ethane	Tetra- chloro- ethene	Tri- chloro- ethene
Albania	12	0.7	–	(100)	(150)	(200)
Austria	12	3.6	–	450	280	130
Belgium/Luxemb.	18	4.6	83	560	400	290
Bulgaria	12	1.8	56	(100)	(150)	(200)
Czechoslovakia	13	3.9	58	(200)	(200)	(300)
Denmark	12	5.7	–	200	100	410
Finland	12	6.3	20	200	120	200
France	16	4.5	26	580	450	580
Germany, D.R.	13	5.4	27	(200)	(200)	(300)
Germany, F.R.	15	6.6	34	510	460	490
Greece	12	3.0	–	90	90	200
Hungary	12	1.9	56	(100)	(150)	(200)
Ireland	12	3.6	–	–	250	170
Italy	15	3.7	25	350	380	330
Netherlands, the	14	4.9	76	230	330	130
Norway	12	3.2	85	320	290	200
Poland	12	2.4	16	(100)	(150)	(200)
Portugal	12	1.8	15	110	140	200
Romania	14	2.1	38	(100)	(150)	(200)
Spain	15	2.8	16	110	180	340
Sweden	12	4.5	42	480	480	1200
Switzerland	30	3.9	–	692	1077	523
United Kingdom	15	6.7	11	530	200	530
U.S.S.R. <sup>1)</sup>	13	2.6	19	(100)	(150)	(200)
Yugoslavia	12	1.9	17	(100)	(150)	(200)

1) In the area of study.

2) Emission factors calculated by dividing the total emission of a country by its number of inhabitants.

### A3 BENZENE

The emission factors presented by Huygen et al. (1987) are given in Tables A5 and A6. They are averages in which no distinction has been made e.g. between different types of vehicles, or between traffic in towns and that on motor ways.

Several data on emissions from combustions differ from those given by Huygen et al., as one of the authors (C. Veldt) presented us recently new values which he regards to be more reliable. For all countries the consumption of diesel by railways and ships is included.

The emission for Switzerland was given by: Der Schweizerische Delegation in der Untergruppe Kd der Internationale Kommission zum Schutze des Rheins gegen Verunreinigung (IKSR).

The emission fluxes from the different source types calculated from the consumption data and the above emission factors have been listed in Tables A7 and A8. The total emission fluxes (the sum of the figures in the last columns) are given in Table A9, together with the emission fluxes per inhabitant. It is seen that the total emission flux per inhabitant varies between 0.3 and 2.0 kg.cap<sup>-1</sup>.y<sup>-1</sup>.

**Table A5** Benzene emission factors for traffic in European countries (excl. Belgium/Luxemb., the F. R. Germany and the Netherlands). Emission factors for Belg/Lux., the FRGermany. and the Netherlands is more specifically given in Huygen (1987).

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Light duty cars:

Italy, Switzerland, United Kingdom	1.7	g.kg <sup>-1</sup> (gasoline)
Eastern Europe	1.8	g.kg <sup>-1</sup> (gasoline)
Sweden	2.5	g.kg <sup>-1</sup> (gasoline)
rest of Europe	2.0	g.kg <sup>-1</sup> (gasoline)
Fuel distribution	0.05	g.kg <sup>-1</sup> (gasoline)
Fuel evaporation	200	g.veh <sup>-1</sup> .y <sup>-1</sup>
Heavy duty cars	0.15	g.kg <sup>-1</sup> (Diesel)

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**Table A6** Benzene emission factor for other sources in European countries.

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refineries	2% of VOC emissions <sup>1)</sup>	Western Europe 0.01 g.kg <sup>-1</sup> (crude oil)
		Eastern Europe 0.04 g.kg <sup>-1</sup> (crude oil)
		USSR 0.18 g.kg <sup>-1</sup> (crude oil)
cokes factories	5% of VOC emissions <sup>2)</sup>	0.045 g/kg <sup>-1</sup> (cokes)
production of ethyl benzene (EB)		0.15 g.kg <sup>-1</sup> (EB)
production of cumene (CU)		0.30 g.kg <sup>-1</sup> (CU)
production of cyclohexane (CH)		0.25 g.kg <sup>-1</sup> (CH)
production of maleic anhydride (MA)		5.0 g.kg <sup>-1</sup> (MA)
domestic space heating		
by combustion of coal		1.0 g.kg <sup>-1</sup>
by combustion of lignite		0.5 g.kg <sup>-1</sup>
by combustion of light oil		0.01 g.kg <sup>-1</sup>
by combustion of wood		0.4 g.kg <sup>-1</sup> <sup>3)</sup>

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1) From: Schaff 1989, Sexton 1983, Edwards 1986

2) From: Schade 1980, Luftminhultung 1988, Dutch Emission registration project.

3) Value assumed based on results of Rudling, Ahling and Löfroth (1982) and of Den Boeft et al. (1984)

**Table A7** Emissions of benzene from traffic sources, in tons.y<sup>-1</sup>.

Country	Gasoline automobile	Diesel	Gasoline distribution	Gasoline evaporation	Total
Albania	360	48	10	54 <sup>1)</sup>	472
Austria	4810	226	120	494	5650
Belgium/Luxemb.	4669	436	145	689	5939
Bulgaria	3240	128	90	360 <sup>1)</sup>	3818
Czechoslovakia	3438	345	96	528	4407
Denmark	3026	205	76	288	3595
Finland	3014	211	75	295	3613
France	35552	1662	889	4638	42741
Germany, G.D.R.	6300	240	175	631	7346
Germany, F.R.G	32636	1922	1172	5044	40774
Greece	3472	223	87	231	4013
Hungary	2340	180	65	269	2854
Ireland	1682	85	42	142	1951
Italy	18875	1790	555	4078	25298
Netherlands, the					9196
Norway	3134	175	78	286	3673
Poland	5400	458	150	685	6693
Portugal	1708	187	43	421	2359
Romania	2484	285	69	437 <sup>1)</sup>	3275
Spain	11788	1014	295	1775	14872
Sweden	9375	236	187	616	10414
Switzerland					4000
United Kingdom	34685	1334	1020	3366	40405
U.S.S.R. <sup>2)</sup>	31950	938	888	1926	35702
Yugoslavia	4840	390	121	575	5926

- 1) Emission calculated from a number of vehicles which is estimated assuming an average gasoline consumption of 1000 tons.y<sup>-1</sup> per vehicle.
- 2) Data estimated with the assumption that 25 % of the total gasoline consumption is in the area of study. A larger consumption in the Asian part is assumed because of the relative large distances and because engines may often not be stopped because of cold.

**Table A8** Emissions of benzene from non-traffic sources, in tons.y<sup>-1</sup>.

Country	Crude	Cokes	Production of				Dom. space heating by combustion of				Total
			EB	CU	CH	MA	coal 1)	lignite 2)	oil	wood	
Albania	120	1	-	-	-	-	760	-	4	384	1269
Austria	120	79	-	-	-	-	350	415	9	2120	3093
Belgium/Luxemb.	330	268	51	-	20	10	203	-	34	128	1044
Bulgaria	520	49	2	9	-	-	2000	650	23	420	3673
Czechoslovakia	896	465	8	12	-	-	1370	15000	33	332	18116
Denmark	68	0	-	-	-	-	700	25	17	80	890
Finland	98	0	-	15	-	-	529	-	15	1000	3275
France	980	391	38	87	13	120	3800	75	-	2500	8004
Germany, G.D.R.	1180	57	-	-	-	-	0	12500	64	136	13937
Germany, F.R.G.	821	1045	107	87	40	195	500	1500	215	920	5430
Greece	140	-	-	-	-	-	4	55	8	460	667
Hungary	312	27	-	-	-	25	600	30	35	580	1609
Ireland	20	-	-	-	-	-	1169	850	1	8	2048
Italy	820	333	44	144	6	200	160	-	-	1840	3547
Netherlands											1117
Norway	68	14	-	-	-	-	23	-	3	600	1386
Poland	640	731	4	15	-	-	33000	-	21	840	35251
Portugal	55	12	-	-	-	-	5	-	-	1440	1512
Romania	840	213	4	14	-	-	2200	375	20	1080	4746
Spain	335	155	-	18	12	-	680	21	10	540	1771
Sweden	168	54	-	-	-	-	416	-	25	5200	5863
Switzerland											1000
United Kingdom	850	417	-	42	-	-	6500	-	5	40	7854
U.S.S.R. 3)	21080	1575	6	24	-	-	30000	750	276	8400	62111
Yugoslavia	980	160	5	-	-	-	2300	515	13	1000	4973

- 1) Because of its low emission factor the emission from anthracite is neglected. For countries where no separate consumption data on anthracite and other hard coal are known it is assumed that only a negligible part of the hard coal consumption refers to anthracite.
- 2) Including of briquettes.
- 3) In the area of study.
- 4) Data from the Dutch Emission Registration project.

**Table A9** Total emissions of benzene, population and emissions of benzene per inhabitant in European countries (1984).

Country	Total emission flux (tons.y <sup>-1</sup> )	Population (10 <sup>6</sup> Inh.)	Emission flux per inhabitant (kg.cap <sup>-1</sup> .y <sup>-1</sup> )		
			Traffic	Other	Total
Albania	1741	3.0	0.16	0.42	0.58
Austria	8743	7.5	0.75	0.41	1.17
Belgium/Luxemb.	6983	10.2	0.58	0.10	0.68
Bulgaria	7491	9.0	0.42	0.41	0.83
Czechoslovakia	22523	15.4	0.29	1.18	1.46
Denmark	4485	5.1	0.70	0.17	0.88
Finland	6888	4.9	0.74	0.67	1.41
France	50745	54.9	0.78	0.15	0.92
Germany, G.D.R.	21283	16.9	0.43	0.82	1.26
Germany, F.R.G.	46204	61.1	0.67	0.09	0.76
Greece	4680	9.9	0.41	0.07	0.47
Hungary	4463	10.7	0.27	0.15	0.41
Ireland	3999	3.6	0.54	0.57	1.11
Italy	28845	57.0	0.44	0.06	0.51
Netherlands, the	10313	14.4	0.64	0.08	0.72
Norway	5059	4.1	0.90	0.34	1.23
Poland	41944	36.9	0.18	0.96	1.14
Portugal	3871	10.0	0.24	0.15	0.39
Romania	8021	22.6	0.14	0.21	0.35
Spain	16643	38.5	0.39	0.05	0.43
Sweden	16277	8.3	1.25	0.71	1.96
Switzerland	5000	6.5	0.62	0.15	0.77
United Kingdom	48259	56.4	0.72	0.14	0.86
U.S.S.R. <sup>1)</sup>	98214	103.3	0.35	0.61	0.95
Yugoslavia	10899	23.0	0.26	0.22	0.47

1) In the area of study.

## A4 POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

Emission factors (of the six of Borneff PAH) for the different types of source, calculated from those of total PAH and the emission profiles according to Duiser and Veldt (1989), are given in Tables A10 and A11.

The PAH emissions by aluminium and coke production are localized at specific production sites.

The emission of PAH is divided in emission of volatile PAH and non-volatile PAH due to the different atmospheric behaviour of the two. The emitted fluoranthene and 50% of the emitted benzofluoranthenes are considered to be in the gaseous phase and are subjected to atmospheric chemical degradation reactions. The other 50% of the emitted benzofluoranthenes, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene are considered to exist only in the aerosol phase and to be stable under atmospheric conditions. Total emissions of the six of Borneff PAH are given in Table A13.

**Table A10** Emission factors of six PAH for different source types, in  $\text{mg.kg}^{-1}$  (Duiser and Veldt, 1989)

PAH	Residential combustion				Production of coke (uncontrolled)	Production of aluminium	
	antra-ciet	hard coal	brown coal briq.	wood		pre-baked anodes	Söderberg process
fluoranthene	0.1	6	2.3	12	1.4	7	220
benzo[b+k]fluoranthene	0.07	3	0.7	5	0.5	2.5	80
benzo[a]pyrene	0.01	2	0.25	3	0.5	0.6	20
benzo[ghi]perylene	0.01	1	0.35	3	0.3	0.3	30
indeno[1,2,3-cd]pyrene	0.01	2	0.85	3	0.3	0.1	5
total six of Borneff	0.18	14	4.45	26	3.0	10.5	355

*Table A11 Emission factors of six PAH for different source types, in mg.kg<sup>-1</sup> (Duiser and Veldt, 1989)*

PAH	Mobile sources	
	gasoline fueled	diesel fueled
fluoranthene	0.56	0.74
benzo[b+k]fluoranthene	0.14	0.19
benzo[a]pyrene	0.04	0.05
benzo[ghi]perylene	0.06	0.08
indeno[1,2,3-cd]pyrene	0.04	0.05
total six of Borneff	0.84	1.11

**Table A12** *Used or produced quantities as sources of PAH emissions in European countries, in 1000 tons.y<sup>-1</sup>.*

Country	Residential combustion				Transport		Industrial production		
	anthr.	hard c.	brown coal	wood	gasoline	diesel	aluminium		coke
							pre-baked	Söderberg	
Albania				960	200	320			20
Austria	1	350	830	5300	2405	1512		120	1751
Belgium/Luxemb.	1300	203		320	2804	2905			5964
Bulgaria		2000	1300	1050	1800	850			1087
Czechoslovakia		1370	30000	830	1910	2300		32	10340
Denmark		700	49	200	1513	1364			
Finland		529		2500	1507	1404			
France		3800	150	6250	17776	11081	80	215	8691
Germany, G.D.R.			25000	340	3500	1600		60	1257
Germany, F.R.G.	2400	500	3000	2300	23430	12814	490	255	23232
Greece		4	110	1150	1736	1488	145		
Hungary		600	60	1450	1300	1200		74	607
Ireland		1169	1700	30	841	564			
Italy		160		4600	11103	11920	220		7410
Netherlands	100		45	500	3392	2992	250		2973
Norway		23		1500	1567	1164	420	325	312
Poland		33000		2100	3000	3050		50	16239
Portugal		5		360	854	1245			275
Romania		2200	750	2700	1380	1900	245		4743
Spain		680	42	1350	5894	6758	170	200	3440
Sweden		416		13000	3750	1572		80	1203
Switzerland		25	31	900	3026	691	35	35	
United Kingdom	4200	6500		100	20403	8895	255	25	9276
U.S.S.R. <sup>1)</sup>		15456	775	10847	17750	6250		920	3500
Yugoslavia		2300	1030	2500	2420	2600	240	60	3545

1) In the area of study.

**Table A13** Emissions of total (six of Borneff) PAH in European countries, in tons.y<sup>-1</sup>.

Country	Emission flux (tons.y <sup>-1</sup> )
Albania	25.5
Austria	197.9
Belgium/Luxemb.	34.9
Bulgaria	66.8
Czechoslovakia	220.8
Denmark	18.0
Finland	75.2
France	346.8
Germany, G.D.R.	149.9
Germany, F.R.G.	279.9
Greece	35.1
Hungary	76.9
Ireland	26
Italy	168.9
Netherlands, the	30.9
Norway	162.7
Poland	589
Portugal	12.4
Romania	124.4
Spain	140.4
Sweden	380.7
Switzerland	40.0
United Kingdom	160.7
U.S.S.R. <sup>1)</sup>	955.2
Yugoslavia	141.2

1) In the area of study.

## A5 POLYCHLORINATED BIPHENYLS (PCB)

PCB may enter the environment during their production, use, and disposal by release into the air, water or soil. An estimate of possible routes of PCB into the environment of North America has been made by Nisbet and Sarofim (1972). According to the authors the emission into the atmosphere by vaporization amounted 10-20% of the sales for platicizing products.

From the data of Nisbet and Sarofim, Duiser and Veldt (1989) concluded that the emission of PCB into the atmosphere of the USA amounted about 1000 tons in 1970. In relation to the number of inhabitants it would be about  $4 \text{ g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$ . Since the production and consumption of PCB have been largely reduced in course of time the authors expect the emission will nowadays be no more than half this value. According to them emissions of PCB in European countries may be estimated from sales by using emission factors, relating the quantities dumped or incinerated to emitted quantities by using the following assumptions:

1. The emissions into the air only originate from vaporization from open systems containing small amounts of PCB which are still manufactured. The quantities of PCB which are used for these applications are equal to the annual sales of PCB which are not used for transformers and large capacitors (emission to air because of leakage or disposal of these objects are supposed to be negligible).
2. The quantities emitted from the products mentioned before are 7% of their PCB contents (half the value used by Nisbet and Sarofim). In other words, it is assumed that the remaining 93% is either destroyed by incineration or open burning, or is released to soil or water.
3. According to this assumption made by Nisbet and Sarofim 2% of this quantity is emitted by open burning (it is assumed that nowadays no capacitor or transformer fluids are subject to open burning). Together with the 7% this will give an emission of 9% of the PCB contents of the products mentioned before.
4. The emission of PCB in a certain area is proportional to its number of inhabitants.
5. Emissions from incineration of domestic refuse and from incineration of refuse liquids containing PCBs which have to be disposed of will be relatively small.

Annual production, domestic sales and exports in some OECD member countries of PCB for usage in transformers, large capacitors, and other applications have been presented by Bletchly (1984). From his results it follows that in the European OECD member countries

maximally 7500 tonnes of PCB may still be produced for use in open systems and small capacitors. It is assumed that this quantity serves to replace the present quantity. If 9% of this quantity is released into the air, the emission from open systems will be about 700 tonnes. With  $315 \times 10^6$  inhabitants the emission factor for vaporization from open systems is about  $2 \text{ g.cap}^{-1}.\text{y}^{-1}$ . This emission factor is half as large as that, calculated for the U.S.A. in the year 1970.

For this study we adopt the value of  $2 \text{ g.cap}^{-1}.\text{y}^{-1}$  for estimating the emission flux density. Emissions in European countries estimated in this way are given in Table A14.

**Table A14** *Populations of European countries and emissions of PCB estimated from them (by multiplying them with a factor of  $2 \text{ g.cap}^{-1}.\text{y}^{-1}$ ).*

Country	Population ( $10^6$ inh.)	Emission (tons. $\text{y}^{-1}$ )
Albania	3.0	6
Austria	7.5	15
Belgium/Luxemb.	10.2	20
Bulgaria	9.0	18
Czechoslovakia	15.4	31
Denmark	5.1	10
Finland	4.9	10
France	54.9	110
Germany, D.R.	16.9	34
Germany, F.R.	61.1	122
Greece	9.9	20
Hungary	10.7	21
Ireland	3.6	7
Italy	57.0	114
Netherlands, the	14.4	29
Norway	4.1	8
Poland	36.9	74
Portugal	10.0	20
Romania	22.6	45
Spain	38.5	77
Sweden	8.3	17
Switzerland	6.5	13
United Kingdom	56.4	113
U.S.S.R. <sup>1)</sup>	103.3	207
Yugoslavia	23.0	46

1) In the area of study.

## A6 PESTICIDES

Emissions of pesticides into air are caused by volatilization. They have been estimated by multiplying the emission flux density (the emission per unit of area and per unit of time) with the area of the region regarded.

In formula, the emission flux density (the emission per unit of area per unit of time) can be calculated from:

$$EFD = \sum P_i \cdot E_i$$

Since most of the emissions of pesticides involved in this study are due to their use in agriculture the emission flux density in a region (EFD) was estimated as the product of the application density (P) (the amount used per unit of area used for agriculture), the fraction of arable land and permanent crops in the region regarded, and the emission factor. In case that the pesticide was used only for one species of crop, the application density was related to the fraction of area used for its culture. Fractions of arable land and permanent crops and of some specific cultures per country are given in Table A15. These fractions (for two cultures given in Table A15) differ largely between the European countries. If no data are available for the separate emission grids, the fraction used for a certain culture was assumed to be equal to that of the country involved.

For pesticides the emission factor is the fraction volatilized during or after application.

Experiments on volatilization of pesticides have been made by several authors. Table A16 shows some results, they regard the losses from the crop after a period of about one month. From these data it follows that most (60-90 %) of the pesticide intercepted by the crop (which is usually less than a quarter to about half of the total quantity applied) is evaporated during the first month after application. This suggests that roughly a third of the total quantity applied has been evaporated after that time. In a recent study on lindane (Sloof and Matthijsen, 1987) some assumptions have been made about the emission factors in dependence on the substrate to which the pesticide is applied.

In this study we used the emission factors, based on the compounds vapour pressure and way of application, suggested by the contractor. Their values were between 0.2 and 0.5 kg.kg<sup>-1</sup>.

*Table A15 Areas of agriculture in European countries (1986) (FAO,1987).*

Country	Area of total agriculture		Area of maize culture		Area of potato culture	
	10 <sup>3</sup> km <sup>2</sup>	% of total area	10 <sup>3</sup> km <sup>2</sup>	% of area of agriculture	10 <sup>3</sup> km <sup>2</sup>	% of area of agriculture
Albania	7.1	24.9	0.95	13.4	0.16	2.3
Austria	15.1	18.0	2.17	14.4	0.35	2.3
Belgium/Luxemb.	8.1	24.3	0.07	0.9	0.41	5.1
Bulgaria	41.3	37.3	5.74	13.9	0.40	1.0
Czechoslovakia	51.4	40.2	2.10	4.1	1.81	3.5
Denmark	26.1	60.6			0.31	1.2
Finland	23.9	7.1			0.39	1.6
France	189.9	34.7	18.84	9.9	2.01	1.1
Germany, D.R.	49.6	45.8			4.59	9.3
Germany, F.R.	74.6	30.0	1.87	2.5	2.32	3.1
Greece	39.4	29.9	2.03	5.2	0.45	1.1
Hungary	52.9	56.9	11.46	21.7	0.68	1.3
Ireland	7.7	11.0			0.31	4.0
Italy	121.8	40.4	8.43	6.9	1.34	1.1
Netherlands, the <sup>1)</sup>	8.8	24.9	1.96	22.2	1.68	19.1
Norway	8.5	2.6			0.17	2.0
Poland	148.2	47.4	0.22	0.1	20.09	13.6
Portugal	27.5	29.9	2.58	9.4	1.24	4.5
Romania	106.5	44.9	29.76	27.9	3.52	3.3
Spain	204.2	40.5	5.24	2.6	2.96	1.4
Sweden	29.7	6.6			0.39	1.3
Switzerland	4.1	10.0	0.22	5.4	0.19	4.6
United Kingdom	70.2	28.7	0.01	0.0	1.79	2.5
U.S.S.R. <sup>2)</sup>	1232.5	10.4	21.1	1.8	33.28	2.7
Yugoslavia	77.8	30.4	23.69	30.4	2.83	3.6

1) Berends (1987)

2) In area of study

*Table A16 Volatilization of pesticides from crops.*

Author(s)	Crop	Pesticide	Vapour pressure* (mPa)	Intercepted by crop (%)	Time (days)	Evaporated from crop (%)
Taylor et al. (1977)	grass	dieldrin	1.8	43	22	83
		heptachlor	42.6	66	22	ca. 90
Willis et al. (1983)	cotton	toxaphene	0.4	28	33	60
		DDT	0.1	19	33	58
Grover et al. (1985)	wheat	2,4-D (iso-octyl ester)	1.2	52	35	80

\* At a temperature which is the mean value of the maximum air temperatures

### A6.1 Atrazine

Atrazine is a chlorinated triazine with a molecular mass of 215.7 kg.kMol<sup>-1</sup> and a specific mass of 1187 kg.m<sup>-3</sup>. Its vapour pressure (20°C) is 40 µPa, its solubility in water (20°C) is 30 mg.l<sup>-1</sup>. It is slowly hydrolysed at 70°C under neutral conditions, and more rapidly in acid or in alkali.

Atrazine can be used as a herbicide in asparagus, forestry, grasslands, grass crops, maize, pineapple, sorghum, sugarcane and non-crop areas (Worthing, 1983).

In the Netherlands, atrazine is admitted for use as a herbicide for asparagus, maize, on field borders, and on permanently uncultivated terrains.

#### *Application densities*

For an estimate of the application density only data of the Netherlands are available. From the data of Berends (1988) it follows that in the Netherlands atrazine is used almost exclusively in maize culture the area of which is 22 % of the total area of agriculture. The application rate densities are 58-100 kg.km<sup>-2</sup>.y<sup>-1</sup>. The amount used as estimated by us from his data regarding the year 1987 is 134 tons per year. According to the Dutch Ministry of Housing, Physical Planning and Environment the amounts of tons in the years 1984-87 were between 192 and 204 tons annually (VROM, 1989) with no tendency to lower. Assuming that the mean of the latter data (200 tons.y<sup>-1</sup>) is a representative for the annual consumption the following application rate densities have been calculated:

Related to the area of maize culture :  $P = 103 \text{ kg.km}^{-2}.\text{y}^{-1}$

Related to the total area of agriculture :  $P = 23 \text{ kg.km}^{-2}.\text{y}^{-1}$ .

No data on the use of atrazine in other European countries except for Denmark are available. For some countries application densities are given regarding the total quantity of (5-6) triazines of which atrazine is one, possibly together with those of triazinons (see Table A17). Most of the application densities of triazines calculated from these data, if related to the total area of agriculture, are about twice the value given here for the application density of atrazine in the Netherlands. If related to the area of maize culture they are 2 to 26 times the value for the Netherlands. As the cultures to which atrazine is used may not be limited to maize, and maize culture areas are known for only ten European countries, we suggest to relate the application density to the total area of agriculture. If only triazine consumption is known, 50% of the triazine consumption is estimated to consist of atrazine.

**Table A17** *Triazines consumptions and application densities in European countries in 1985, related to the total area of agriculture and to the area of maize culture (FAO, 1984, 1987).*

Country	Consumption (tons.y <sup>-1</sup> )	Area of agriculture (10 <sup>3</sup> km <sup>2</sup> )	Application density (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Area of maize culture (10 <sup>3</sup> km <sup>2</sup> )	Application density (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Remarks
Austria	700	15.1	46	2.08	337	
Czechoslovakia	1514	51.4	29	2.05	739	
Denmark	700 <sup>1)</sup>	26.1	27			in 1986
Finland	25	23.9	1			
Hungary	3076	52.9	58	11.46	268	in 1986
Italy	4298	121.8	35	9.23	466	
Netherlands	200 <sup>2)</sup>	8.8	23	1.96	102	
Norway	28	8.5	3			
Poland	714	148.2	5	0.22	3245	in 1986
Sweden	270	29.7	9			

1) Atrazine: 100 tons (1987) (Ministry of the Environment, National Agency of Environmental Protection, Copenhagen)

2) Atrazine: 200 tons (mean of values 1984-87) (VROM, 1989)

### *Emission flux densities*

Atrazine is used for crop treatment only (as a herbicide). On suggestion of the contractor it is assumed that emission flux densities of atrazine can be calculated from application densities by multiplying them with an emission factor of 0.25 which is, in view of its low vapour pressure, not unrealistic. Then the following emission fluxes are found:

Related to the total area of agriculture :  $EFD = 5.75 \text{ kg.km}^{-2}.\text{y}^{-1}$ .

Related to the consumption of atrazine:  $EFD = 0.25 \text{ kg/kg}$  applied atrazine

Related to the consumption of triazine :  $EFD = 0.125 \text{ kg/kg}$  applied triazine

## **A6.2 1,3-dichloropropene**

1,3-dichloropropene is a chlorinated hydrocarbon with a molecular mass of 111.0  $\text{kg.kMol}^{-1}$  and a specific mass of 1217  $\text{kg.m}^{-3}$ . It is a liquid with a comparatively high vapour pressure: 3.7 kPa at 20°C; its solubility in water is 1  $\text{g.l}^{-1}$ . It is non-persistent and is hydrolysed in soil to the corresponding 3-chloroallyl alcohols (Worthing, 1983).

1,3-Dichloropropene is used as nematicide (against root knot, meadow, sting and dagger, spiral and sugar beet nematodes). It is injected on a depth of 0.15-0.30 m, from where it evaporates thus working as a soil fumigant. The prescribed dosing rate of 1,3-dichloropropene containing fumigants is 15000-25000  $\text{kg.km}^{-2}$  (once per four years), depending on its 1,3-dichloropropene content.

In the Netherlands, 1,3-dichloropropene is admitted for several agricultural uses: potatoes, strawberries, flower bulbs, vegetables, sugar beets, onions, orchard replanting, etc. According to Berends (1988), it is used mainly in culture of potatoes, strawberries, and parks. As the culture of potatoes takes for the greatest area, we restrict ourselves to that application. According to Berends (1988) the total area for cultivating potatoes in the Netherlands is about 168200 ha (75400 ha for consumption potatoes, 58300 ha for industrial potatoes, and 34500 ha for seed-potatoes). However, only a part of this area (the part which is used only for industrial potatoes culture) is treated since the culture in the other areas is alternated with that of other crops which makes a soil fumigation unnecessary. Besides that, other nematicides (e.g. metam-sodium) are also used.

### *Application densities*

It is not known whether, as in the Netherlands, in other European countries the use of nematicides for the cultivation of potatoes is limited to that of industrial potatoes.

Therefore we suggest to relate the application rate of 1,3-dichloropropene simply to the whole area of potato culture. We also neglect the possibility that in other countries the fraction of the potato culture area which is treated with other fumigants than 1,3-dichloropropene differs from that in the Netherlands.

For an estimation of the amount of 1,3-dichloropropene used in the Netherlands annually two sources are available. The first is the prescribed quantity to use per unit of area, 170 kg.ha<sup>-1</sup> (Berends, 1988), together with the fumigated area which was, according to the Dutch Plant Pathology Service (priv. comm.), 12092 ha (in 1985). These data yield an annual amount of 2060 tons. Related to the total area of potato culture (1683 km<sup>2</sup>) the application density in the Netherlands is then:

$$P = 1220 \text{ kg.km}^{-2}.\text{y}^{-1}$$

Secondly there are the amounts of fumigantia excluding metam-sodium used in the years 1984-1987 as presented by the Dutch Ministry of Housing, Physical Planning and Environment (VROM, 1989). The values given were 6741, 5682, 5795 and 3130 tons, respectively. We suggest to use the average of these values (5337 tons) as a representative value for the annual consumption. This is probably an overestimate as it includes the amounts of some other fumigant (e.g. methyl bromide). The application density based on potato area calculated from this value is:

$$P = 3170 \text{ kg.km}^{-2}.\text{y}^{-1}$$

According to state authorities the total sales of 1,3-dichloropropene amounted to 14 tons in Denmark (1987) and 162 tons in Norway (1987). Together with the areas of potato culture these values correspond to 45 and 950 kg.km<sup>-2</sup>.y<sup>-1</sup>, respectively.

### *Emission flux densities*

As 1,3-dichloropropene is used as a fumigant, emission flux densities may be calculated from application densities by multiplying them with an assumed factor of 0.5. By multiplying the application rate calculated from the value of VROM with this factor the following emission flux density is found:

$$\text{Related to the area of potato culture : EFD} = 1590 \text{ kg.km}^{-2}.\text{y}^{-1}.$$

### A6.3 Endosulfan

Endosulfan is a chlorinated cyclic sulfite with a molecular mass of  $406.9 \text{ kg.kMol}^{-1}$ . It is a solid with a vapour pressure of 1.2 Pa at  $80^\circ\text{C}$ . Its solubility in water is  $0.32\text{-}0.33 \text{ mg.l}^{-1}$  ( $22^\circ\text{C}$ ). It is stable to sunlight, unstable in alkaline media and subject to slow hydrolysis to the corresponding diol and sulphur dioxide (Worthing, 1983). Endosulfan is used as an insecticide and acaricide in the culture of a wide variety of crops: cereals, coffee, cotton fruit, oilseeds, potatoes, tea, vegetables.

Endosulfan is nowadays only admitted for the integrated treatment in fruit. It is to be prohibited per 1-1-1990.

#### *Application densities*

Data on actual applications are scarce. Berends (1988) mentions the possibility of its use in apple culture ( $0.47 \text{ kg.ha}^{-1}$ ). In 1976 endosulfan was mainly applied in the culture of mushrooms and several species of cabbage; the amount of endosulfan, together with that of dicofol and dienochlor used in the Netherlands was estimated to be 46 tons (Curatorium Landbouwemissie, 1980). Assuming that these three pesticides were used in equal quantities, the quantity of endosulfan used would have been about 15 tons.

According to the Dutch Ministry of Housing, Physical Planning and Environment the emission of chlorinated hydrocarbons excluding Lindane were in the years 1984-1987 63, 70, 54 and 29 tons, respectively (VROM, 1989). Taking the average of the latter two amounts (42 tons) as representative for the annual consumption (because of the tendency to lower the use of these compounds) and again assuming that one third of this quantity is endosulfan, an amount of 14 tons would follow. Related to the whole agriculture area in the Netherlands ( $8800 \text{ km}^2$ ) this quantity corresponds with an application density of  $1.7 \text{ kg.km}^{-2}.\text{y}^{-1}$ . Except from a private communication from the Danish Ministry of the Environment, National Agency of Environmental Protection, that in Denmark 1.5 ton endosulfan had been sold in 1987, no information on other European countries is available.

### *Emission flux densities*

On the proposal of the contractor a factor of 0.25 has been adopted, although not well supported by the value of the vapour pressure which is "average". By multiplying the application density by this factor the following emission flux has been calculated for the Netherlands:

Related to the total area of agriculture :  $EFD = 0.43 \text{ kg.km}^{-2}.\text{y}^{-1}$ .

### **A6.4 Fentin acetate/ fentin hydroxide**

Fentin hydroxide and fentin acetate are the usual names of triphenyl tin hydroxide and its acetic acid ester, respectively.

Fentin hydroxide has a molecular mass of  $367.0 \text{ kg.kMol}^{-1}$ . It is a solid with a vapour pressure of  $0.047 \text{ mPa}$  at  $20^\circ\text{C}$ ; its solubility in water is  $1 \text{ mg.l}^{-1}$  (at a pH of 7.0, greater at lower pH). It is slowly decomposed by sunlight. Fentin acetate has a molecular mass of  $409.0 \text{ kg.kMol}^{-1}$ . It is a solid with a vapour pressure of  $0.177 \text{ mPa}$  at  $20^\circ\text{C}$ ; its solubility in water is  $9 \text{ mg.l}^{-1}$ . It is stable when dry but is easily decomposed on exposure to air or sunlight, finally forming insoluble tin compounds (Worthing, 1983).

Fentin compounds are used as fungicides in the culture of celery, sugar beets and potatoes (application to crops). In the Netherlands, the use of fentin acetate is only admitted in combination with other pesticides. According to Berends (1988) the main applications of fentin acetate regard potatoes (consumption, industrial and seed-potatoes).

### *Application densities*

An estimation of the amounts of fentin acetate used in the Netherlands for the categories consumption potatoes, industrial potatoes and seed-potatoes was made based on data of Berends (1988). According to this author fentin acetate is not used in celery and sugar beet culture. From these data it follows that areas of agriculture which is used for the potato cultures and the application densities in the Netherlands (in 1987) were (Table A18):

*Table A18 Application densities and amounts used in the Netherlands (Berends, 1988).*

Potato category	Area (km <sup>2</sup> )	Application density (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Amount used (tons.y <sup>-1</sup> )
consumption potatoes	755	258	195
industrial potatoes	583	6	3.5
seed potatoes	345	88	30.5
Total	1683	136	229

If for a given region the areas of the potato cultures are known, the consumption of fentin acetate may be calculated by multiplying them with the application densities (given in Table A18, third column), and adding up. If only the total area of potato culture is known, this area may be multiplied with an average application density. For the Netherlands the average application density had been calculated by dividing the total amount used (229 tons.y<sup>-1</sup>) by the total area of potato culture (1683 km<sup>2</sup>).

According to the Dutch Ministry of Housing, Physical Planning and Environment, amounts of 317, 388, 302 and 383 tons of the triphenyl tin compounds, fentin acetate and fentin hydroxide have been consumed as fungicides for agricultural use in the Netherlands in the years 1984-7, respectively (VROM, 1989). (Other tin compounds, cyhexatin and azocyclotin, which are cyclohexyltin compounds, are used as insecticide/acaricide in relatively small amounts and have been left out of consideration). Therefore the total amount of fentin hydroxide and fentin acetate used in the Netherlands as pesticides will be about 350 tons annually. The application density calculated from this value and the area of potato culture (1683 km<sup>2</sup>) is 206 kg.km<sup>-2</sup>.y<sup>-1</sup>. The estimate of Berends relating to fentin acetate (136 kg.km<sup>-2</sup>.y<sup>-1</sup>) is only two third of this value. So, 70 kg.km<sup>-2</sup>.y<sup>-1</sup> of the estimated 206 kg.km<sup>-2</sup>.y<sup>-1</sup> must regard fentin hydroxide in order to give an agreement with Berends' results. However, as Berends does not mention any use of fentin hydroxide in agriculture this is unlikely.

In Denmark and Norway the use of triphenyltin compounds is prohibited.

### *Emission flux densities*

The emission flux density has been estimated for the total of triphenyl tin compounds. As these compounds are used for crop treatment, the emission flux density has been calculated

from application density by multiplying it by an emission factor of 0.4, taking into consideration that a small part of the pesticide is applied by spraying from aeroplanes of which a relatively large fraction may evaporate. Together with the value derived from the consumption data of VROM ( $206 \text{ kg.km}^{-2}.\text{y}^{-1}$ ) this gives the following emission flux density:

Related to the area of potato culture :  $\text{EFD} = 82 \text{ kg.km}^{-2}.\text{y}^{-1}$ .

## A6.5 Lindane

Lindane is the common name of a substance containing 99.0 % or more of the gamma isomer of hexachlorocyclohexane (gamma-HCH). The compound has a molecular mass of  $290.8 \text{ kg.kmol}^{-1}$ . Its vapour pressure is 5.6 mPa at  $20^\circ\text{C}$ . It is slightly soluble in water:  $7 \text{ mg.l}^{-1}$ . At  $22^\circ\text{C}$ , 50 % loss occurs in 191 days at pH 7, in 11 hours at pH 9 (Worthing, 1983).

Lindane is used as an insecticide, on crops as well as in soil. It is not only used in agriculture but it has also veterinary use (cattle-breeding), household use and treatment of wood against insects.

In agriculture lindane finds its applications in soil, on seed and on crops. However, some restrictions are made to its use in many countries.

### *Application densities*

For this study, we refer to a recent report of a literature study on emission data of some organic pollutants of which lindane was one made by Duiser and Veldt (1989). In this study the emission of lindane has been estimated based on its applications in agriculture as well as in other uses. It was found that although data on the consumption of lindane were available for most of the European countries not always consumption data were given for agricultural/ veterinary use and other uses separately. It was recommended in the study to assume then that 5 % of the total consumption regards other uses. For nine out of the 25 countries no data were available at all. The consumption rates presented in the study regard the years 1982 and 1983. Many of the data in literature, however, refer to consumptions of 1977. These data had been corrected by multiplying them with a factor of 0.6, thus accounting for the downwards trend in the use of lindane as a result of replacement of lindane by alternatives. In the meantime some data regarding later years have been found. The consumption rates (FAO production data) for some countries are given in Table A19,

together with application rate densities calculated from them. The latter values vary largely; for some countries they show a sharp decrease with time whilst other values remain nearly constant.

**Table A19** *Lindane consumptions and application densities for agricultural use in European countries in 1985 (FAO, 1987).*

Country	Consumption (tons.y <sup>-1</sup> )	Area of agriculture (10 <sup>3</sup> km <sup>2</sup> )	Application density (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Remarks
Austria	35.5	15.1	2.1	
Czechoslovakia	0.7	51.4	0.0	1979-81, mean value
Denmark	10 <sup>1)</sup>	26.1	0.4	in 1987
Finland	23.4	23.9	1.0	1979-81, mean value
Hungary	195.3	52.9	3.7	in 1982
Italy	1622.9	121.8	13.3	2)
Netherlands	24	8.8	2.8	in 1987 (VROM)
Poland	56.5	148.2	0.4	3)
Portugal	6.1	27.5	0.2	in 1984
Sweden	4.5	29.7	0.2	

1) information of the Danish state authority

2) probably the formulation (20% Lindane)

3) 1984: 166.2 tons, 1986: 1.6 tons

According to Duiser and Veldt default values may be used for countries of which no data were available. These default values have been obtained by averaging the consumption rates in the other European countries. These values are:

Application density of lindane for agricultural and veterinary use (from the area of arable land and permanent crops):

$$\text{application density} = 2 \text{ kg.km}^{-2}.\text{y}^{-1}$$

Application density of lindane for abatement of insects and wood preservation in buildings (from the number of inhabitants):

$$\text{application density} = 0.2 \text{ g.inhabitant}^{-1}.\text{y}^{-1}$$

Applying these relations to the Netherlands an annual use of 20 tons results. This amount is only slightly lower than the amounts presented by the Dutch Ministry of Housing, Physical Planning and Environment for the years 1984-7, which were 27, 29, 34 and 24 tons, respectively (VROM, 1989). For simplicity, we will use the average of the latter values (29 tons annually), and relate this consumption to agriculture only. Then the application density is given by:

$$\text{application density} = 3.3 \text{ kg.km}^{-2}.\text{y}^{-1}.$$

#### *Emission flux densities*

Emission flux densities can be estimated from the application densities by multiplying them with an emission factor. For this a factor of 0.5 has been suggested by the contractor which seems to be reasonable because of the relatively high vapour pressure. Then the following emission flux densities are found:

$$\text{Related to the total area of agriculture} : \text{EFD} = 1.65 \text{ kg.km}^{-2}.\text{y}^{-1}.$$

### **A6.6 Parathion**

Parathion is the common name of dimethyl or diethyl nitrophenyl phosphorothionate. The diethylated derivate is usually called simply parathion.

Parathion-ethyl ( $M = 291.3 \text{ kg.kMol}^{-1}$ ) is a liquid (density  $1265 \text{ kg.m}^{-3}$ ) with a vapour pressure of 5 mPa at 20°C. Its solubility in water is  $0.024 \text{ g.l}^{-1}$ . It is hydrolysed at 25°C and pH 5-6 with a rate of 1 % in 62 days. Parathion-methyl ( $M = 263.2 \text{ kg.kMol}^{-1}$ ) is a solid (density  $1358 \text{ kg.m}^{-3}$ ) with a vapour pressure of 1.3 mPa at 20°C. Its solubility in water is  $0.055\text{-}0.060 \text{ g.l}^{-1}$ . It is hydrolysed by alkali (Worthing, 1983).

Both compounds are (cholesterinase inhibiting) insecticides with some fumigant action. They are admitted for a wide application on crops as well in soil and used for the same purposes.

In the Netherlands the main applications regard agriculture (sugar beets, consumption potatoes and seed-potatoes, peas, onions, beans, leek, horticulture (rose, chrysanthemum, gerbera) and arboriculture (Berends, 1988). The use in the last two cultures are, however, of minor importance (each about 1 %). For this reason the application density may be related to agriculture as a whole or, if possible, to some specified types of agriculture.

### *Application densities*

An estimation of the amounts of parathion used in the Netherlands for the various categories was made based on data of Berends (1988). The application densities in the Netherlands (in 1987) following from these data (which, however relate only to a part of the total area used for the cultures) are given in Table A20.

For a given region the application density of parathion may be estimated by multiplying the fractions of area used in that region for the various categories by the relevant application density given in the third column, and adding up. If no areas for the separate categories of potatoes are known, an average application density may be used related to the total area used for agriculture. For this average the value of about  $8 \text{ kg.km}^{-2}.\text{y}^{-1}$ , obtained by adding up the figures of the fourth column, may be used. From this value and the total area used for agriculture the total amount used in that region can be calculated. For the Netherlands, with a total area for agriculture of  $8840 \text{ km}^2$ , this quantity was estimated to be about 70 tons annually.

According to the Dutch Ministry of Housing, Physical Planning and Environment the amounts of parathion used in the years 1984-1987 were 99, 110, 64 and 64 tons respectively (VROM, 1989). From the average of these values (84 tons) an average application density of  $9.5 \text{ kg.km}^{-2}.\text{y}^{-1}$  has been calculated. The latter value has been adopted for estimating a default value for the average application density.

For some European countries application densities may be calculated from the consumptions presented by FAO (1987) (see Table A21).

An emission factor of 0.25 results in an emission flux density related to total area of agriculture of  $2.4 \text{ kg.km}^{-2}.\text{y}^{-1}$ .

**Table A20** Application densities of parathion in the Netherlands (Berends, 1988).

Potato categorie	Fraction of area used for agriculture (%)	Application density (average) <sup>1)</sup> (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Amount used per unit of area used for agriculture (kg.km <sup>-2</sup> .y <sup>-1</sup> )
sugar beets	14.3	3.7	0.53
consumption potatoes	8.5	25.5	2.17
peas	4.0	41	1.65
seed-potatoes	3.9	13	0.51
onions	1.9	60.5	1.15
beans	1.2	75	0.90
rape-seed	1.1	50	0.55
leek	0.3	15	0.05
horticulture	0.2	40	0.08
arboriculture	0.4	15	0.06
Total	35.8		7.65

1) Related to the area of the type of agriculture in regard.

**Table A21** Parathion consumptions and application densities in European countries in 1985 (FAO, 1987).

Country	Consumption (tons.y <sup>-1</sup> )	Area of agriculture (10 <sup>3</sup> km <sup>2</sup> )	Application density (kg.km <sup>-2</sup> .y <sup>-1</sup> )	Remarks
Austria	15	15.1	1.0	
Czechoslovakia	14	51.4	0.3	
Denmark	21 <sup>1)</sup>	26.1	2.2	in 1987 <sup>1)</sup>
Hungary	1314	52.9	24.8	in 1986
Italy	1982	121.8	16.3	
Netherlands	64	8.8	7.2	in 1987 (VROM)
Portugal	58	27.5	2.1	in 1984
Switzerland	70	4.1	17.1	1979-81, mean value

1) information of the Danish state authority ; the use of parathion has been reduced strongly in course of years: in 1984: 171.4 tons, in 1985: 95.4 tons.

## A6.7 Azinphos-methyl

Azinphos-methyl is an organic phosphor containing compound with a molecular mass of 317.1 g/mol and a specific mass of 1440 kg.m<sup>-3</sup>. The vapour pressure is lower than 1 µPa. The solubility in water is 33 mg.l<sup>-1</sup> (at 20°C).

Azinphos-methyl is an insecticide with its main use in fruit (apple) treatment.

Data on the use in the Netherlands were supplied by VROM (1989) and Berends (1988). There is no data available on the use in other European countries. According to VROM the average consumption in 1984-1987 amounted to 8 tons per year. Berends mentioned a use of 0.23 kg.ha<sup>-1</sup>.y<sup>-1</sup> in the Dutch regions Gelderland, Limburg and the eastern part of Noord-Brabant, which together cover an area of about 7100 ha. There is no available data for the other regions.

Assuming that the application density applies to the total Dutch apple-culture area (15.132 ha), a annual use of 3.5 ton can be calculated. In this study we used an average of the data by VROM and Berends: 6 ton/year, which result in an application density of 0.4 kg.ha<sup>-1</sup>.y<sup>-1</sup>.

The use of an application density for the other European countries was prohibited by the lack of data on the areas of apple culture in those countries. The use of azinphos-methyl was therefore related to the apple production. The use in the Netherlands than result in de-

fault value of 17 kg per 1000 ton apples produced. The apple production data was taken from FAO, 1987. Emissions are calculated by multiplying the use with an emission factor of 0.2, due to the compounds low vapour pressure.

### A6.8 Simazine

Simazine is a triazine with a molecular weight of 201.7 g/mol. It has a specific mass of 1302 kg.m<sup>-3</sup>. It has a vapour pressure of 0.81 μPa and its solubility in water is 5 mg.l<sup>-1</sup> (at 20°C).

Simazine is a herbicide with a wide application in agriculture. Data of the use of simazine is only available for the Netherlands. The application densities given by Berends (1988) for use on various cultures like beans, strawberries, lilies, lawn and parl trees etc. These application densities vary up to a factor twentyfive for the different applications. For the Netherlands however an averaged application density calculated of 0.15 kg.ha<sup>-1</sup>.y<sup>-1</sup>. When applied to a area of 62846 ha this results in an annual use of 9.2 ton.

Data provided by VROM on the total use of triazines (of which simazine is one compound) during 1984-1987 is a factor 1.8 higher than the total triazine use provided by Berends. We chose to estimate the use of the total triazines by averaging the data from Berends and VROM and apply a correction factor to the data of Berends of 1.4 to obtain the averaged total triazine use. This factor can than also be applied to Berends' data on the use of simazine resulting in an annual use of simazine in the Netherlands of 13 ton. Due to the wide range of applications, the use of simazine is related to the total area of agriculture, resulting in a default application density of 1.57 kg.km<sup>-1</sup>.y<sup>-1</sup>.

The emission is calculated by multiplying the application density with a factor 0.2, based on the compounds low vapour pressure.

### A6.9 Bentazone

Bentazone is a thiodiazine oxide with a molecular weight of 2050.3 g/mol. The vapour pressure is low, less than 0.02 μPa at 20°C. The solubility in water is 500 mg.l<sup>-1</sup> (20°C).

Bentazone is a herbicide with a wide application in agriculture, its main application is on cereals.

Except for the Netherlands no data on its use was availalbe. Berends (1988) gives an annual use of 156 ton. Related to the total area of agriculture this results in an default appli-

cation density of  $0.18 \text{ kg}\cdot\text{ha}^{-1}$ . The emission is calculated by multiplying the application density with an emission factor 0.1, based on the compounds low vapour pressure.

### A6.10 Trifluralin

Trifluralin is a dinitro-aniline with a molecular weight of  $335.5 \text{ g/mol}$ . The vapour pressure at  $25^\circ\text{C}$  is  $13.7 \text{ mPa}$ , the solubility in water less than  $1 \text{ mg}\cdot\text{l}^{-1}$  ( $27^\circ\text{C}$ ).

Trifluralin is a herbicide. Its main application is in the treatment of wheat and burley cultures. In the Netherlands its use is allowed only in combination with isoproturon (a 1:1 mixture) and with linuron (trifluralin : linuron : 2 : 1).

VROM (1989) provided an average annual use of isoproturon during 1984-1987 of 37 ton and an annual use of linuron of 12 ton. Isoproturon is also used in mixtures other than with trifluralin. Only one third of the isoproturon and linuron use is estimated to be in combination with trifluralin. A use of 20 ton per year can thus be calculated for the Netherlands. Related to the area of wheat and barley culture this result in a default application density of  $0.13 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ .

Multiplied with an emission factor of 0.3 the emission density is  $3.9 \text{ kg}\cdot\text{km}^{-2}\cdot\text{y}^{-1}$ , related to the area of wheat and barley culture.

### A6.11 Dichlorvos

Dichlorvos is a phosphorus containing compound with molecular weight of  $221 \text{ g/mol}$ . At  $20^\circ\text{C}$  it is a liquid with a specific mass of  $1415 \text{ kg}\cdot\text{m}^{-3}$  and a vapour pressure of  $1.6 \text{ Pa}$ . The solubility in water is  $10 \text{ mg}\cdot\text{l}^{-1}$ .

Dichlorvos is an insecticide mainly used in greenhouses and is used against internal and external parasites on cattle and against insects in buildings etc. Sixty percent of its use is in agriculture, percent is used against parasites and 10% in the protection of stored goods.

The use in the Netherlands shows a strong increase during 1984-1987:

1984	0.4	$\text{g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$
1985	0.5	$\text{g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$
1986	0.7	$\text{g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$
1987	2.2	$\text{g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$

The increase is probably caused by the replacement of parathion by dichlorvos. There is no data available on the use in other countries. For the Netherlands a consumption of 2

$\text{g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$  is used. Due to the absence of major applications in greenhouses in the other countries, a default consumption of  $1 \text{ g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$  is used.

The emission was calculated by multiplying the consumption data with a emission factor of 0.5.

### **A6.12 Pentachlorophenol**

Pentachlorophenol (PCP) has a molecular weight of 266.4 g/mol. The vapour pressure at 20°C is  $2\cdot 10^{-3}$  Pa, the solubility in water is pH dependant: at pH 5 = 0.014  $\text{g}\cdot\text{l}^{-1}$  and at pH 7 = 2  $\text{g}\cdot\text{l}^{-1}$ .

Pentachlorophenol is an effective widely applicable biocide. Its main use is in wood preservation. It is also used as protective agent for textile goods (rope, canvas sails), leather, waterbased paints and glues. It has been used worldwide since 1940. Since the eighties its adverse effect on human health and the environment have been recognised and in use has been strongly reduced.

The use of pentachlorophenol is prohibited in the Netherlands, West-Germany, Denmark and Sweden. In spite of this, some tens of thousand tons are used in the Netherlands. The use of PCP in some European countries is given in Table A22. France is still using very large amounts (several thousands of tons per year) of PCP. To a lesser extend this also is true for Spain and Portugal which use in the order of a thousand ton per year.

Thirty to eighty percent of the used amount in surface treatment of pine wood is lost by evaporation (WHO, 1989). We used an emission factor of 0.5 to calculate the emission.

Of those countries for which no data was available on the use of PCP, emissions were calculated using a default emission of  $3 \text{ g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$  for Eastern European countries and for Western European countries which have prohibited or restricted the use of PCP. For the other countries a default value of  $4 \text{ g}\cdot\text{cap}^{-1}\cdot\text{y}^{-1}$  was used. The use in Eastern European countries is lower due to the use of other wood preservation compounds as thiourem.

**Table A22** *The use of PCP in some European countries and default emissions used in this study.*

	<b>Use of PCP (1980) ton/year</b>	<b>Emission g.cap<sup>-1</sup>.y<sup>-1</sup></b>	<b>Total emission ton/year</b>
Albanie		3	10
Austria		4	30
Belgium/Luxembourg	125		62
Bulgaria		3	30
Crechoslovakia		3	45
Denmark		3	15
Finland		4	20
France	several thousands of tons		2800
Germany (GDR)		3	50
Germany (FRG)	750	3	180
Greece		4	40
Hungary		3	30
Ireland		3	10
Italy	250-280		120
Netherlands the	30-40	3	45
Norway		3	15
Poland		3	100
Portugal	500		250
Romania		3	25
Spain	some thousands of tons		900
Sweden		3	25
Switzerland		4	25
United Kingdom	500-1000		500
USSR		3	295
Yugoslavia		3	70

## A7 SUMMARY OF RESULTS

Default values of the emission flux densities in the other countries have been summarized in Table A23.

Table A24 shows the emission fluxes of the pesticides of which the emission is related to the total area of agriculture. Some of them have been calculated from annual consumptions (FAO, 1987). In the cases where no consumption data were available the default values for the emission flux densities have been used.

The amount of lindane used in Italy as given by the FAO has been reduced by a factor of 5 as it is assumed that this amount regards the formulation which contains only 20% lindane. The emission fluxes of 1,3-dichloropropene and of fentin acetate, related to the areas of potato culture, are given in Table A25. The emissions of azinphos-methyl, trifluralin dichlorvos and pentachlorophenol are given in Table 26.

The estimation of the annual use of the pesticides on which the emission data is based is given in Tables A26 and A27.

*Table A23 Emission flux densities of some pesticides (derived from their use in the Netherlands).*

Pesticide	Emission related to		
atrazine	total agriculture area	5.75	kg.km <sup>-2</sup> .y <sup>-1</sup>
bentazone	"	1.8	"
endosulfan	"	0.43	"
lindane	"	1.65	"
parathion (methyl + ethyl)	"	2.4	"
simazine	"	0.314	"
1,3-dichloropropene	potato culture area	15.9	kg.ha <sup>-1</sup> .y <sup>-1</sup>
fentin (acetate + hydroxide)	"	0.82	"
dichlorvos	total inhabitants	0.5-1.0	g.cap <sup>-1</sup> .y <sup>-1</sup>
pentachlorophenol	"	3.0-4.0	g.cap <sup>-1</sup> .y <sup>-1</sup>
azinphos-methyl	apple production	3.4	kg.(10 <sup>3</sup> ton apples produced) <sup>-1</sup>
trifluralin	wheat/barley culture area	3.9	kg.ha <sup>-2</sup> .y <sup>-1</sup>

**Table A24** Emissions of some pesticides in European countries estimated from their consumption data or from default values of the emission flux densities (then given between parentheses) related to their areas of agriculture.

	Area of agriculture (10 <sup>3</sup> km <sup>2</sup> )	Emission (10 <sup>3</sup> kg.y <sup>-1</sup> )					
		atrazine	endosulfan	lindane	parathion	bentazone	simazine
EFD (kg.km <sup>-2</sup> .y <sup>-1</sup> )		5.75	0.43	1.65	2.4	1.8	0.31
Albania	7.1	(41)	(3)	(11)	(17)	(13)	(2.3)
Austria	15.1	87 (87)	(6.5)	18 (24)	3.5 (36)	(27)	(4.8)
Belgium/Luxemb.	8.1	(47)	(3.5)	(13)	(19)	(15)	(2.6)
Bulgaria	41.3	(237)	(18)	(66)	(99)	(74)	(13)
Czechoslovakia	51.4	190 (295)	(22)	0.4 (82)	3.5 (123)	(93)	(16)
Denmark	26.1	25 (150)	0.4 (11)	5 (42)	5.5 (63)	(47)	(8.4)
Finland	23.9	3 (137)	(10)	12 (38)	(57)	(43)	(7.6)
France	189.9	(1092)	(82)	(304)	(456)	(342)	(61)
Germany, G.D.R.	49.6	(285)	(21)	(79)	(119)	(89)	(16)
Germany, F.R.G.	74.6	(429)	(32)	(119)	(179)	(134)	(24)
Greece	39.4	(227)	(17)	(63)	(95)	(71)	(13)
Hungary	52.9	385 (304)	(23)	49 (85)	328 (127)	(95)	(17)
Ireland	7.7	(44)	(3.3)	(12)	(18)	(14)	(2.5)
Italy	121.8	538 (700)	(52)	162 (195)	495 (292)	(219)	(39)
Netherlands, the <sup>1)</sup>	8.8	(51)	(3.8)	(14)	(21)	16	2.8
Norway	8.5	4 (49)	(3.7)	(14)	(20)	(15)	(2.7)
Poland	148.2	89 (852)	(64)	28 (237)	(356)	(267)	(47)
Portugal	27.5	(158)	(12)	3 (44)	15 (66)	(50)	(8.8)
Romania	106.5	(612)	(46)	(170)	(256)	(192)	(34)
Spain	204.2	(1174)	(88)	(327)	(490)	(368)	(65)
Sweden	29.7	34 (172)	(13)	2 (48)	(71)	(53)	(9.5)
Switzerland	4.1	(24)	(1.8)	(7)	18 (10)	(7.4)	(1.3)
United Kingdom	70.2	(404)	(30)	(112)	(168)	(126)	(22)
U.S.S.R. <sup>2)</sup>	1232.5	(7087)	(530)	(2036)	(2958)	(2219)	(387)
Yugoslavia	77.8	(447)	(33)	(124)	(187)	(140)	(25)

1) Berends (1987)

2) In the area of study.

**Table A25** Total emission in  $10^3 \text{ kg.y}^{-1}$  of pesticides related to specific agricultural areas or use in European countries.

	Azinphos-methyl	Trifluralin	Dichlorvos	Pentachlorophenol	1,3-dichloropropene	Fentin compounds
EFD	3,4 kg (1000 ton apples produced) <sup>-1</sup>	3.9 kg.ha <sup>-2</sup> .y <sup>-1</sup> area of wheat and barley culture	0.5-1.0 g inh <sup>-1</sup> .y <sup>-1</sup> ( - -)	3-4 g.inh <sup>-1</sup> .y <sup>-1</sup>	15.9 kg.ha <sup>-1</sup> .y <sup>-1</sup> area of potato culture	0.82 kg.ha <sup>-1</sup> .y <sup>-1</sup> area of potato culture
Albania	0.07	7.70	1.6	10	(260)	(13)
Austria	0.9	24.0	4.0	30	(560)	(29)
Belgium/luxemb.	0.83	13.0	5.2	62	(650)	(34)
Bulgaria	1.60	53.0	5.0	30	(640)	(33)
Czechoslovakia	1.05	80.0	7.5	45	(2870)	(148)
Denmark	0.15	53.0	2.5	15	7	0
Finland	0.03	28.0	2.5	20	(620)	(32)
France	8.20	270.0	27.5	2800	(3190)	(165)
Germany GDR	2.00	65.0	7.5	50	(7280)	(376)
Germany FRG	3.70	137.0	30.0	181	(3680)	(190)
Greece	1.00	44.0	5.0	40	(720)	(37)
Hungary	3.40	59.0	5.0	30	(1080)	(56)
Ireland	0.03	13.0	1.5	10	(429)	(25)
Italy	7.30	138.0	27.5	120	(2120)	(110)
Netherlands, the	1.20	6.20	15.0	45	(2660)	(138)
Norway	0.15	8.10	2.0	15	81	0
Poland	1.70	133.0	20.0	100	(31860)	(1647)
Portugal	0.29	16.0	5.0	250	(2000)	(102)
Romania	3.40	121.0	10.0	70	(5580)	(289)
Spain	3.50	256.0	20.0	900	(4690)	(293)
Sweden	0.40	34.0	5.0	25	(620)	(32)
Switzerland	1.20	5.7	3.5	25	302	16
United Kingdom	1.20	149.0	27.5	500	(2840)	(147)
USSR <sup>1</sup>	8.82	1587.0	49.2	295	52915	(2729)
Yugoslavia	1.40	65	10	70	(4490)	(252)

1) in the area of study: area of potato culture is estimated to be 2.7% of the total agricultural area

Table A26 The use of pesticides on which the emission data is based (tons/y).

	Atra-zine	Endo-sulfan	Lin-dane	Para-thion	Benta-zone	Sima-zine	Azin-phos-methyl	Triflu-ralin	Di-chlorv-os	Penta-chloro-phenol	1,3-dichlo-roprene	Fentin com-pounds
Albania	164	12	22	68	130	11.5	0.4	25.7	3.2	20	520	32.5
Austria	350	26	36	15	270	24	4.5	80.0	8	60	1120	72.5
Belgium/luxemb.	188	14	26	76	150	13	4.1	43.3	10.4	125	1300	85
Bulgaria	948	72	132	396	740	65	8.0	176.7	10	60	1280	82.5
Czechoslovakia	760	88	0.8	14	930	80	5.3	266.7	15	90	5740	370
Denmark	100	1.5	10	21	470	42	0.7	176.7	5	30	14	0
Finland	12	40	24	228	430	38	0.2	93.3	5	40	1240	80
France	4368	328	608	1824	3420	305	41.0	900.0	55	5600	6380	412.5
Germany GDR	1140	84	158	476	890	80	10.0	216.7	15	100	14560	940
Germany FRG	1716	128	238	716	1340	120	18.5	456.7	60	362	7360	475
Greece	908	68	126	380	710	65	5.0	146.7	10	80	1440	92.5
Hungary	1540	92	98	1314	950	85	17.0	196.7	10	60	2160	140
Ireland	176	13.2	24	72	140	12.5	0.2	43.3	3	20	858	62.5
Italy	2150	208	324	1982	2190	195	36.5	460.0	55	250	4240	275
Netherlands, the	200	14	28	84	156	13	6.0	20.0	30	90	5337	345
Norway	14	14.8	28	80	150	13.5	0.7	27.0	4	30	162	0
Poland	356	256	56	1424	2670	235	8.5	443.3	40	200	63720	4117.5
Portugal	632	48	6	58	500	44	1.4	53.3	10	500	4000	255
Romania	2448	184	340	1024	1920	170	17.0	403.3	20	140	11160	722.5
Spain	4696	352	654	1960	3680	325	17.5	853.3	40	1800	9380	732.5
Sweden	135	52	4	284	530	47.5	2.0	113.3	10	50	1240	80
Switzerland	96	7.2	14	70	74	6.5	6.0	19.0	7	50	604	40
United Kingdom	1616	120	224	672	1260	110	6.0	496.7	55	1000	5680	367.5
USSR <sup>1</sup>	28348	2120	4072	11832	22190	1935	44.1	5290.0	98.4	590	105830	6822.5
Yugoslavia	1788	132	248	748	1400	125	7.0	216.7	20	140	8980	630

After the calculations in this study had been made some additional information from the Kd group in the IKSR on the use of pesticides has become available. This concerns an estimation of the agricultural use in the Rhine catchment area the pesticides: parathion, azinphos-methyl, bentazone, simazine, atrazine, dichlorvos, fentin compounds, trifluralin and endosulfan. To compare the estimation of the use in the Rhine catchment area to this study's estimation of the use in the complete individual countries, the estimation of the use in the Rhine catchment part of a country needed to be extrapolated to the use in the total country.

The assumption that the use of pesticides in the Rhine catchment part of a country is representative for the total country, might be correct for Western-Germany, where 40% of the total agricultural area lies in the Rhine catchment area, but is most likely not correct for France where only 3% of the total agricultural area lies in the Rhine catchment area.

As the new information only concerns agricultural use of pesticides, the data for pesticides which have mainly non-agricultural applications like pentachlorophenol is not possible.

The extrapolation of the estimation of the pesticide use shows, in general, compared to this study, a smaller use (of a factor 0.2 to 0.7) of the pesticides except for a larger use (of a factor 7 and 2) of azinphos-methyl and simazine in the FRG, a larger use of simazine and atrazine (of a factor 3 to 1.5) in France and Switzerland and a larger use (of a factor 15 to 8) of parathion, azinphos-methyl, simazine, atrazine and endosulfan in the Netherlands.

The implications of these new estimations of the use of pesticides, which have not been used in the calculations in this study, are briefly discussed in Chapter 4.3.

## APPENDIX B MODEL INPUT PARAMETERS

The deposition velocities of the aerosol phase compounds are dependant on their size distribution. The following standard size distributions and corresponding deposition velocities have been used (v. Jaarsveld 1990):

	<0.95 $\mu\text{m}$	0.95-4 $\mu\text{m}$	4-10 $\mu\text{m}$	10-20 $\mu\text{m}$	>20 $\mu\text{m}$	
Fine	70	20	5.5	2.5	2.0	%
Normal	53	28	11.5	4.2	3.3	%
Coarse	42	33	14.5	5.9	4.6	%
Vd (cm/s)	0.065	0.25	0.71	1.3	6.7	

Deposition velocities and scavenging ratio's unless otherwise stated, are computed from the compounds Henry's Law constant and its diffusion coefficients in air and water according to Liss and Slater (1974).

The diffusion coefficients in air and water have been calculated from the compound structure according to the methods of Hayduk and Laudie and the method of Fuller, Schettler and Giddings (Lyman, W.J. et al., 1982).

For the pesticides the Henry constants have been calculated from the compounds vapour pressure and solubility in water (Worthing, 1983).

The atmospheric degradation is computed from the reaction rate with the hydroxyl radical of the compound using an average OH concentration of  $0.3 \cdot 10^{-7}$  ppb (v. Aalst 1985).

Compounds in the aerosol phase are considered to be stable.

Compound	Gas/aer	Vd (cm/s)	Scav. ratio	Reaction rate %/h
Cadmium <sup>1)</sup>	aer fine			0
Chromium <sup>1)</sup>	aer normal			0
Copper <sup>1)</sup>	aer fine			0
Nickel <sup>1)</sup>	aer fine			0
Lead <sup>1)</sup>	aer fine			0
Zinc <sup>1)</sup>	aer fine			0
Mercury <sup>1)</sup>	gas	49 <sup>4)</sup>	12*10 <sup>4</sup>	0
Carbon tetrachloride	gas	0.004	0.777	0.0001 <sup>7)</sup>
Chloroform	gas	0.0329	6.8	0.0284 <sup>7)</sup>
Dichloroethane	gas	0.021	4.22	0.0568 <sup>7)</sup>
Trichloroethane	gas	0.022	4.74	0.0049 <sup>7)</sup>
Tetrachloroethene	gas	0.004	0.80	0.0439 <sup>7)</sup>
Trichloroethene	gas	0.009	1.94	0.5208 <sup>7)</sup>
Benzene <sup>1)</sup>	gas	9999 <sup>4)</sup>	17	0.54
PAH	gas	0.034 <sup>5)</sup>	50000 <sup>5)</sup>	13.32 <sup>10)</sup>
PAH	aer fine			0
PCB	gas	0.07 <sup>6)</sup>	1000 <sup>6)</sup>	0
Atrazine <sup>3)</sup>	aer fine			0
Dichloropropene <sup>3)</sup>	gas	0.027	5.73	3.6 <sup>8)</sup>
Endosulfan <sup>3)</sup>	gas	0.006	1.55	1.8 <sup>8)</sup>
Fentin compounds <sup>3)</sup>	gas	0.426	2.93*10 <sup>5</sup>	0
Lindane <sup>3)</sup>	gas	0.429	4.53*10 <sup>5</sup>	0.09
Parathion <sup>3)</sup>	gas	0.433	3.88*10 <sup>4</sup>	1.8 <sup>8)</sup>
Azinphosmethyl <sup>3)</sup>	aer fine			0
Dichlorvos <sup>3)</sup>	gas	0.483	6.73*10 <sup>4</sup>	1.8 <sup>8)</sup>
Simazine <sup>3)</sup>	aer fine			0
Bentazone <sup>3)</sup>	aer fine			0
Trifluralin <sup>3)</sup>	gas	0.330	588	30 <sup>9)</sup>
Pentachlorophenol <sup>3)</sup>	gas	0.440	8.83*10 <sup>6</sup>	0 <sup>8)</sup>

1) Van Jaarsveld 1990

2) In the deposition velocity calculation the diffusion coefficient in water estimated according to Hayduk and Laudie (1982). Diffusion coefficient in air estimated according to Fuller, Schettler and Giddings (1982).

3) In the deposition velocity calculation Henry's law constant is calculated from its solubility and vapour pressure as given in Worthing R. (1983).

4) Given as surface resistance (s/m).

5) From Duyzer 1989.

6) From Baart 1991.

7) K(OH) from v. Aalst 1983.

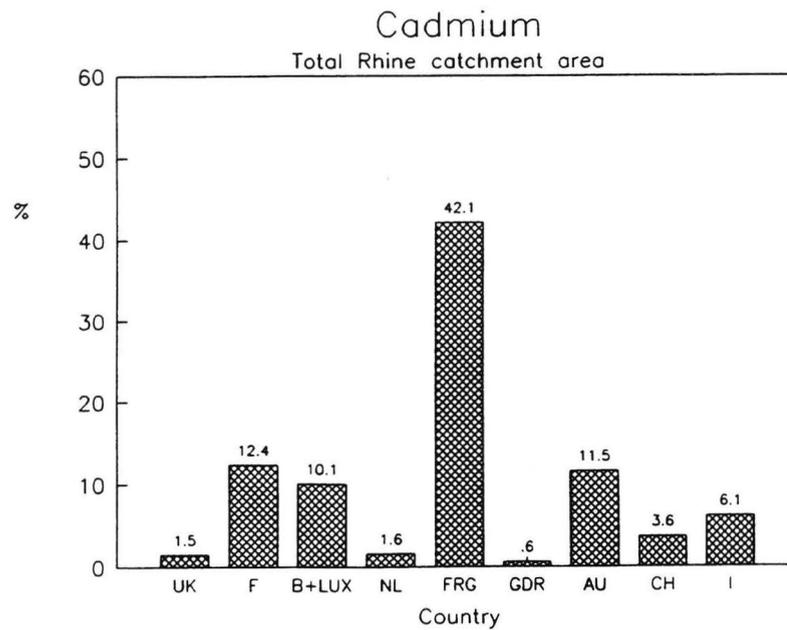
8) Estimated from compound structure.

9) Finlayson Pitts, Pitts (1986).

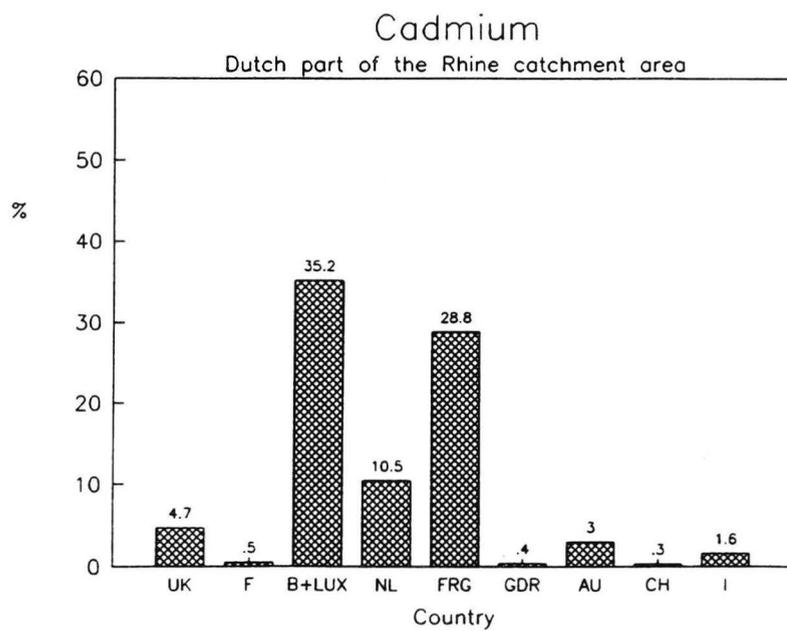
10) Atkinson (1990)

## APPENDIX C

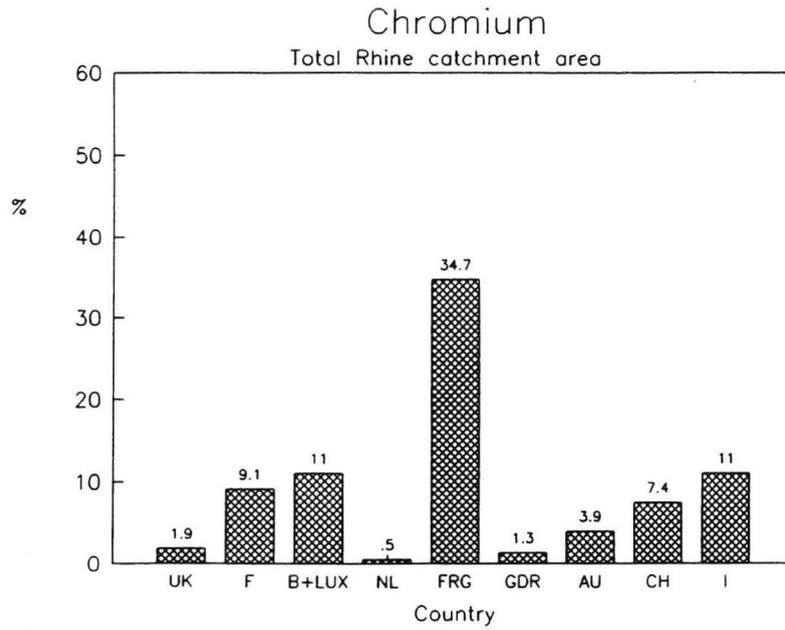




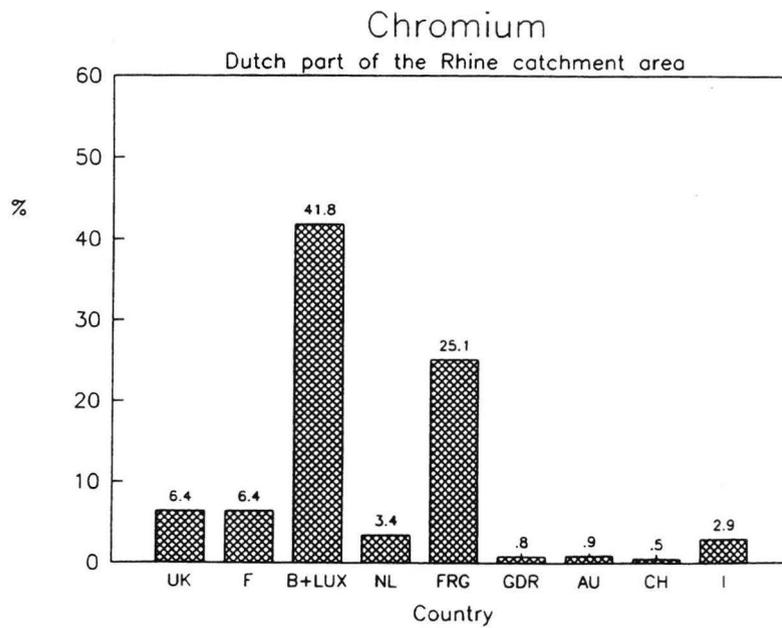
**Figure C1** Relative contributions of the surrounding countries to the total deposition of cadmium on the Rhine catchment area. Total deposition 22 ton/y.



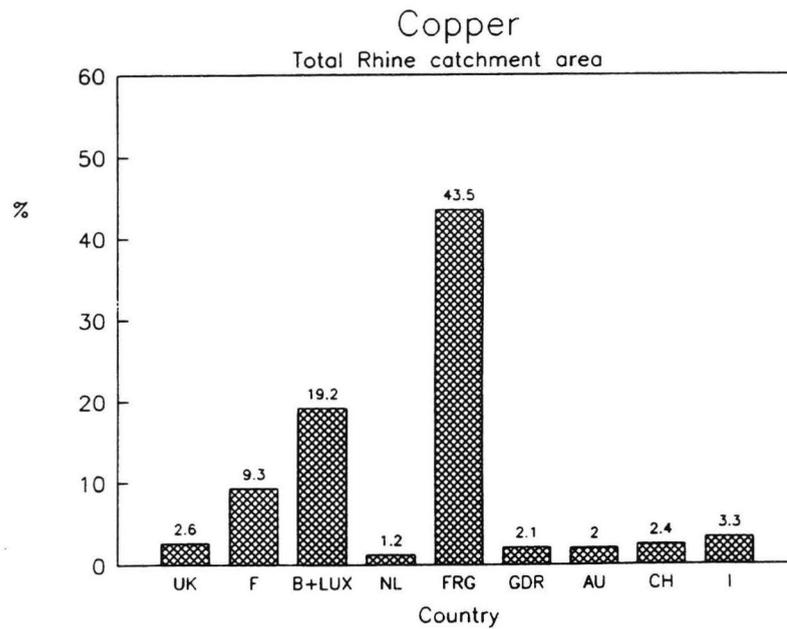
**Figure C2** Relative contributions of the surrounding countries to the total deposition of cadmium on the Dutch part of the Rhine catchment area. Total deposition 0.8 ton/y.



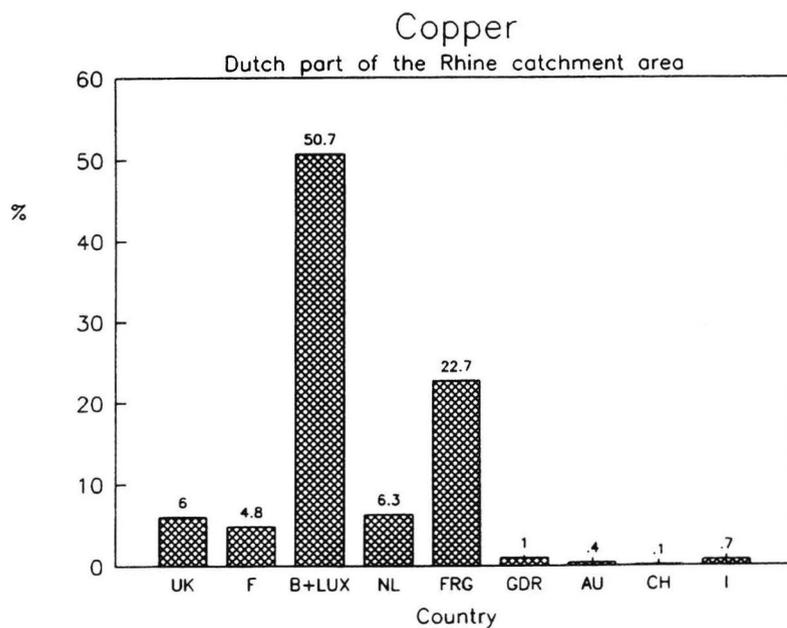
**Figure C3** Relative contributions of the surrounding countries to the total deposition of chromium on the Rhine catchment area. Total deposition 100 ton/y.



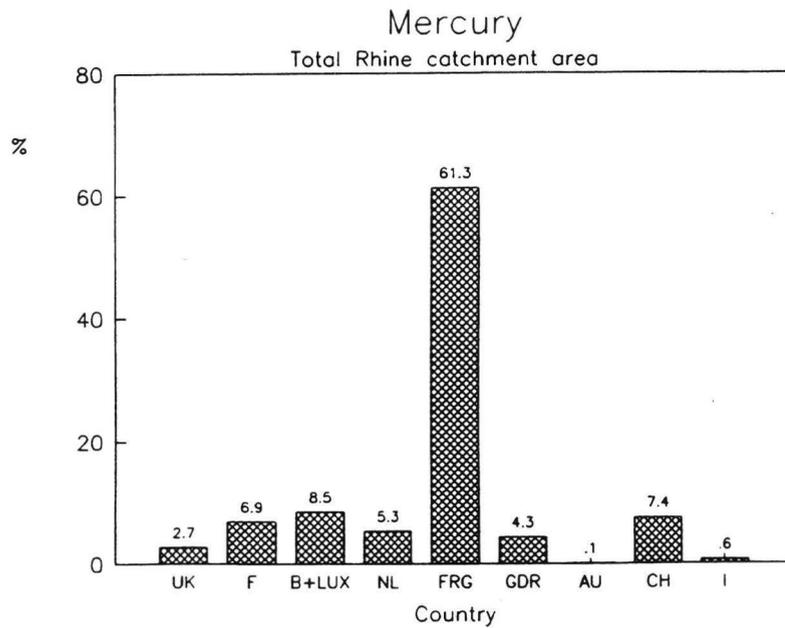
**Figure C4** Relative contributions of the surrounding countries to the total deposition of chromium on the Dutch part of the Rhine catchment area. Total deposition 3.6 ton/y.



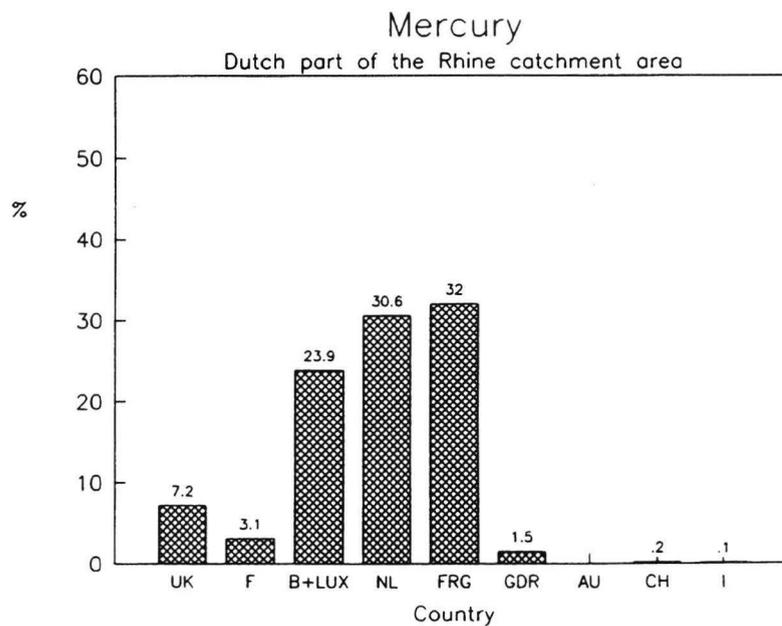
**Figure C5** Relative contributions of the surrounding countries to the total deposition of copper on the Rhine catchment area. Total deposition 120 ton/y.



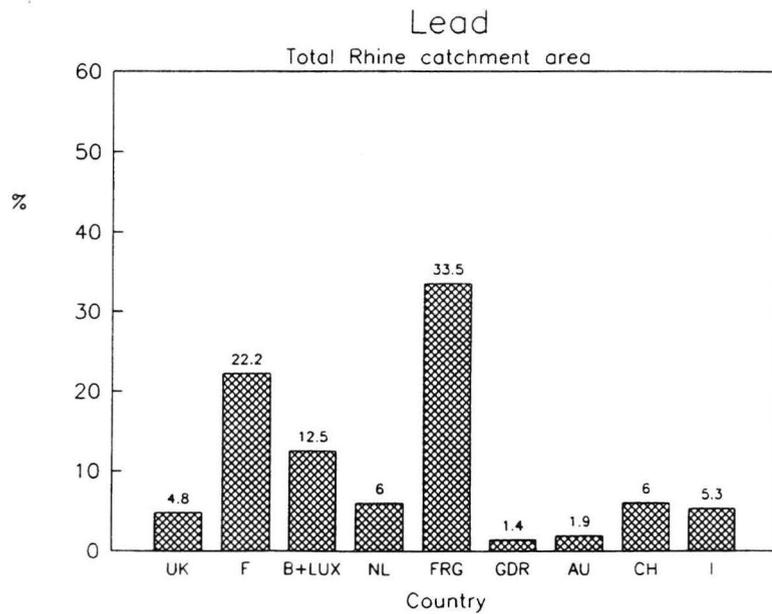
**Figure C6** Relative contributions of the surrounding countries to the total deposition of copper on the Dutch part of the Rhine catchment area. Total deposition 6.3 ton/y.



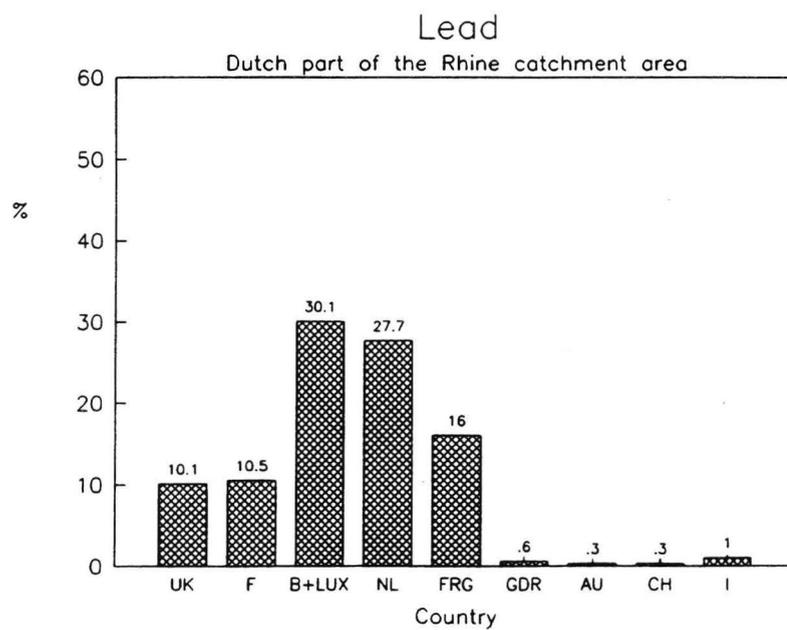
**Figure C7** Relative contributions of the surrounding countries to the total deposition of mercury on the Rhine catchment area. Total deposition 18 ton/y.



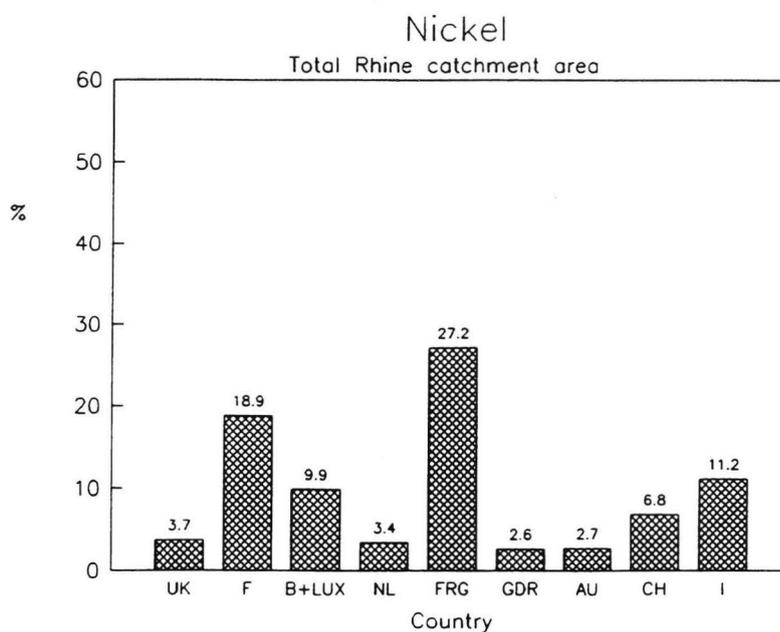
**Figure C8** Relative contributions of the surrounding countries to the total deposition of mercury on the Dutch part of the Rhine catchment area. Total deposition 0.9 ton/y.



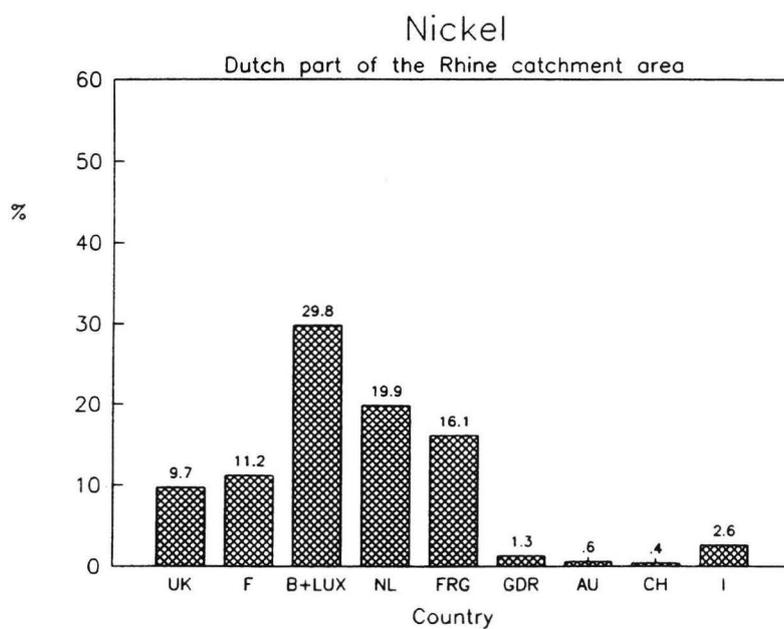
**Figure C9** Relative contributions of the surrounding countries to the total deposition of lead on the Rhine catchment area. Total deposition 1900 ton/y.



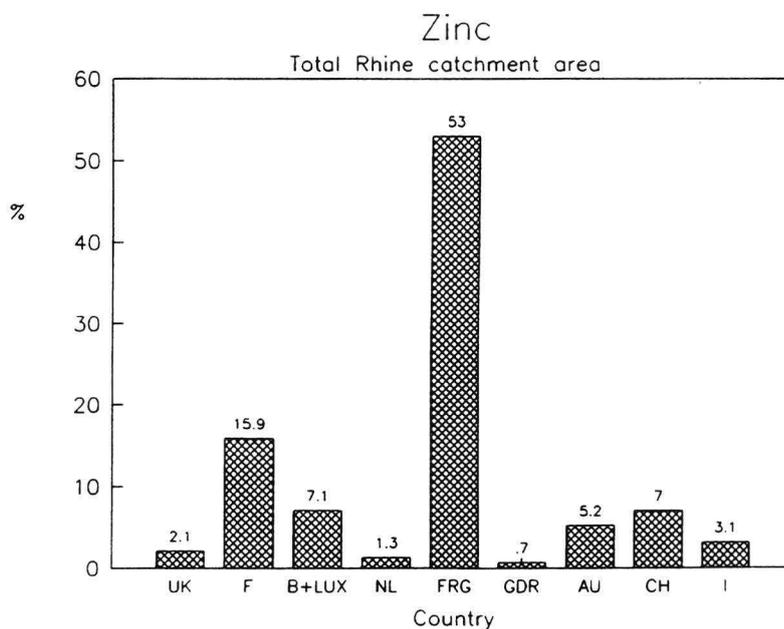
**Figure C10** Relative contributions of the surrounding countries to the total deposition of lead on the Dutch part of the Rhine catchment area. Total deposition 310.1 ton/y.



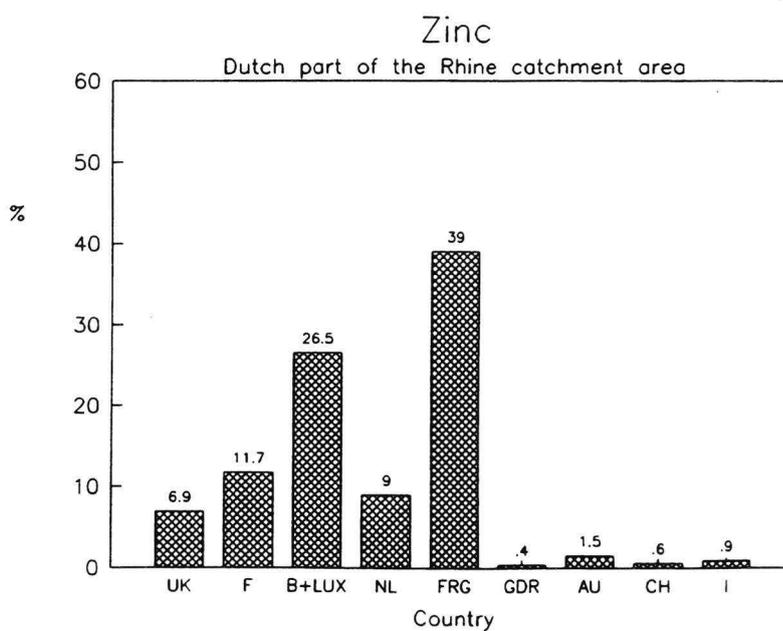
*Figure C11* Relative contributions of the surrounding countries to the total deposition of nickel on the Rhine catchment area. Total deposition 130 ton/y.



*Figure C12* Relative contributions of the surrounding countries to the total deposition of nickel on the Dutch part of the Rhine catchment area. Total deposition 5.6 ton/y.

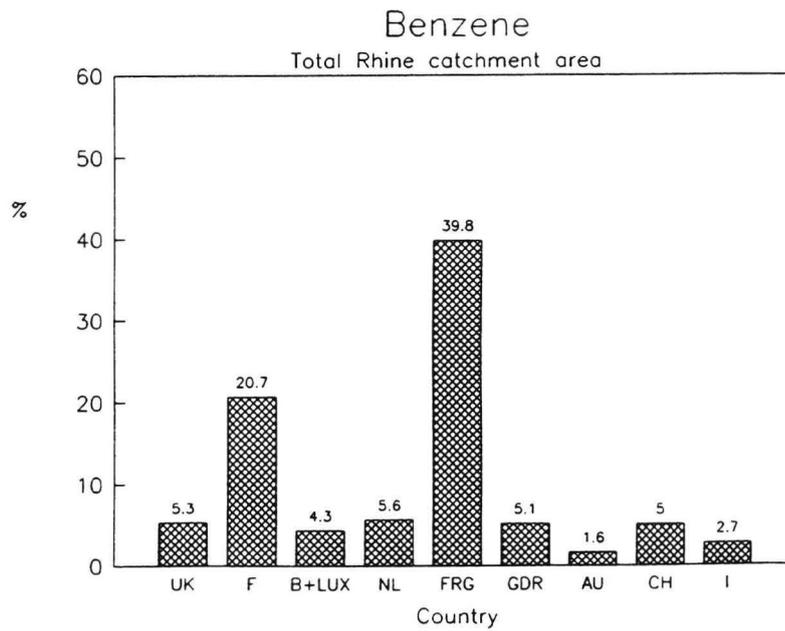


**Figure C13** Relative contributions of the surrounding countries to the total deposition of zinc on the Rhine catchment area. Total deposition 1500 ton/y.

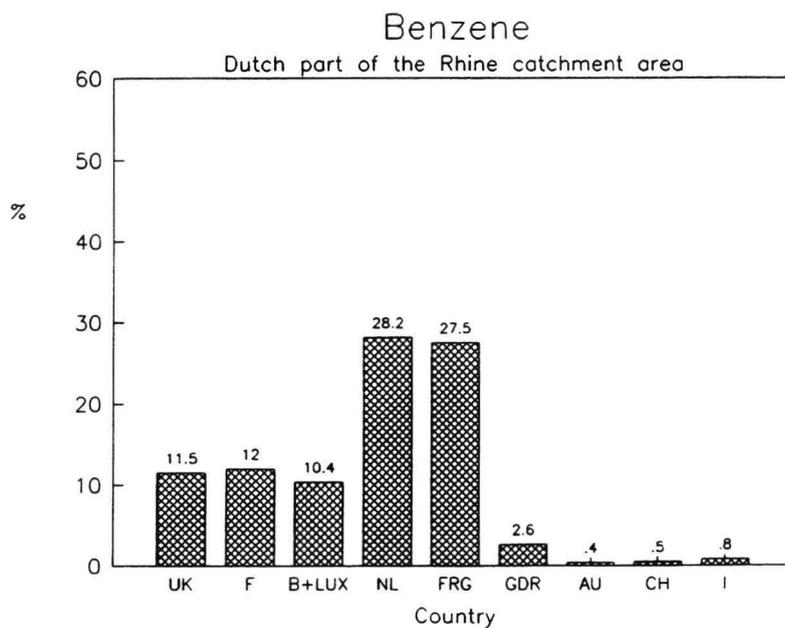


**Figure C14** Relative contributions of the surrounding countries to the total deposition of zinc on the Dutch part of the Rhine catchment area. Total deposition 54.7 ton/y.

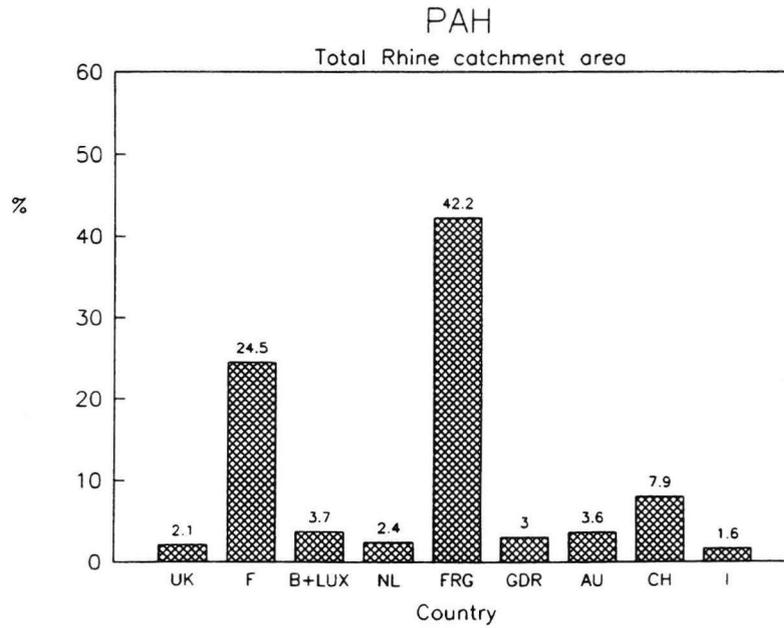




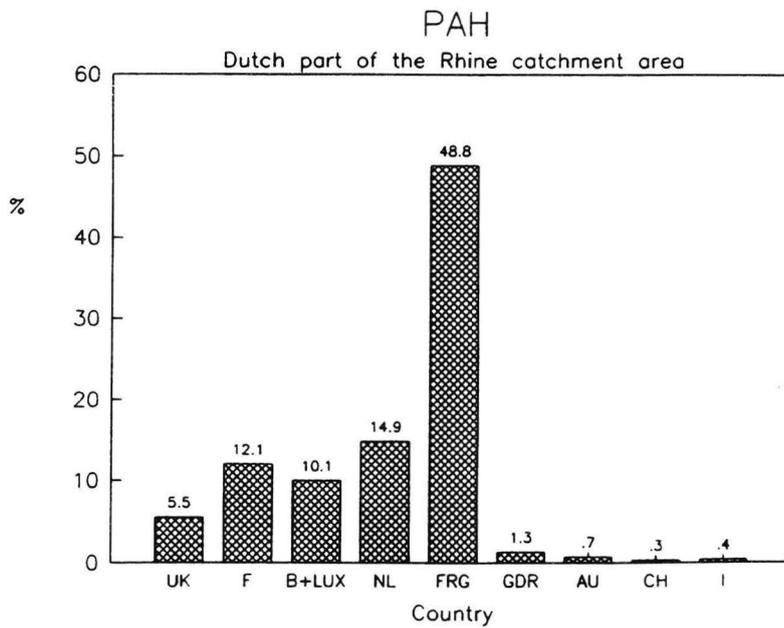
**Figure C15** Relative contributions of the surrounding countries to the total deposition of benzene on the Rhine catchment area. Total deposition 520 ton/y.



**Figure C16** Relative contributions of the surrounding countries to the total deposition of benzene on the Dutch part of the Rhine catchment area. Total deposition 23.7 ton/y.

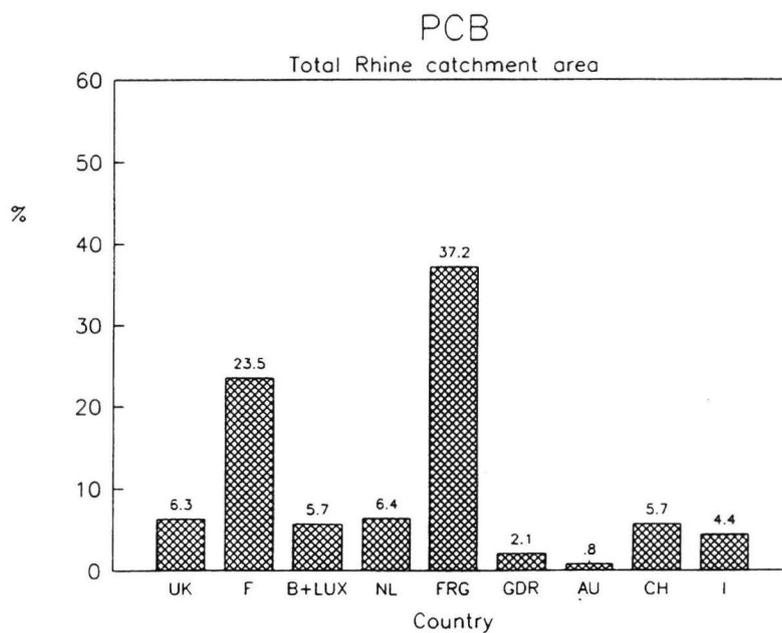


**Figure C17** Relative contributions of the surrounding countries to the total deposition of PAH on the Rhine catchment area. Total deposition 45.5 tonly.

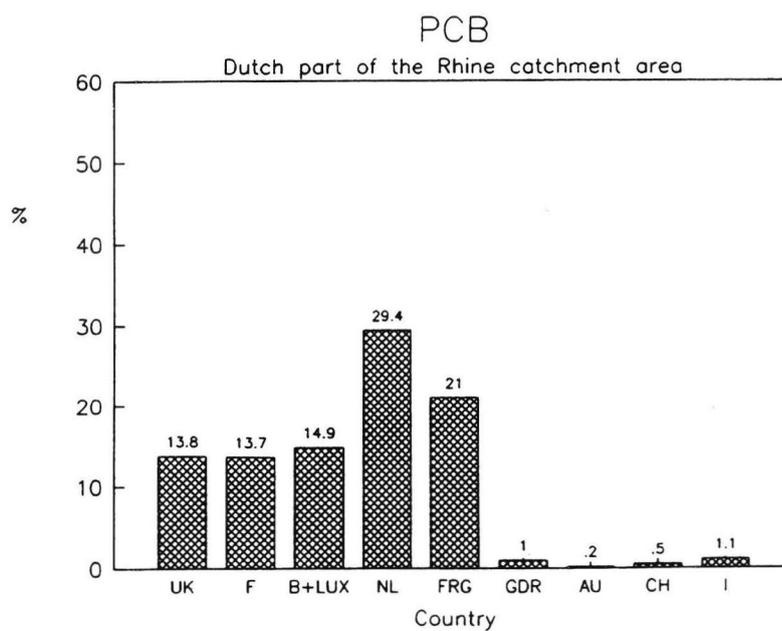


**Figure C18** Relative contributions of the surrounding countries to the total deposition of PAH on the Dutch part of the Rhine catchment area. Total deposition 2.1 tonly.

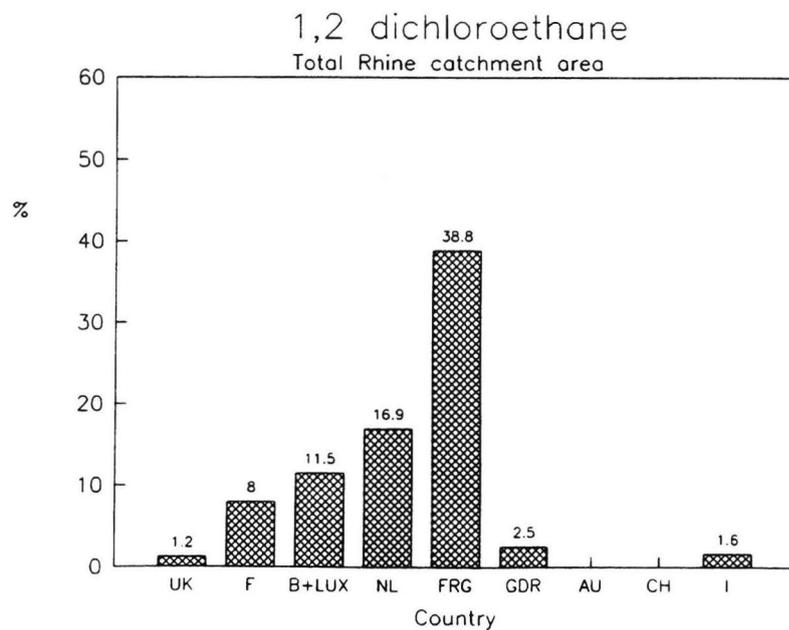




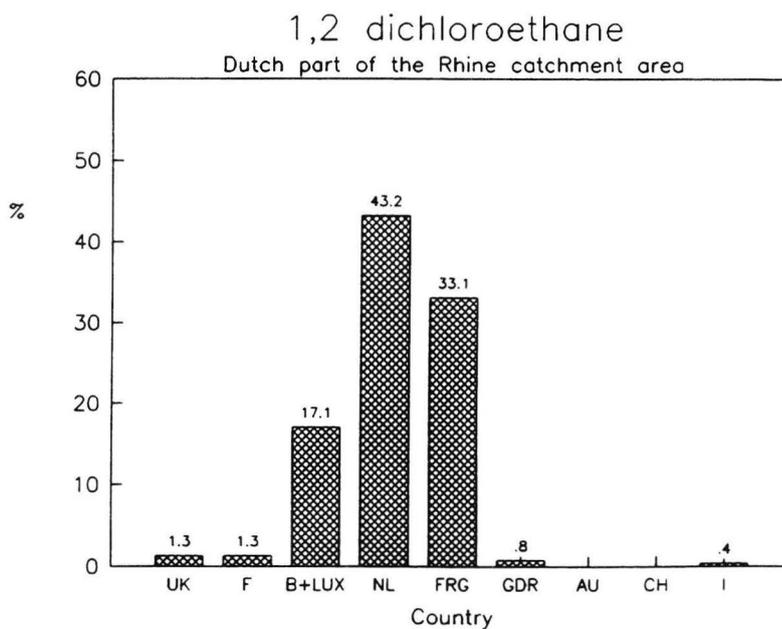
**Figure C19** Relative contributions of the surrounding countries to the total deposition of PCB on the Rhine catchment area. Total deposition 28 tonly.



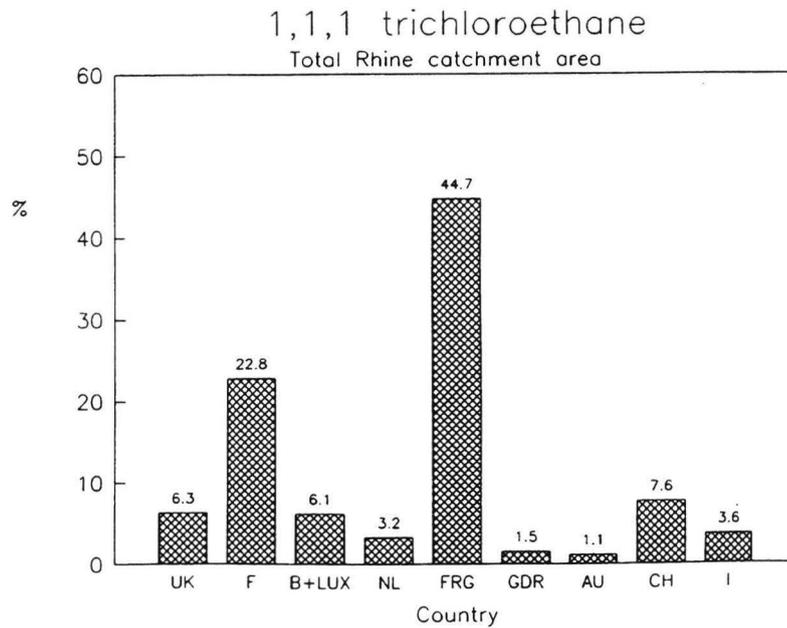
**Figure C20** Relative contributions of the surrounding countries to the total deposition of PCB on the Dutch part of the Rhine catchment area. Total deposition 1.3 tonly.



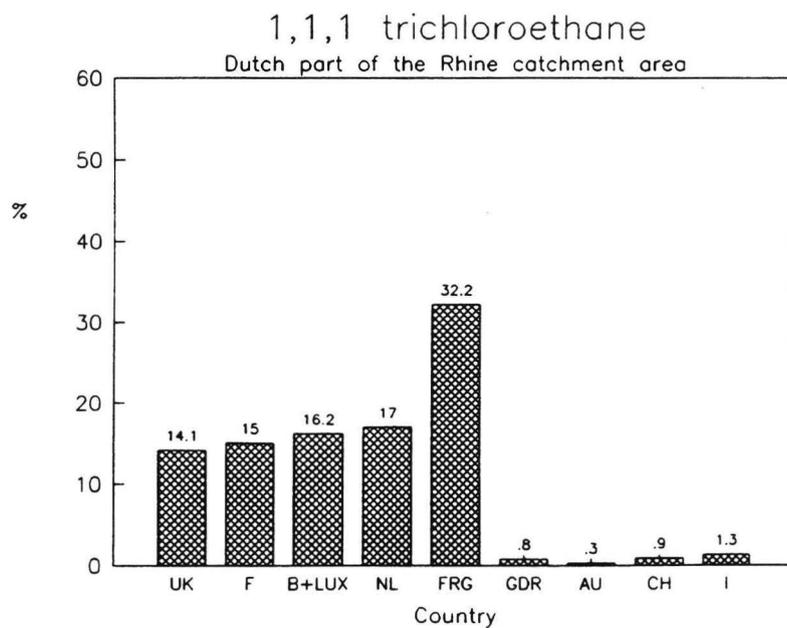
**Figure C21** Relative contributions of the surrounding countries to the total deposition of 1,2-dichloroethane on the Rhine catchment area. Total deposition 63 ton/ly.



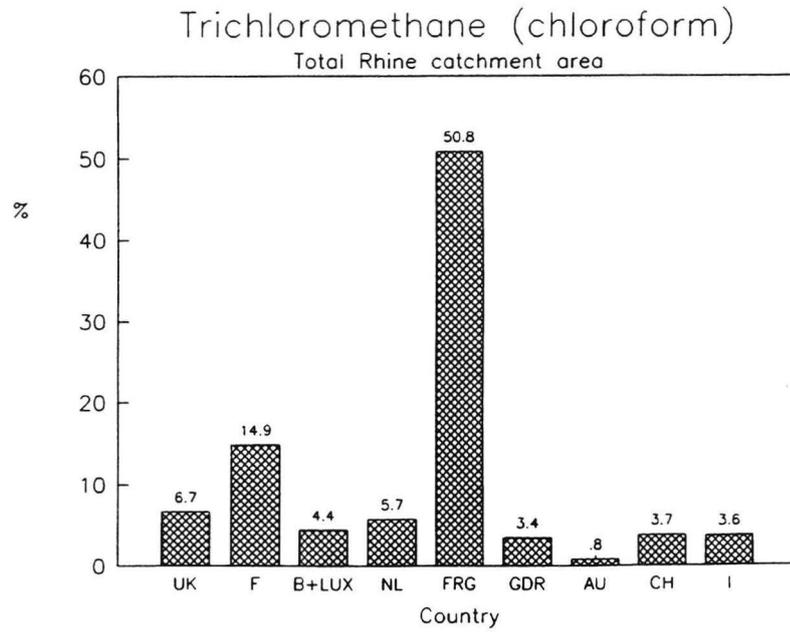
**Figure C22** Relative contributions of the surrounding countries to the total deposition of 1,2-dichloroethane on the Dutch part of the Rhine catchment area. Total deposition 4.3 ton/ly.



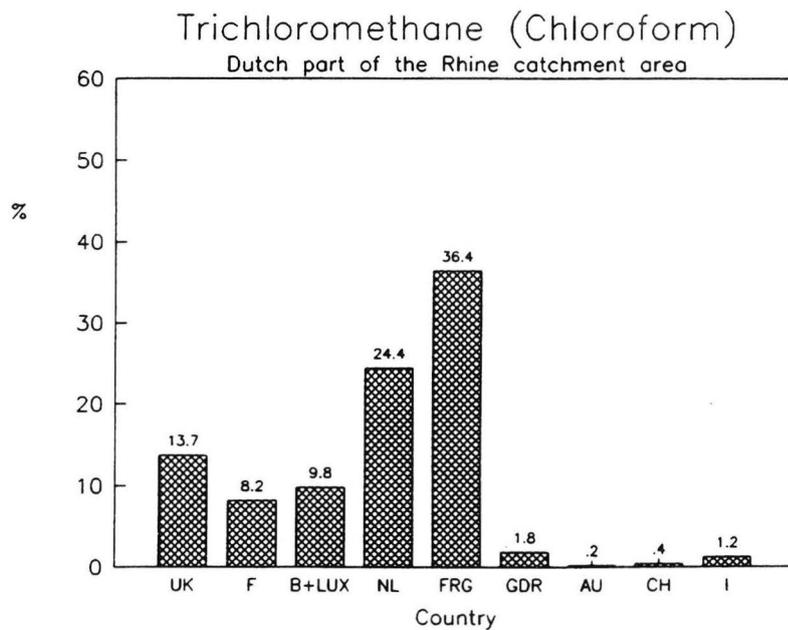
**Figure C23** Relative contributions of the surrounding countries to the total deposition of 1,1,1-trichloroethane on the Rhine catchment area. Total deposition 730 ton/y.



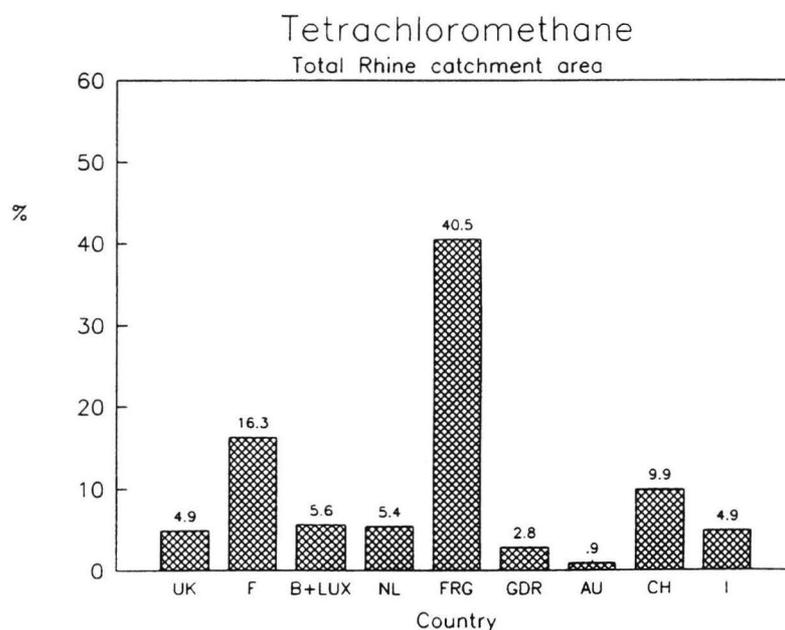
**Figure C24** Relative contributions of the surrounding countries to the total deposition of 1,1,1-trichloroethane on the Dutch part of the Rhine catchment area. Total deposition 30.4 ton/y.



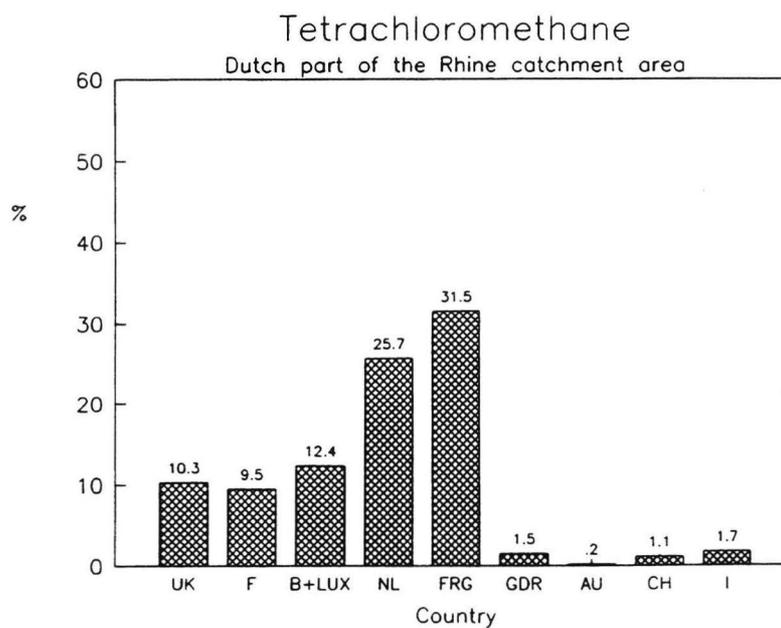
**Figure C25** Relative contributions of the surrounding countries to the total deposition of chloroform on the Rhine catchment area. Total deposition 12 ton/y.



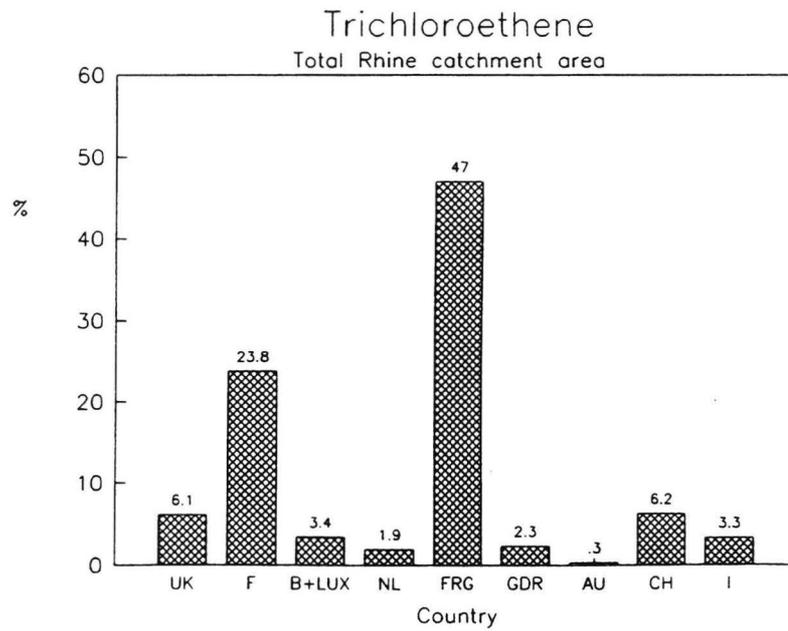
**Figure C26** Relative contributions of the surrounding countries to the total deposition of chloroform on the Dutch part of the Rhine catchment area. Total deposition 0.6 ton/y.



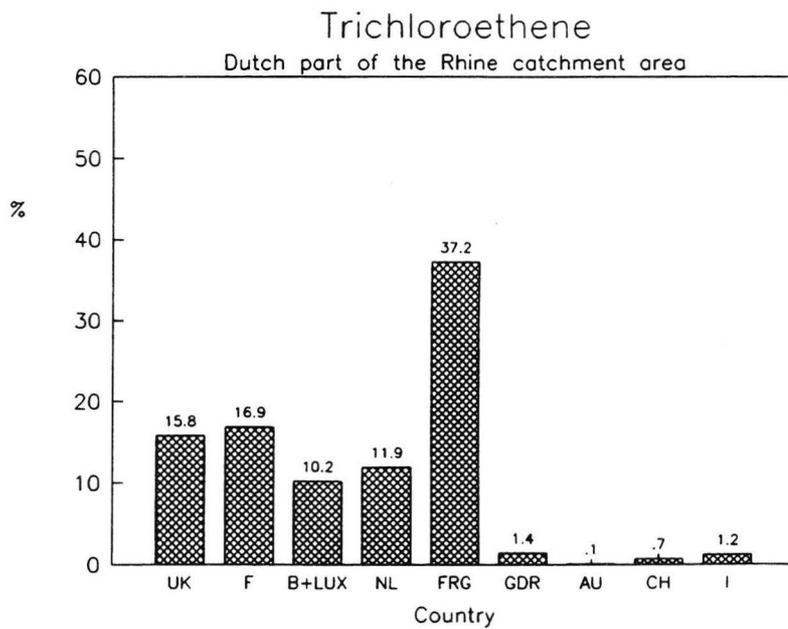
**Figure C27** Relative contributions of the surrounding countries to the total deposition of tetrachloromethane on the Rhine catchment area. Total deposition 4.3 ton/y.



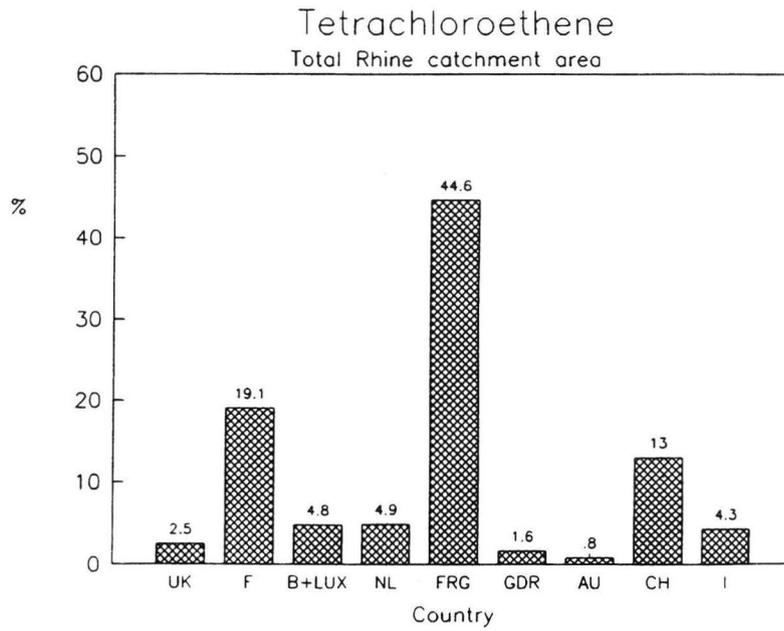
**Figure C28** Relative contributions of the surrounding countries to the total deposition of tetrachloromethane on the Dutch part of the Rhine catchment area. Total deposition 0.2 ton/y.



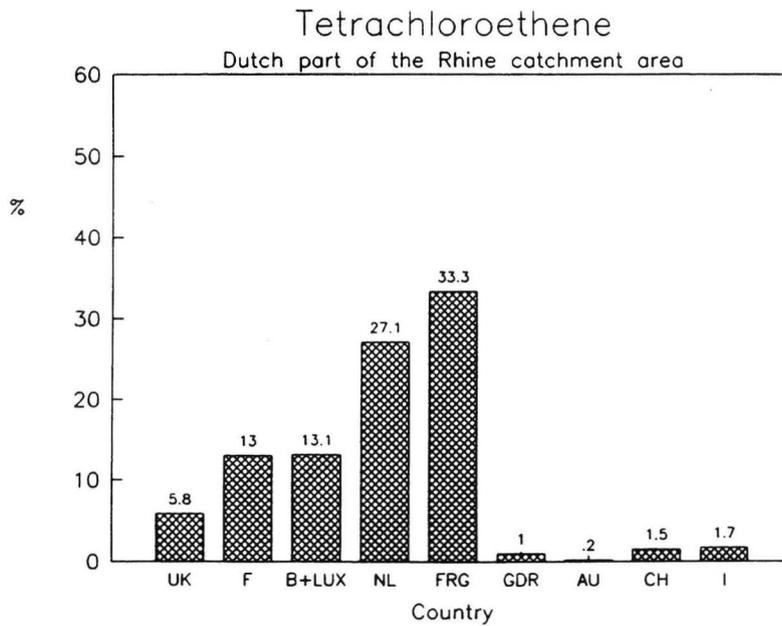
**Figure C29** Relative contributions of the surrounding countries to the total deposition of trichloroethene on the Rhine catchment area. Total deposition 280 ton/y.



**Figure C30** Relative contributions of the surrounding countries to the total deposition of trichloroethene on the Dutch part of the Rhine catchment area. Total deposition 10.4 ton/y.



**Figure C31** Relative contributions of the surrounding countries to the total deposition of tetrachloroethene on the Rhine catchment area. Total deposition 110 ton/y.



**Figure C32** Relative contributions of the surrounding countries to the total deposition of tetrachloroethene on the Dutch part of the Rhine catchment area. Total deposition 4.5 ton/y.



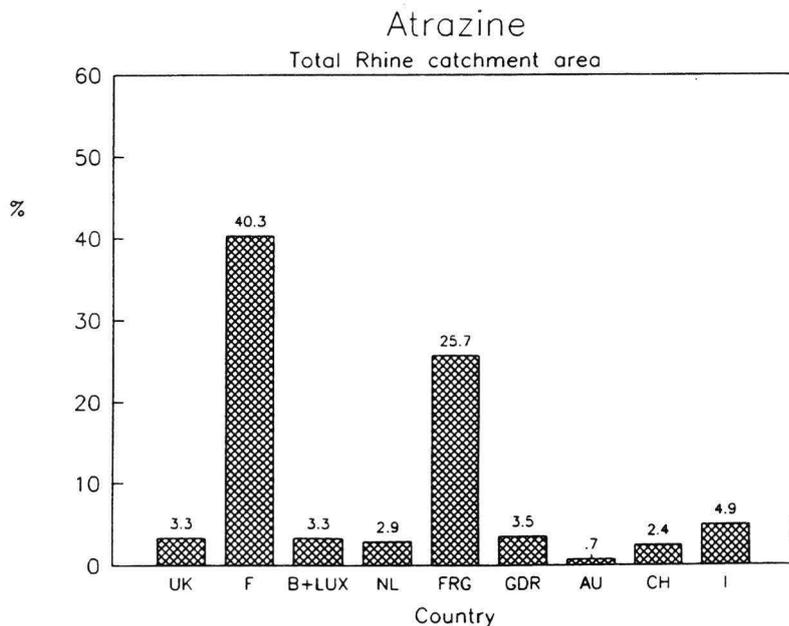


Figure C33 Relative contributions of the surrounding countries to the total deposition of atrazine on the Rhine catchment area. Total deposition 170 ton/y.

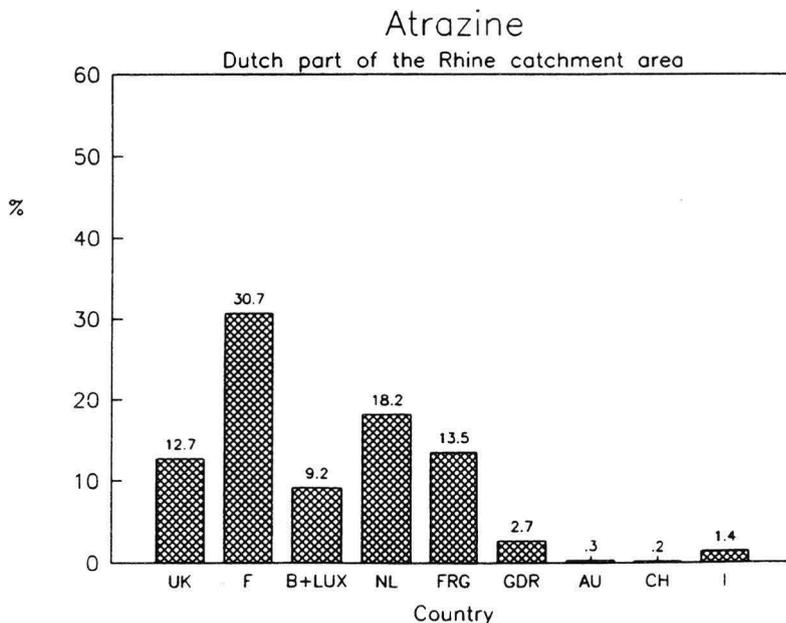
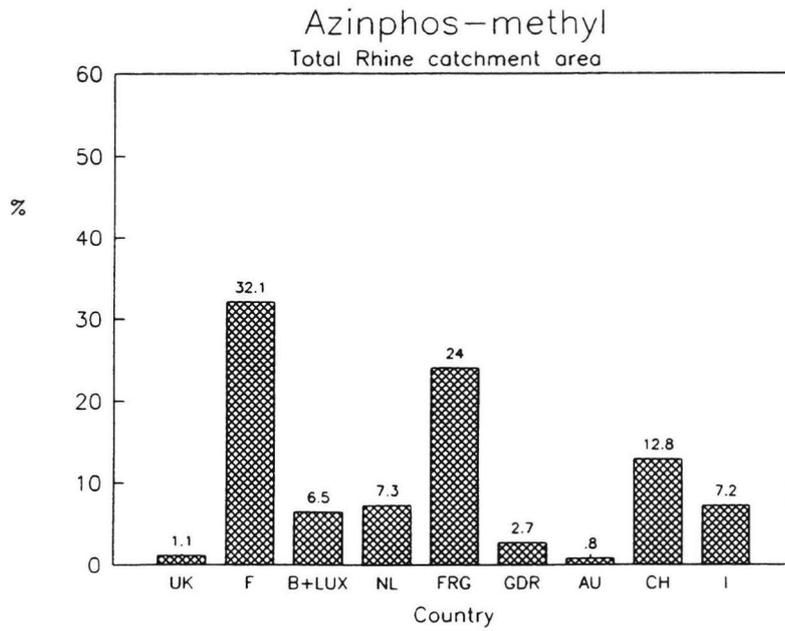
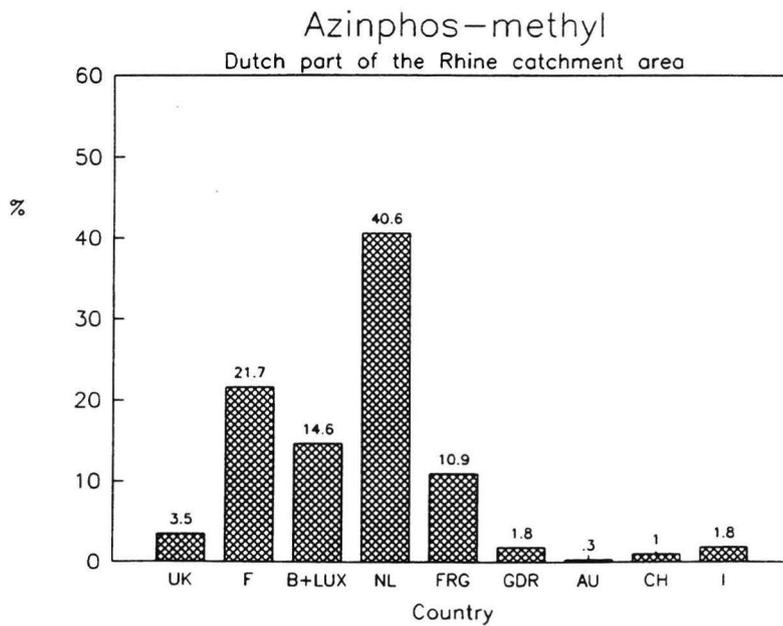


Figure C34 Relative contributions of the surrounding countries to the total deposition of atrazine on the Dutch part of the Rhine catchment area. Total deposition 5.3 ton/y.

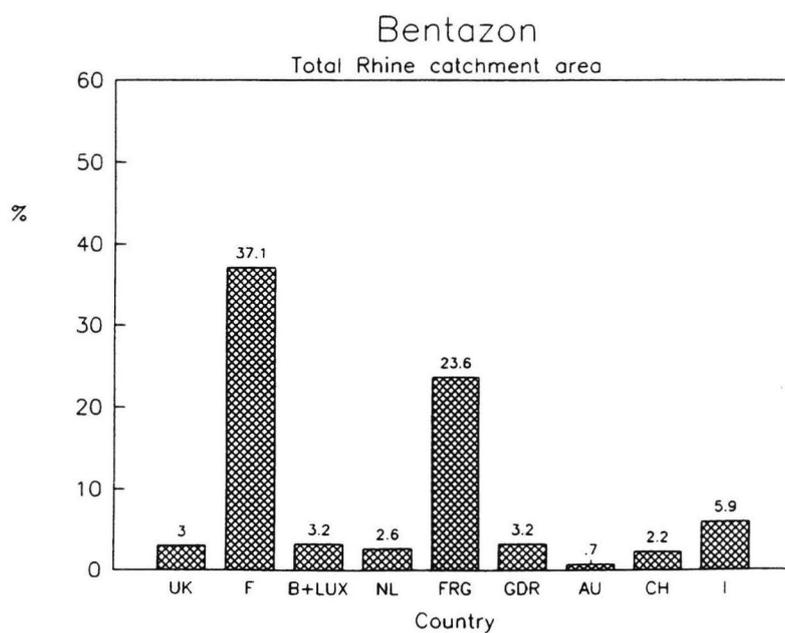




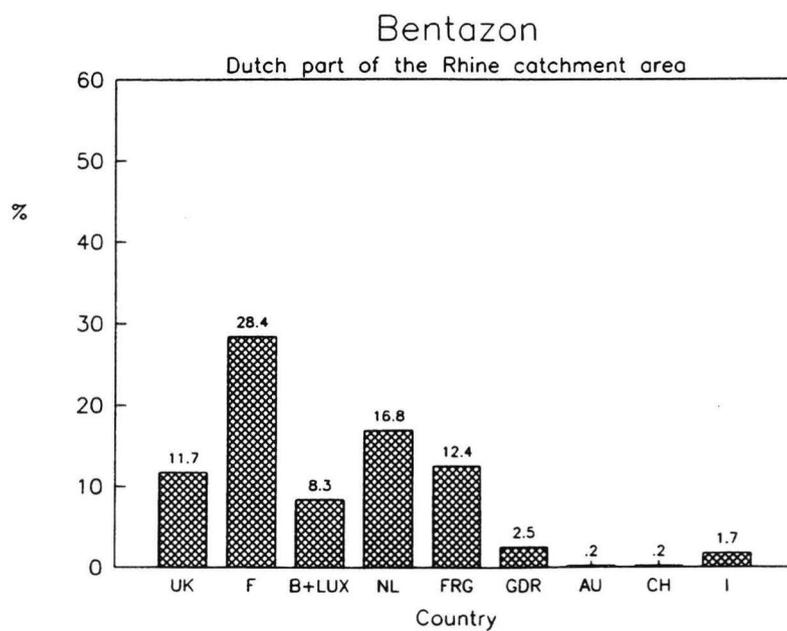
**Figure C35** Relative contributions of the surrounding countries to the total deposition of azinphos-methyl on the Rhine catchment area. Total deposition 1.5 ton/y.



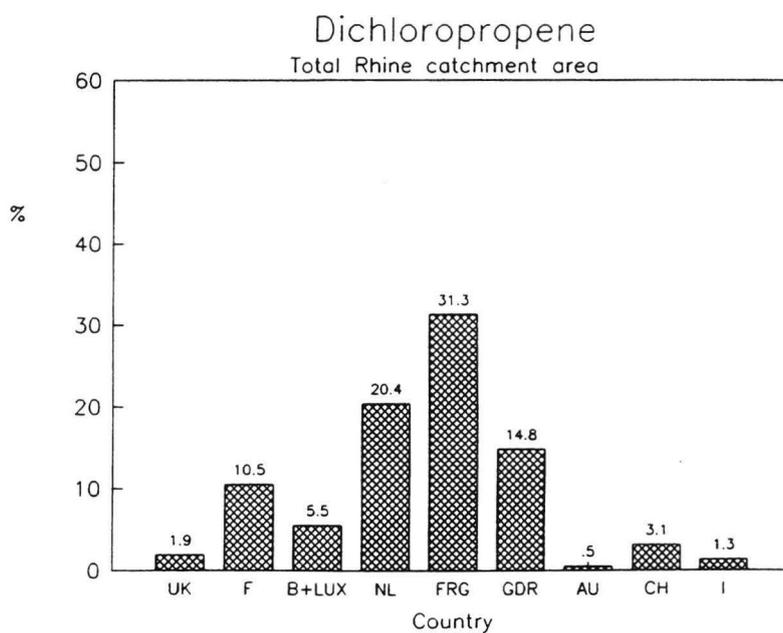
**Figure C36** Relative contributions of the surrounding countries to the total deposition of azinphos-methyl on the Dutch part of the Rhine catchment area. Total deposition 0.1 ton/y.



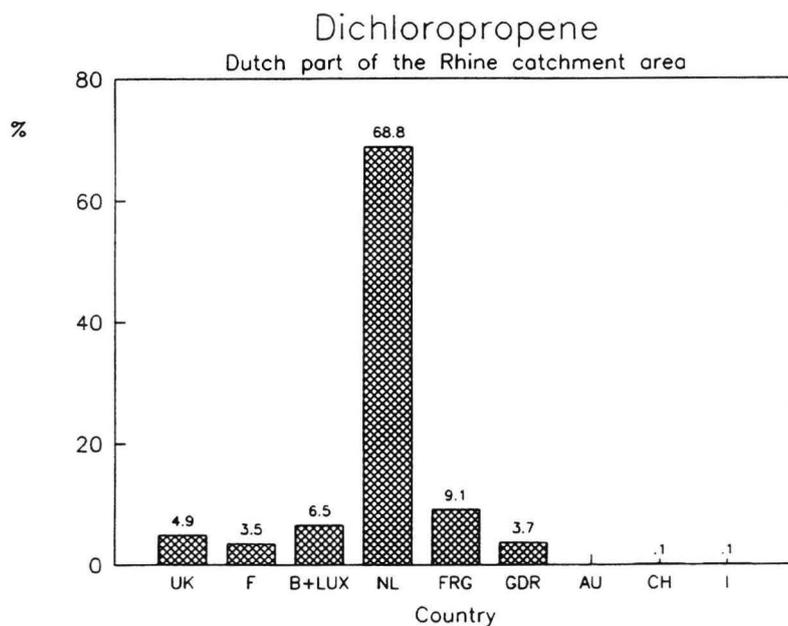
**Figure C37** Relative contributions of the surrounding countries to the total deposition of bentazon on the Rhine catchment area. Total deposition 57 ton/y.



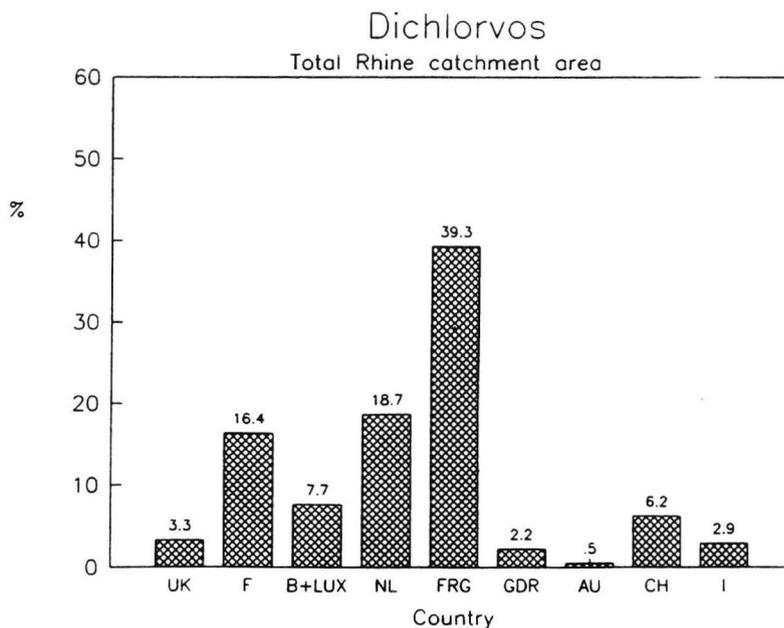
**Figure C38** Relative contributions of the surrounding countries to the total deposition of bentazon on the Dutch part of the Rhine catchment area. Total deposition 1.8 ton/y.



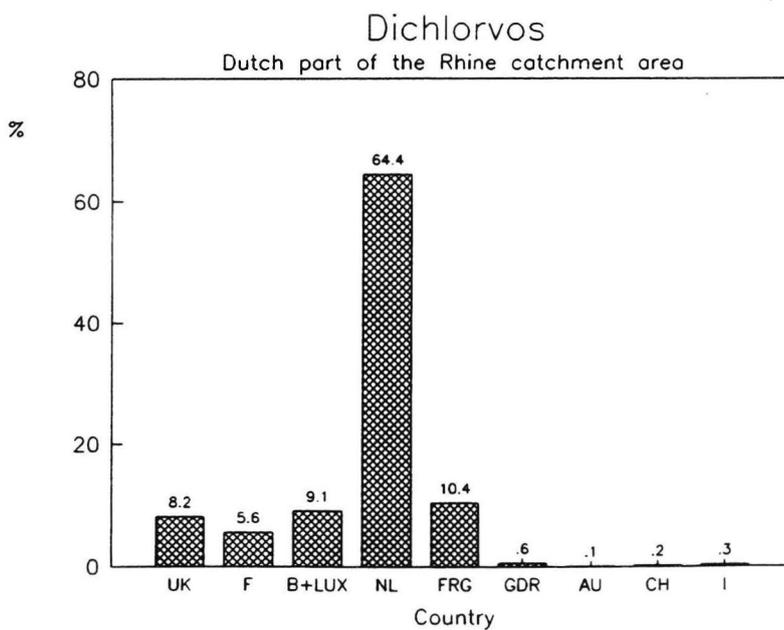
**Figure C39** Relative contributions of the surrounding countries to the total deposition of dichloropropene on the Rhine catchment area. Total deposition 79 ton/y.



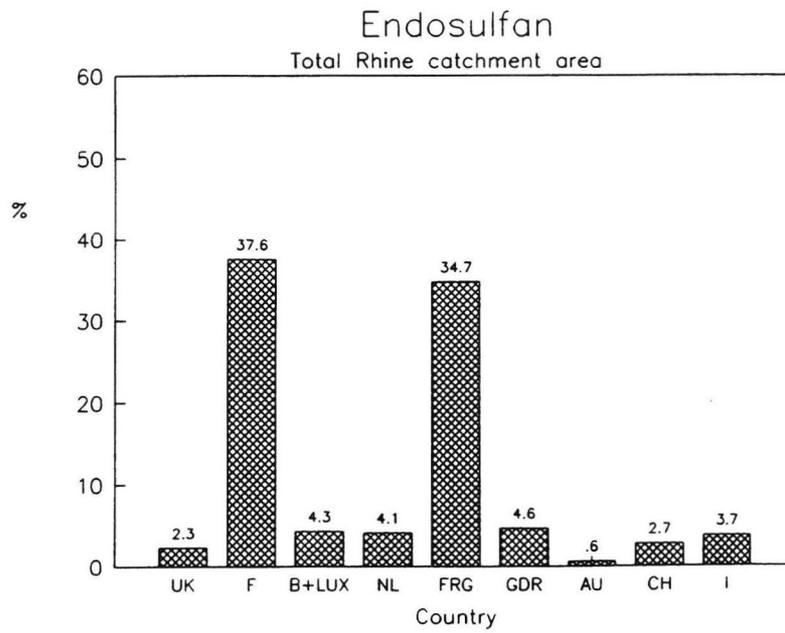
**Figure C40** Relative contributions of the surrounding countries to the total deposition of dichloropropene on the Dutch part of the Rhine catchment area. Total deposition 4.4 ton/y.



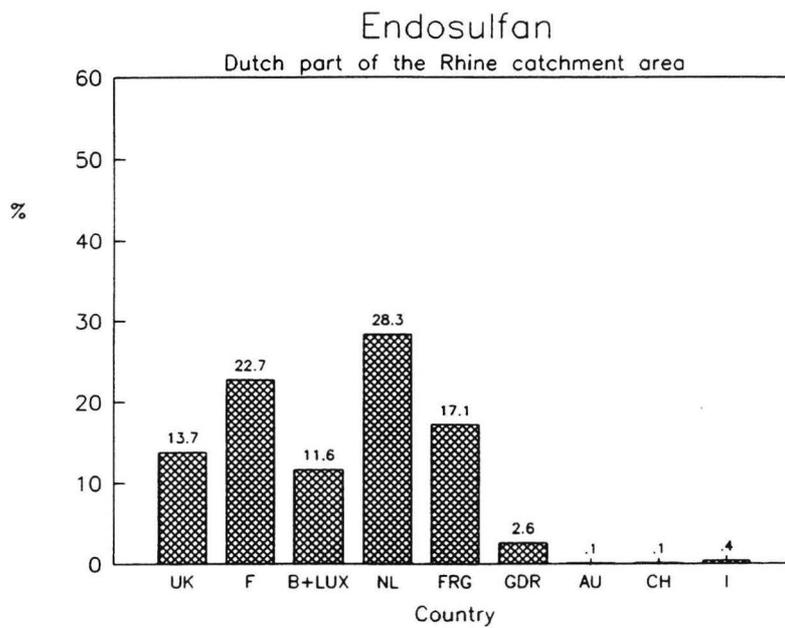
**Figure C41** Relative contributions of the surrounding countries to the total deposition of dichlorvos on the Rhine catchment area. Total deposition 7.3 ton/y.



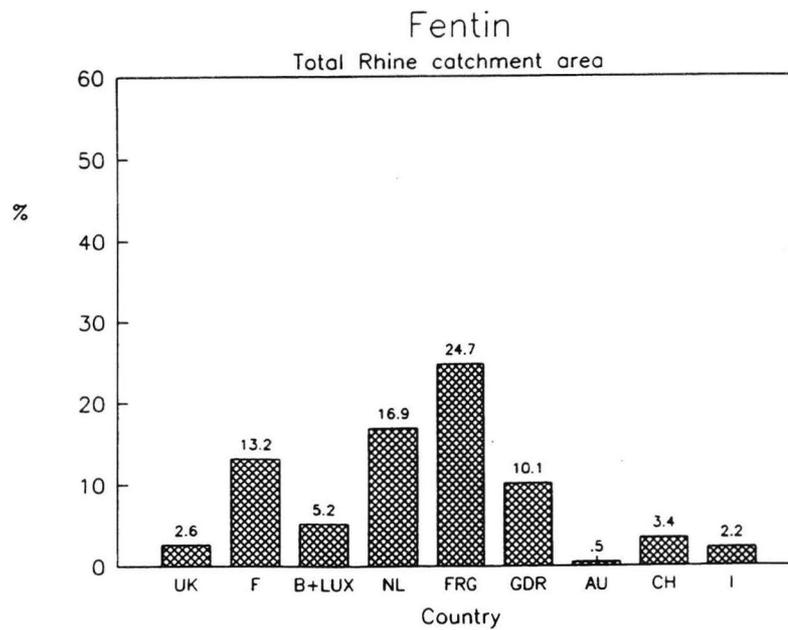
**Figure C42** Relative contributions of the surrounding countries to the total deposition of dichlorvos on the Dutch part of the Rhine catchment area. Total deposition 0.4 ton/y.



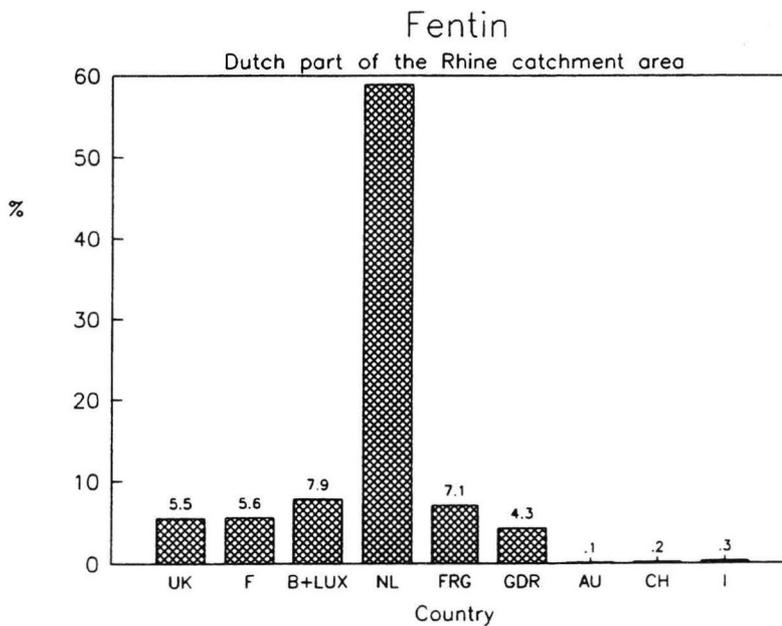
**Figure C43** Relative contributions of the surrounding countries to the total deposition of endosulfan on the Rhine catchment area. Total deposition 12 ton/y.



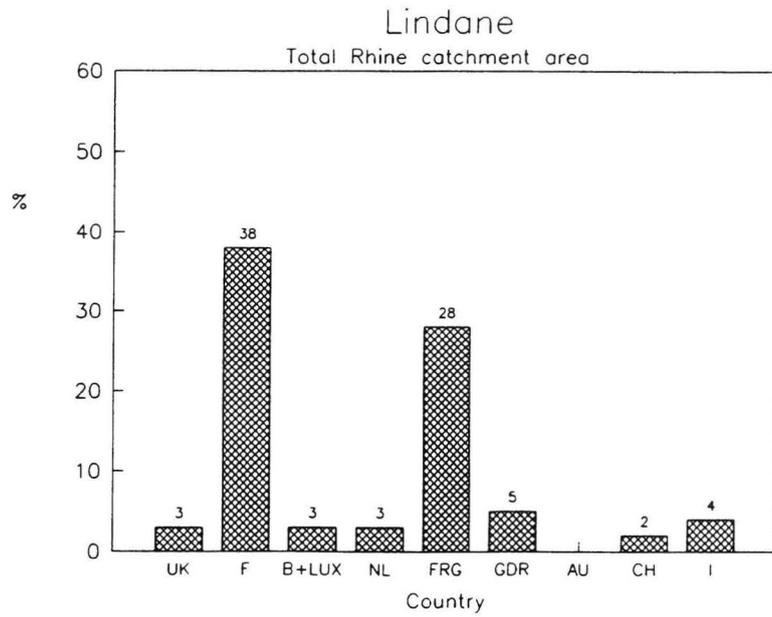
**Figure C44** Relative contributions of the surrounding countries to the total deposition of endosulfan on the Dutch part of the Rhine catchment area. Total deposition 0.3 ton/y.



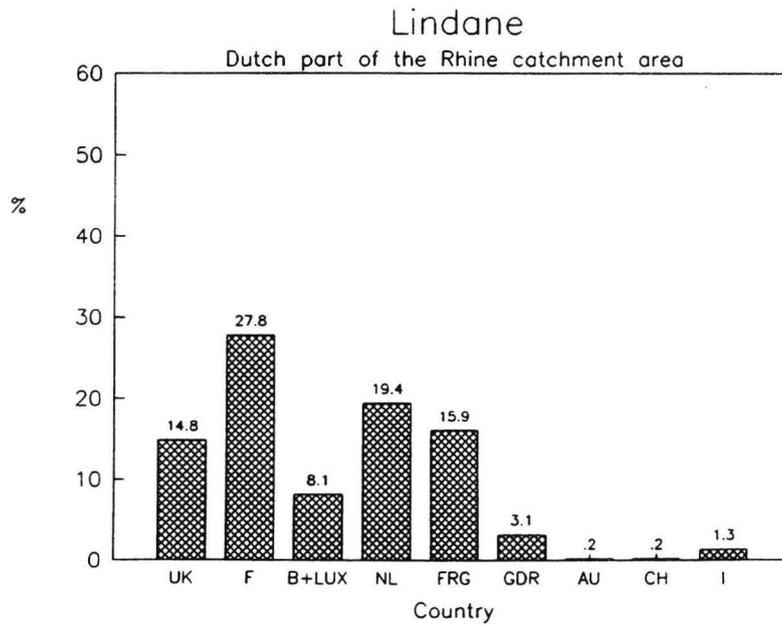
**Figure C45** Relative contributions of the surrounding countries to the total deposition of fentin on the Rhine catchment area. Total deposition 77 ton/y.



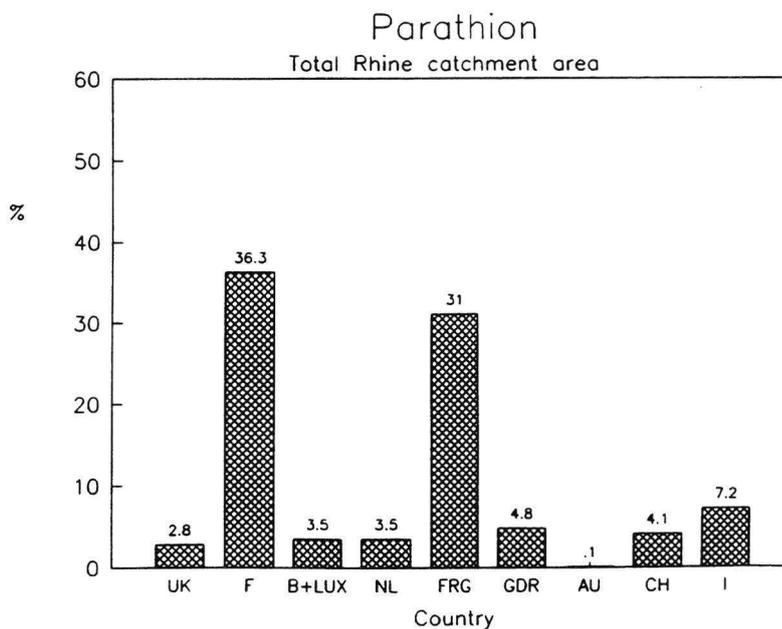
**Figure C46** Relative contributions of the surrounding countries to the total deposition of fentin on the Dutch part of the Rhine catchment area. Total deposition 4.4 ton/y.



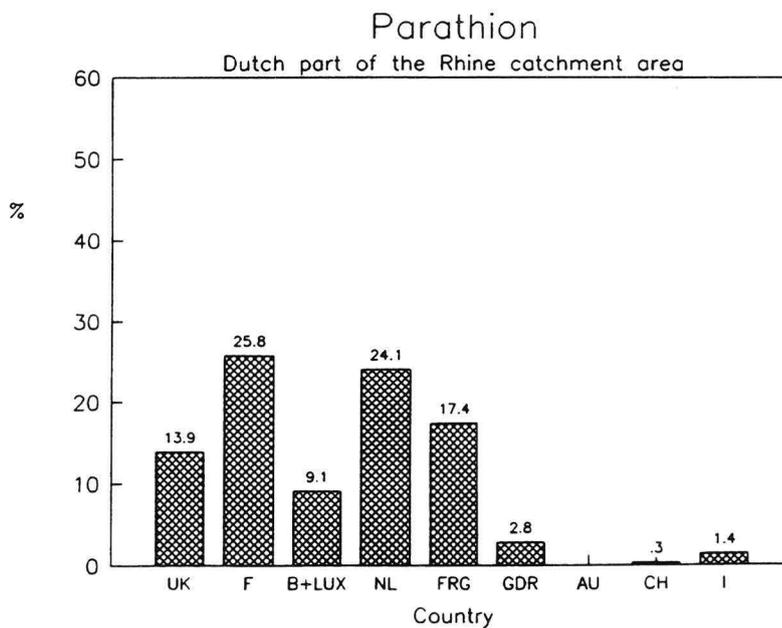
**Figure C47** Relative contributions of the surrounding countries to the total deposition of lindane on the Rhine catchment area. Total deposition 42 ton/y.



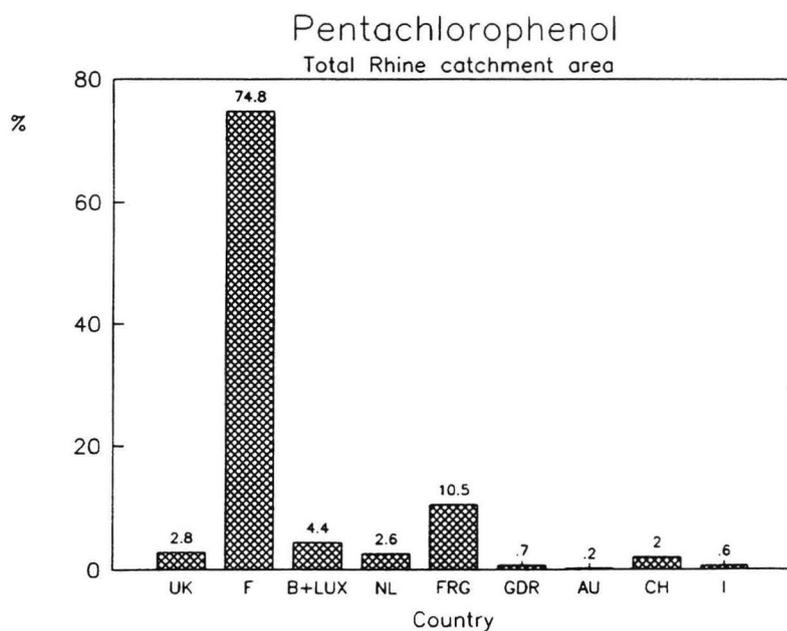
**Figure C48** Relative contributions of the surrounding countries to the total deposition of lindane on the Dutch part of the Rhine catchment area. Total deposition 1.2 ton/y.



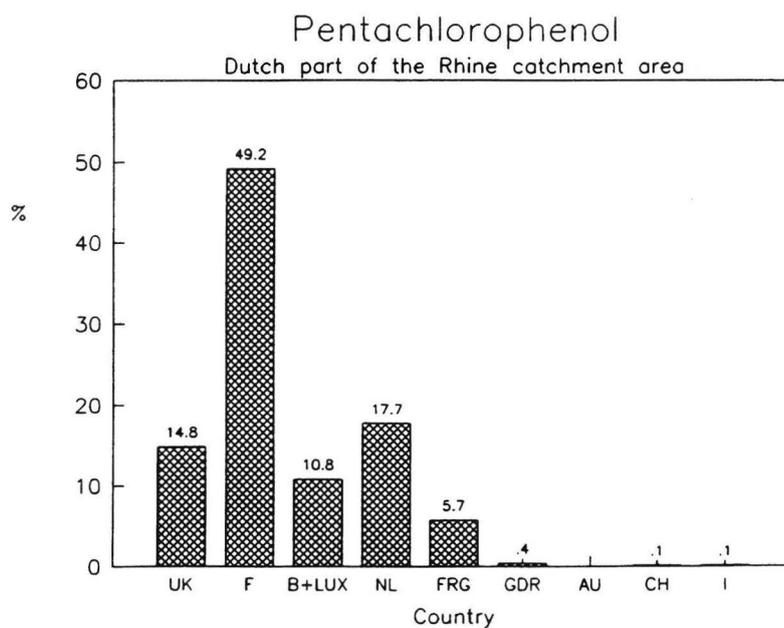
**Figure C49** Relative contributions of the surrounding countries to the total deposition of parathion on the Rhine catchment area. Total deposition 50 ton/y.



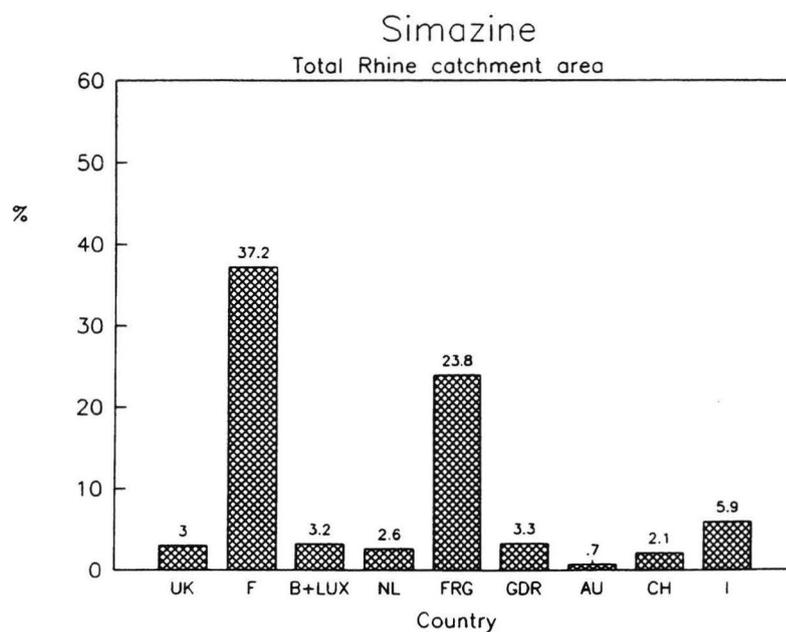
**Figure C50** Relative contributions of the surrounding countries to the total deposition of parathion on the Dutch part of the Rhine catchment area. Total deposition 1.4 ton/y.



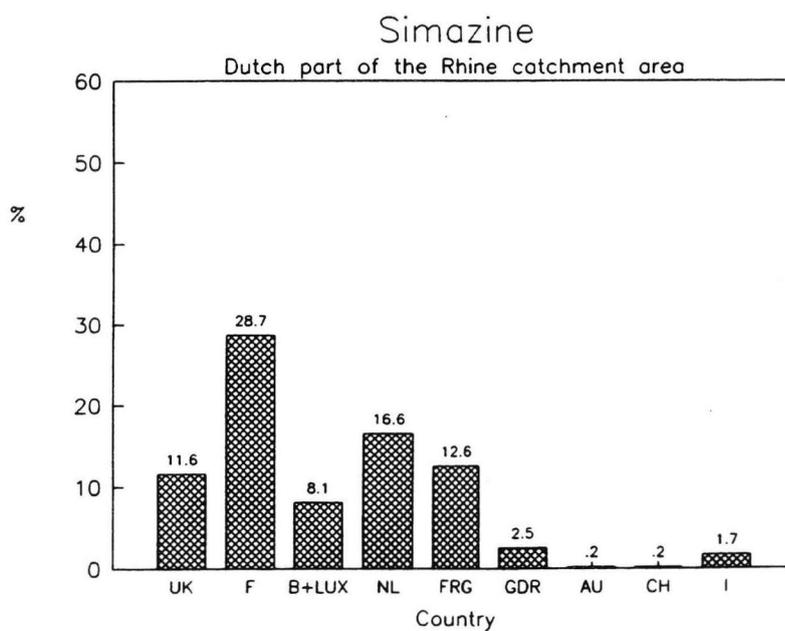
**Figure C51** Relative contributions of the surrounding countries to the total deposition of pentachlorophenol on the Rhine catchment area. Total deposition 260 ton/y.



**Figure C52** Relative contributions of the surrounding countries to the total deposition of pentachlorophenol on the Dutch part of the Rhine catchment area. Total deposition 7 ton/y.



**Figure C53** Relative contributions of the surrounding countries to the total deposition of simazine on the Rhine catchment area. Total deposition 10 ton/y.



**Figure C54** Relative contributions of the surrounding countries to the total deposition of simazine on the Dutch part of the Rhine catchment area. Total deposition 0.3 ton/y.

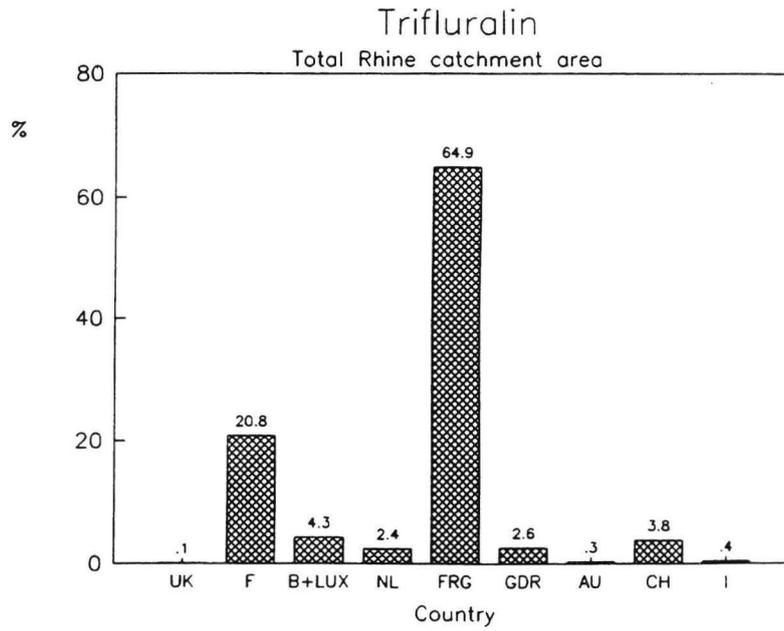


Figure C55 Relative contributions of the surrounding countries to the total deposition of trifluralin on the Rhine catchment area. Total deposition 3.6 ton/y.

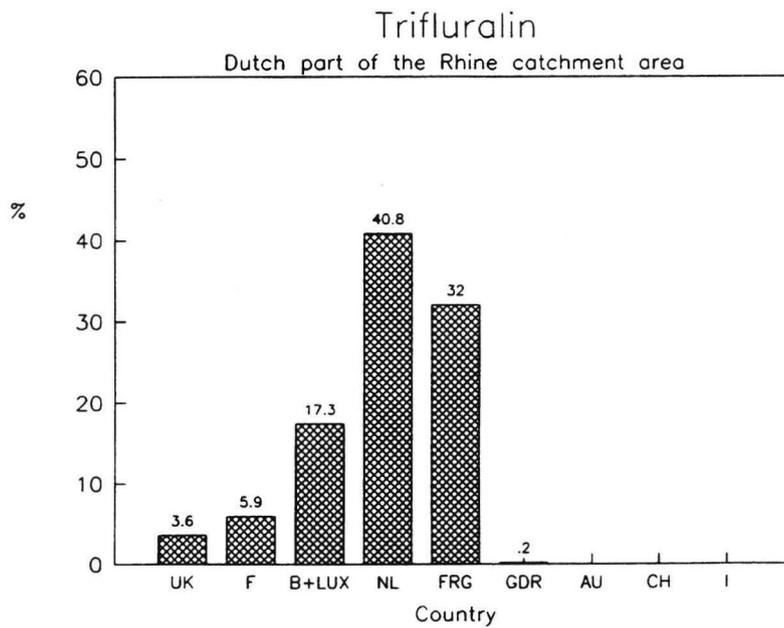
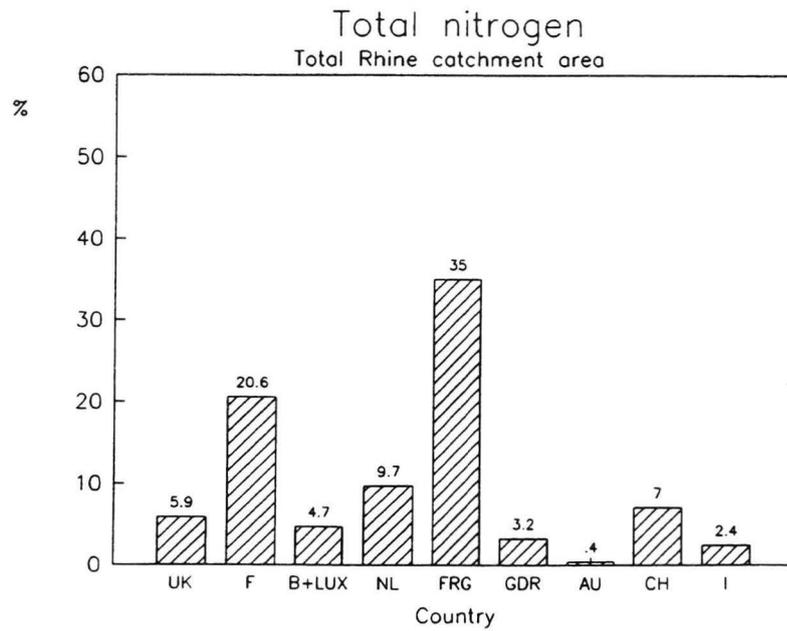
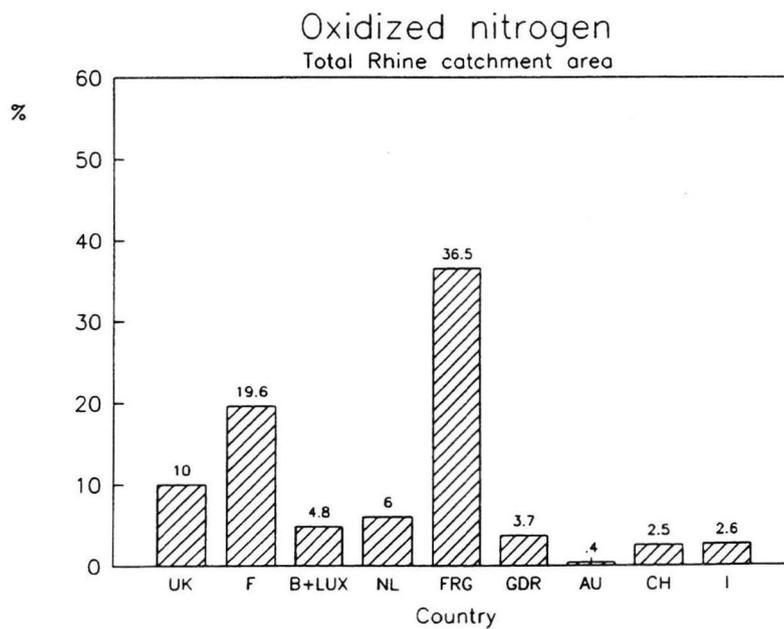


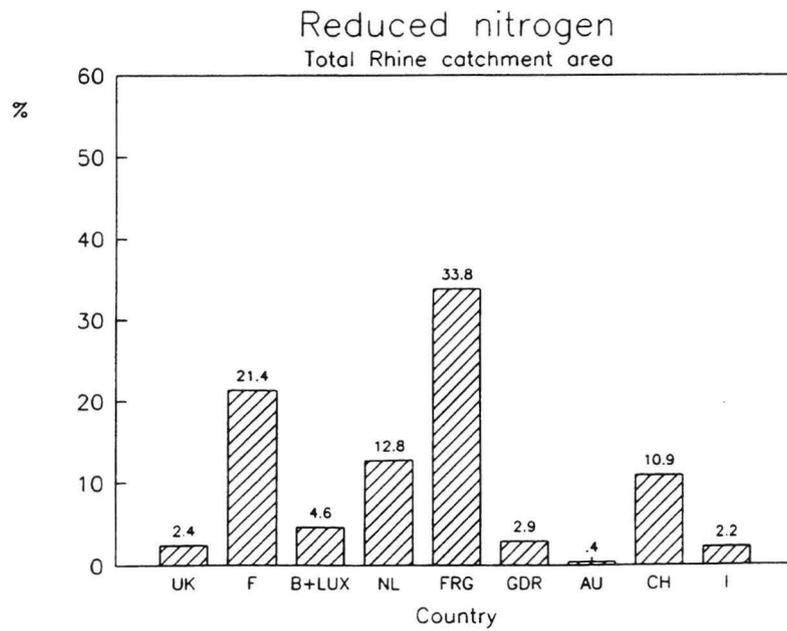
Figure C56 Relative contributions of the surrounding countries to the total deposition of trifluralin on the Dutch part of the Rhine catchment area. Total deposition 0.1 ton/y.



**Figure C57** Relative contributions of the surrounding countries to the total deposition of nitrogen on the Rhine catchment area. Total deposition  $3.4 \cdot 10^5$  ton N/y.



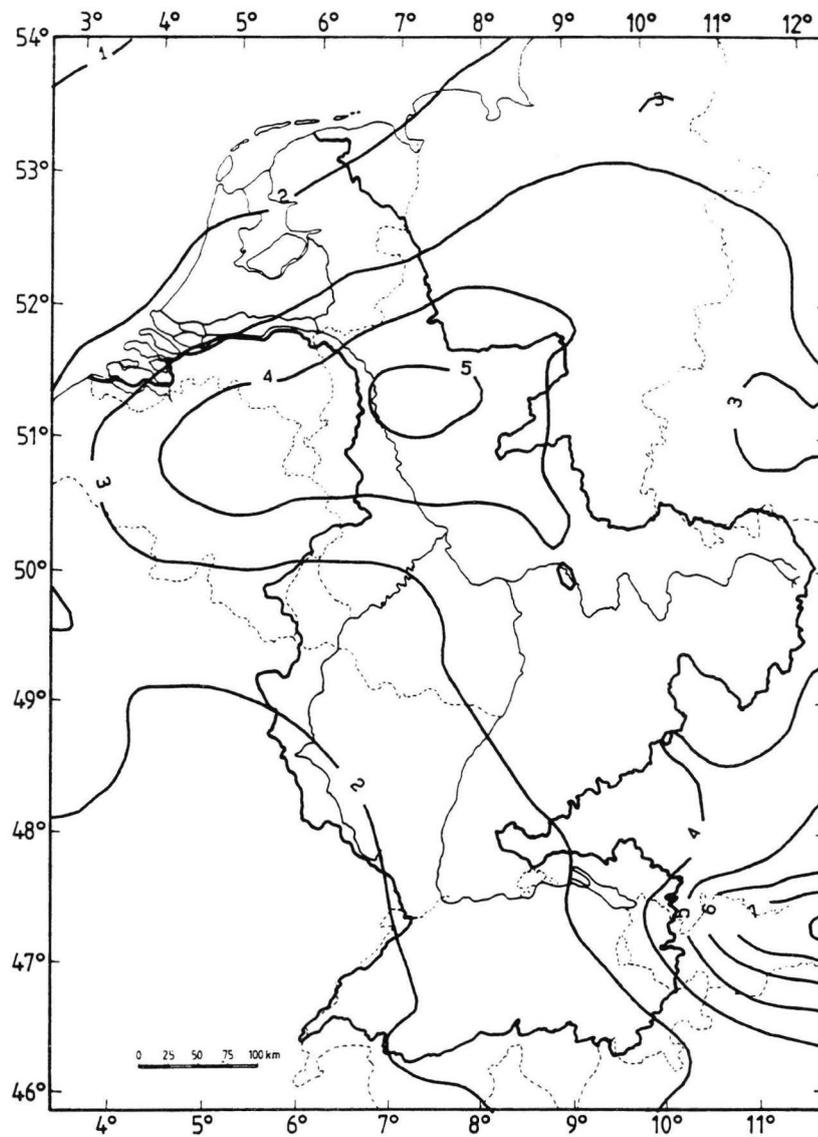
**Figure C58** Relative contributions of the surrounding countries to the total deposition of oxidized nitrogen on the Rhine catchment area. Total deposition  $3.4 \cdot 10^5$  ton N/y.



**Figure C59** Relative contributions of the surrounding countries to the total deposition of reduced nitrogen on the Rhine catchment area. Total deposition  $3.4 \cdot 10^5$  ton N/y.

## APPENDIX D





1	=	.4000E-03
2	=	.8000E-03
3	=	.1200E-02
4	=	.1600E-02
5	=	.2000E-02
6	=	.2400E-02
7	=	.2800E-02
8	=	.3200E-02

**Figure D1** Calculated deposition of cadmium in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

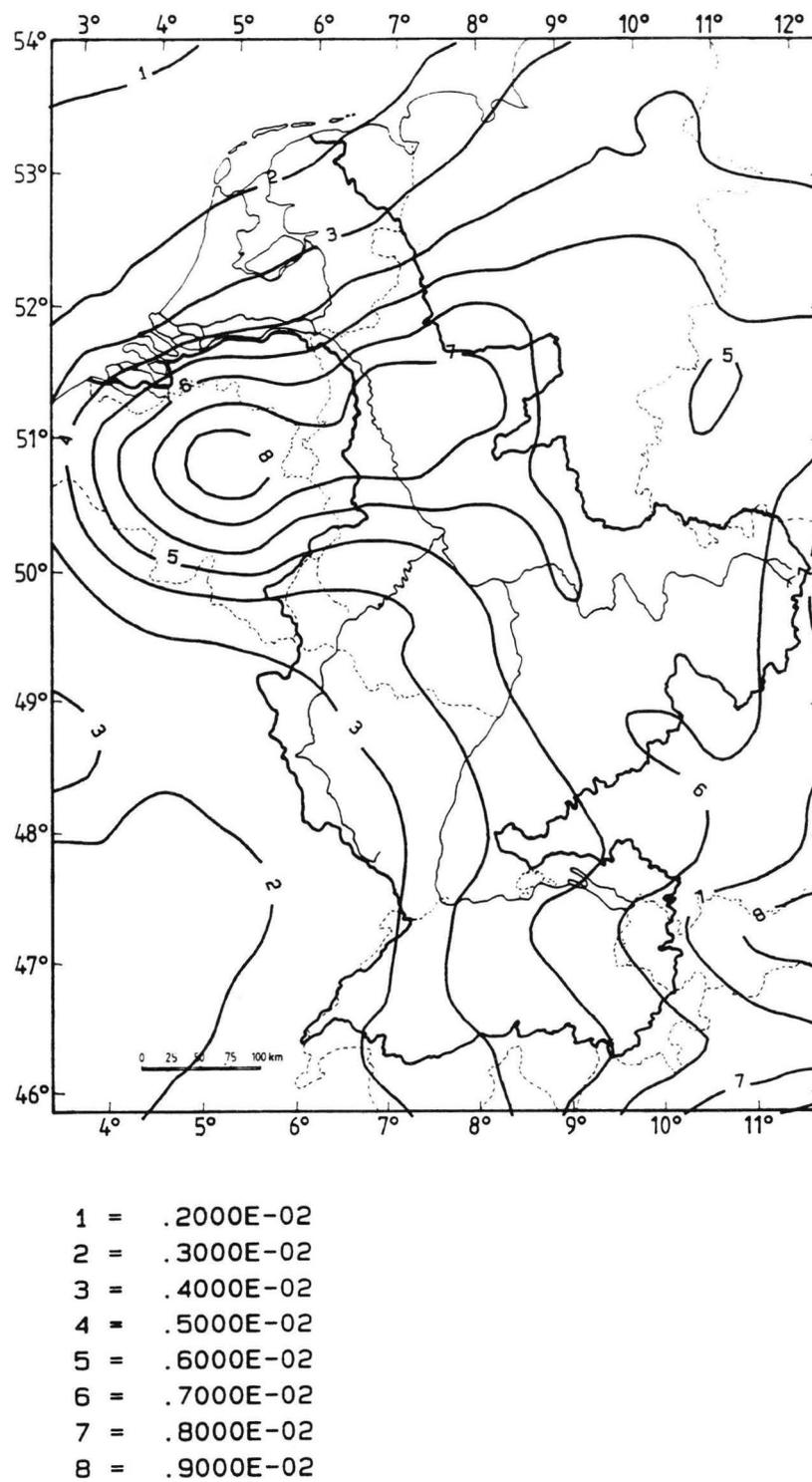
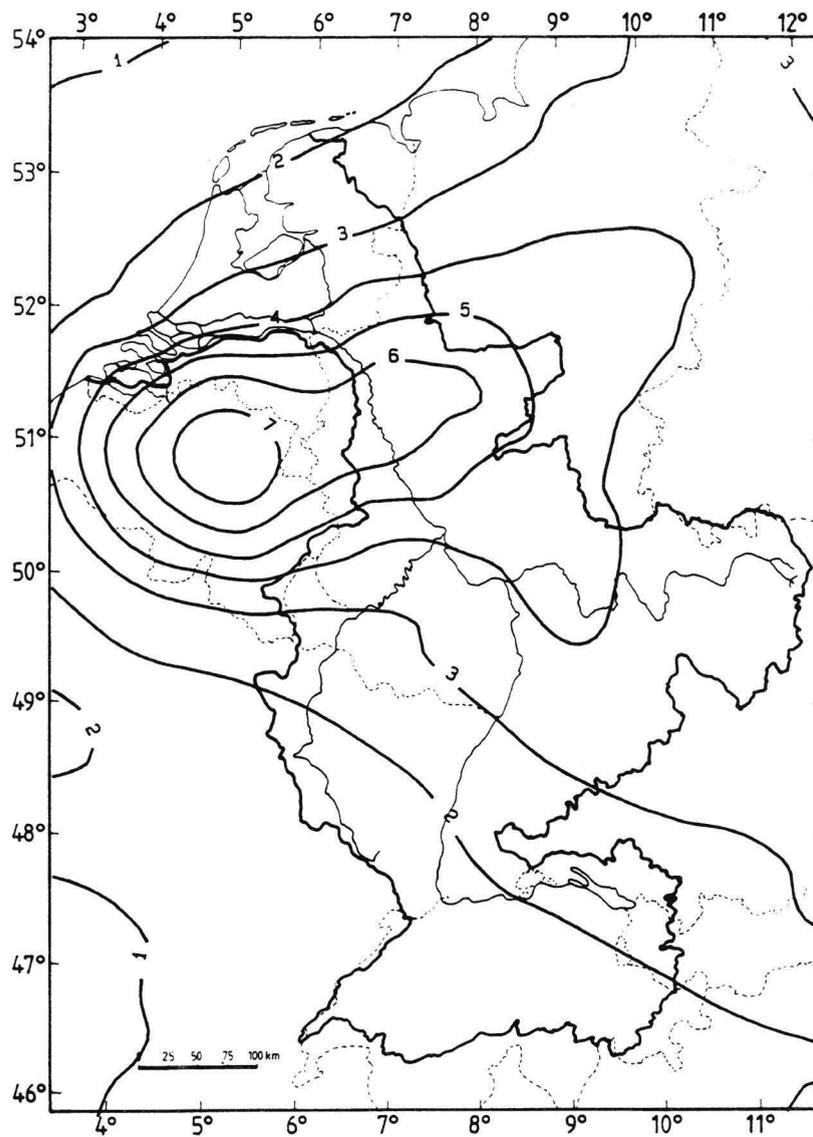
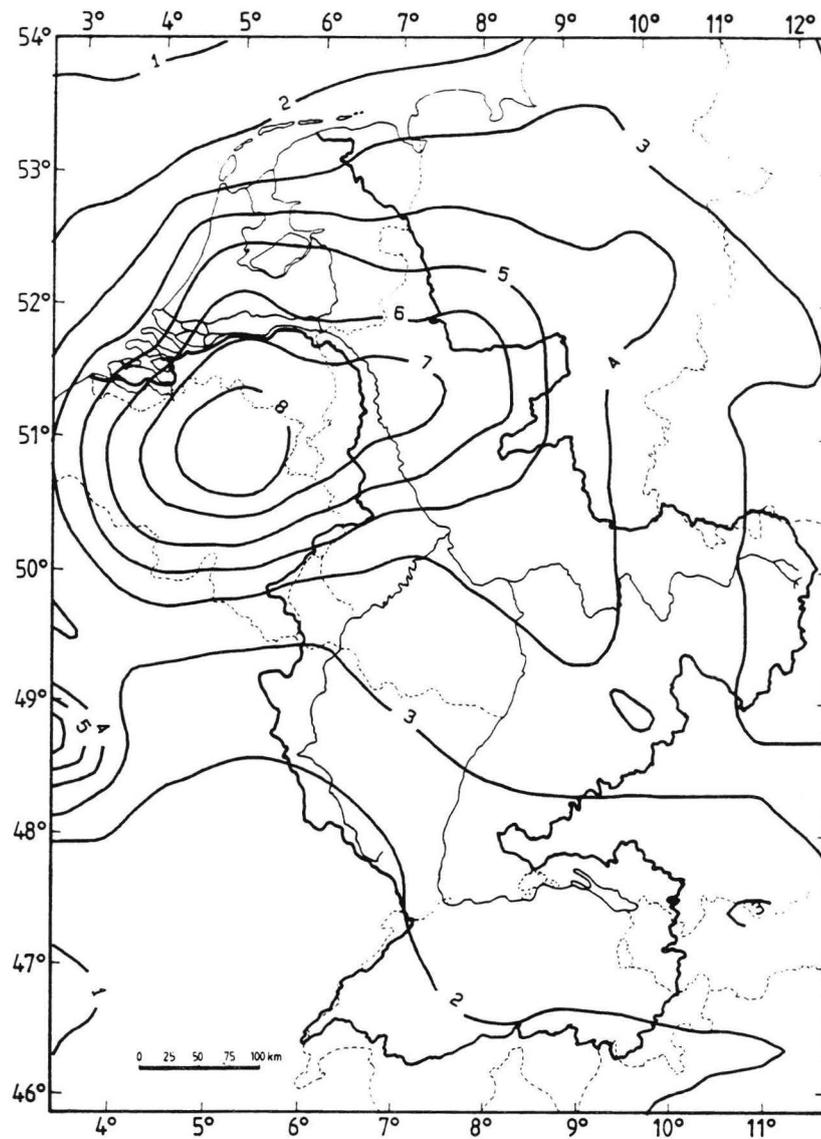


Figure D2 Calculated deposition of chromium in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.3000E-02
2	=	.5000E-02
3	=	.7000E-02
4	=	.9000E-02
5	=	.1100E-01
6	=	.1300E-01
7	=	.1500E-01

**Figure D3** Calculated deposition of copper in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.6000E-01
2	=	.8000E-01
3	=	.1000E+00
4	=	.1200E+00
5	=	.1400E+00
6	=	.1600E+00
7	=	.1800E+00
8	=	.2000E+00

**Figure D4** Calculated deposition of lead in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

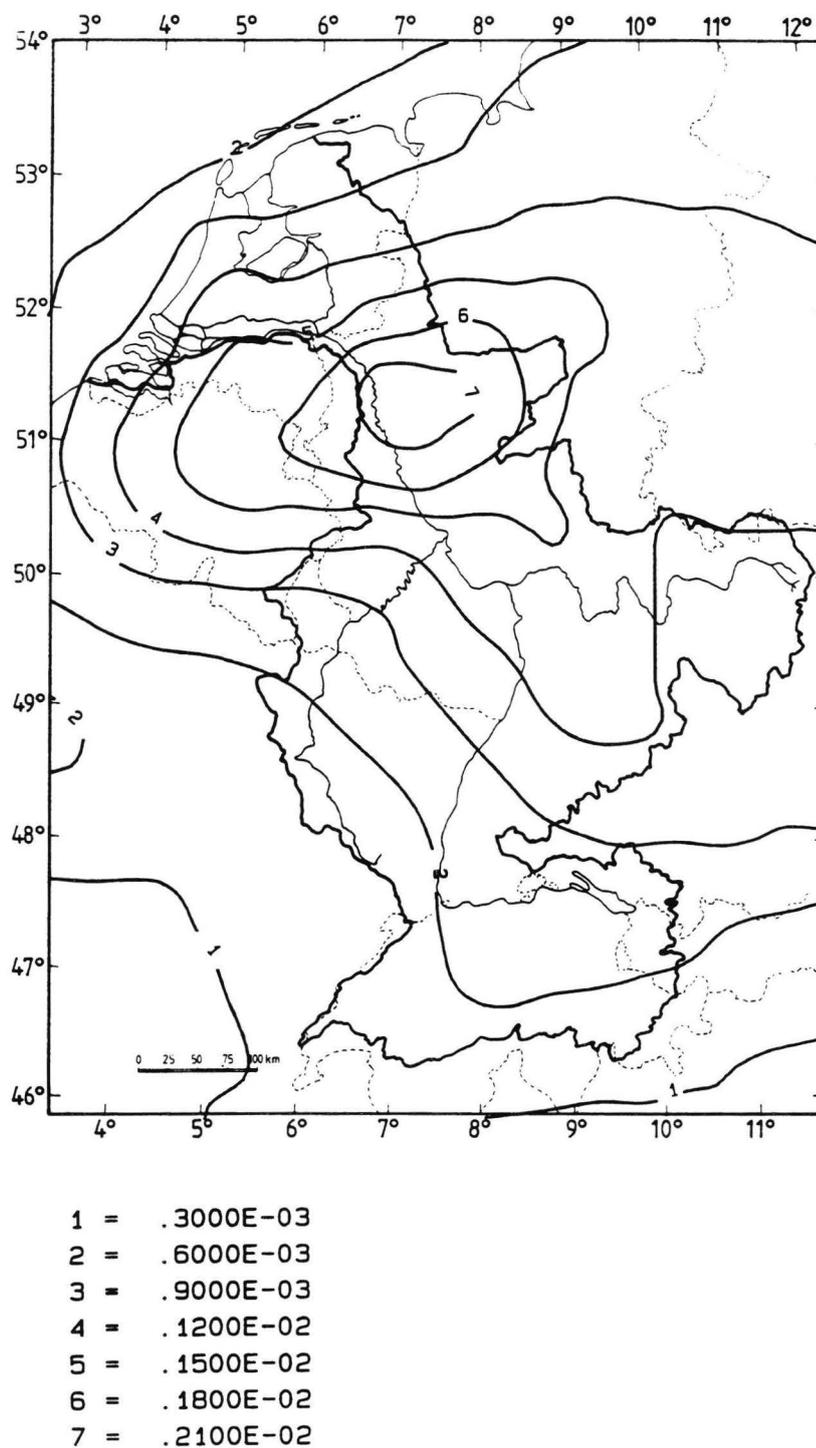
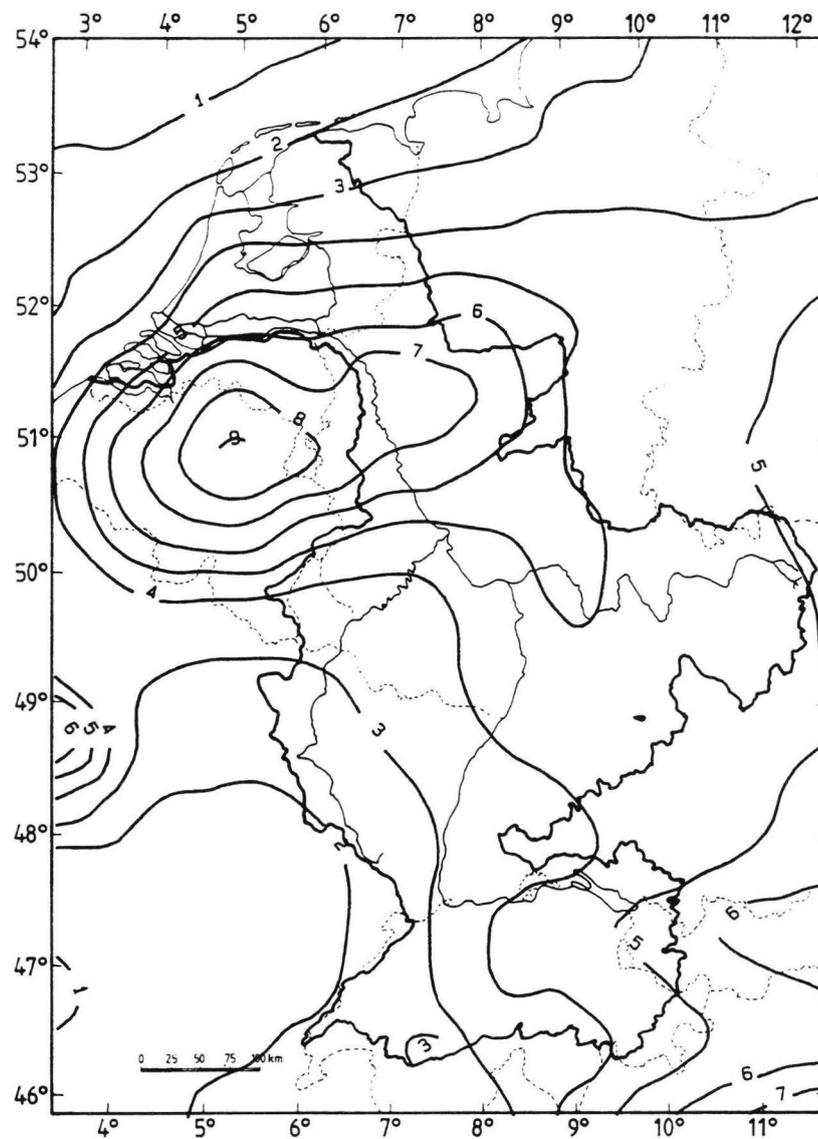
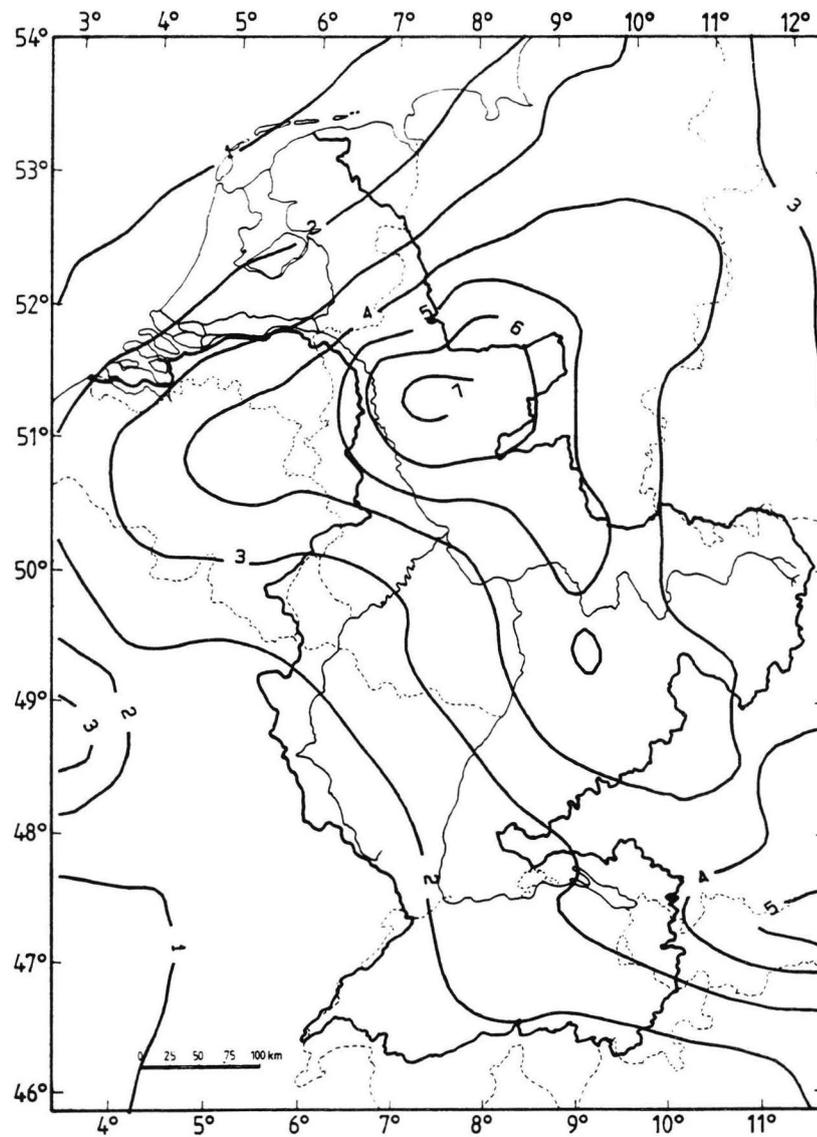


Figure D5 Calculated deposition of mercury in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



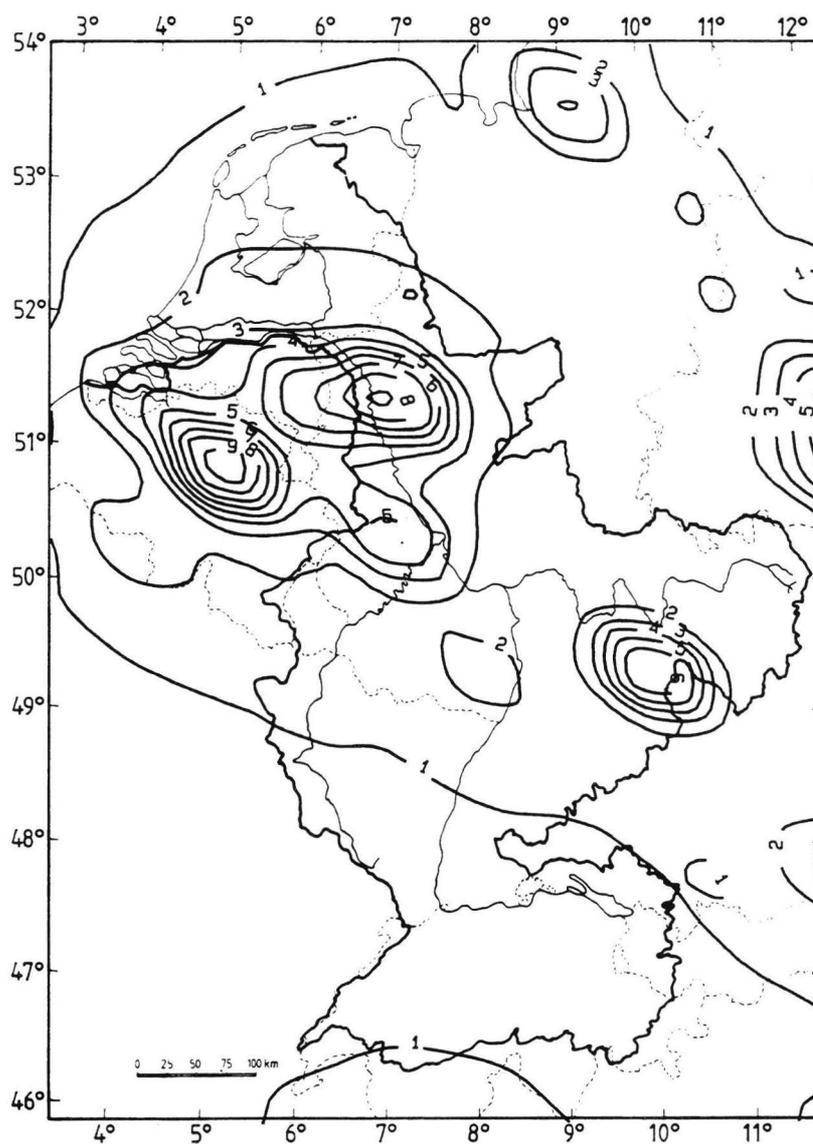
1	=	.4000E-02
2	=	.5000E-02
3	=	.6000E-02
4	=	.7000E-02
5	=	.8000E-02
6	=	.9000E-02
7	=	.1000E-01
8	=	.1100E-01
9	=	.1200E-01

**Figure D6** Calculated deposition of nickel in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.4000E-01
2	=	.6000E-01
3	=	.8000E-01
4	=	.1000E+00
5	=	.1200E+00
6	=	.1400E+00
7	=	.1600E+00

*Figure D7* Calculated deposition of zinc in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.2000E-02
2	=	.4000E-02
3	=	.6000E-02
4	=	.8000E-02
5	=	.1000E-01
6	=	.1200E-01
7	=	.1400E-01
8	=	.1600E-01
9	=	.1800E-01

**Figure D8** Calculated deposition of 1,2-dichloroethane in kg·ha<sup>-1</sup>·y<sup>-1</sup> on the Rhine catchment area.

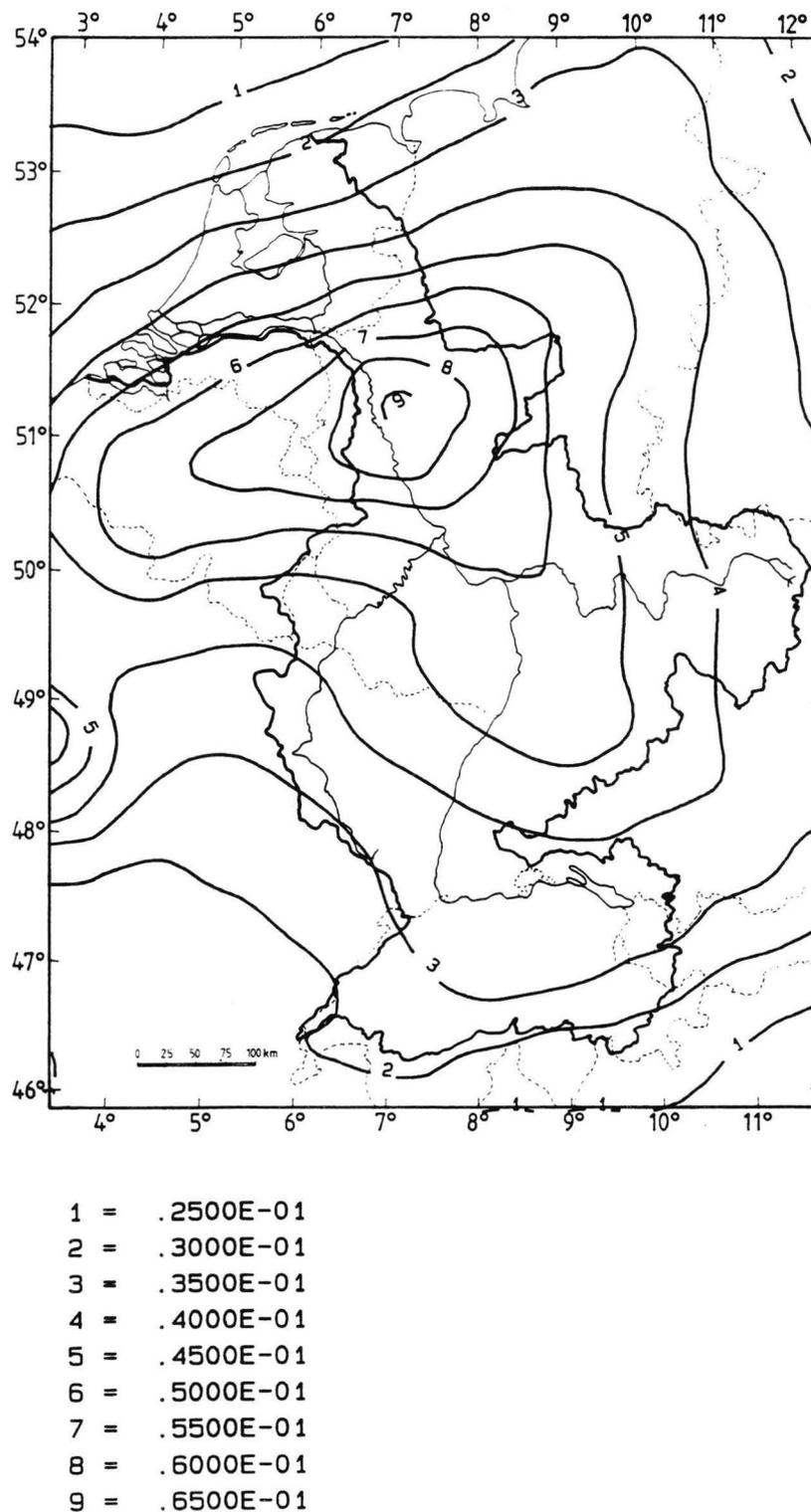


Figure D9 Calculated deposition of 1,1,1-trichloroethane in  $\text{kg.ha}^{-1}.\text{y}^{-1}$  on the Rhine catchment area.

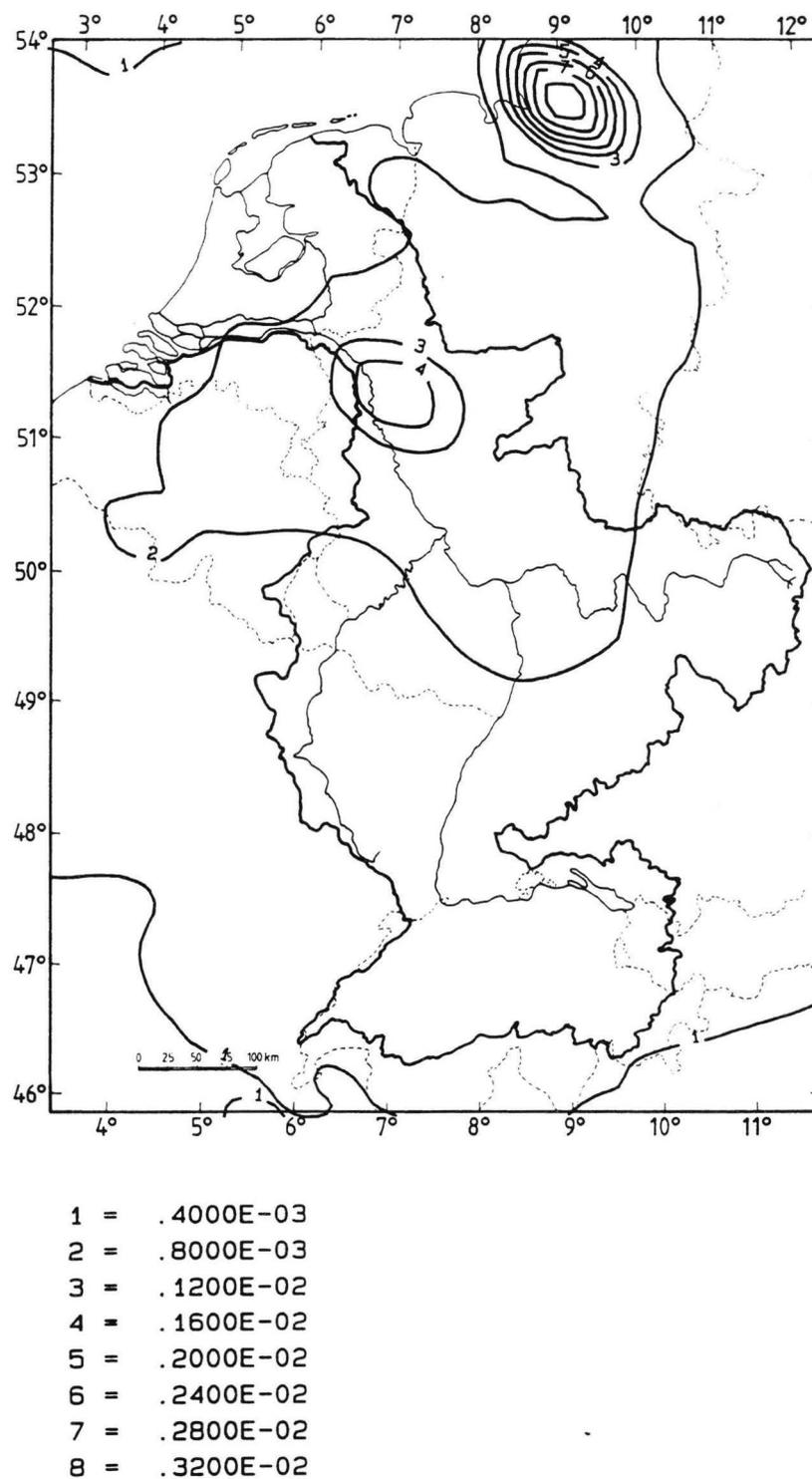
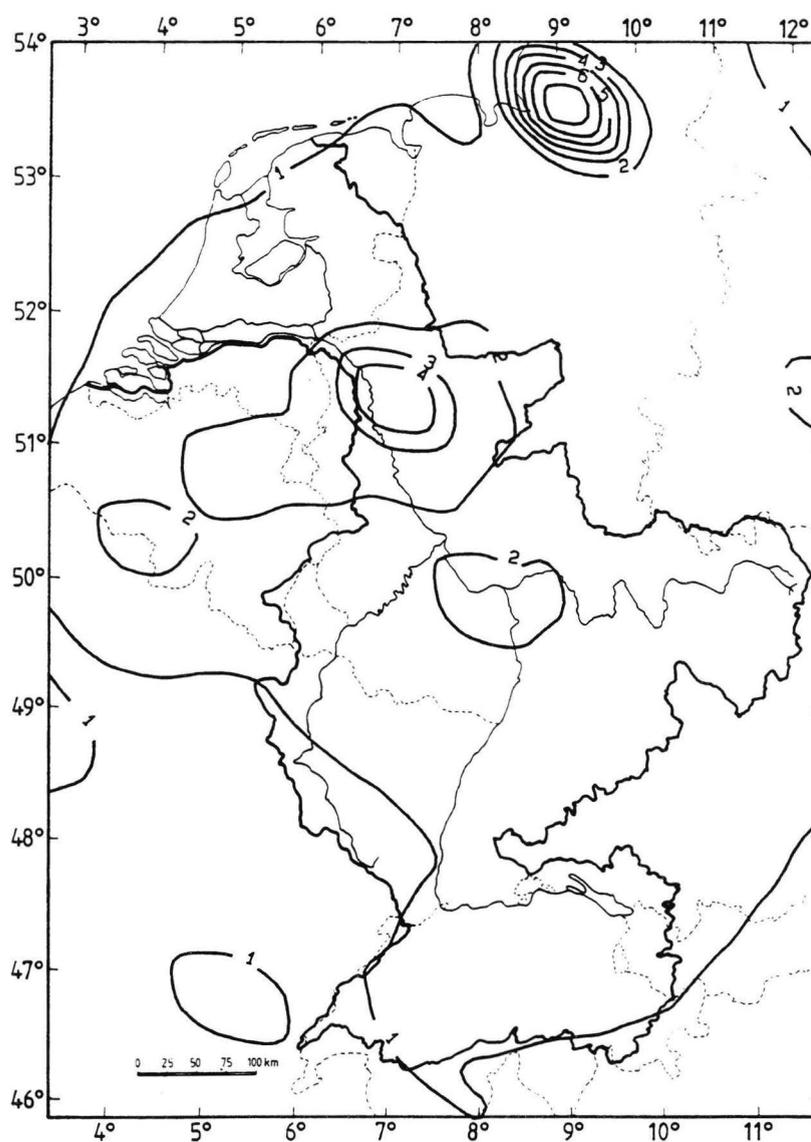
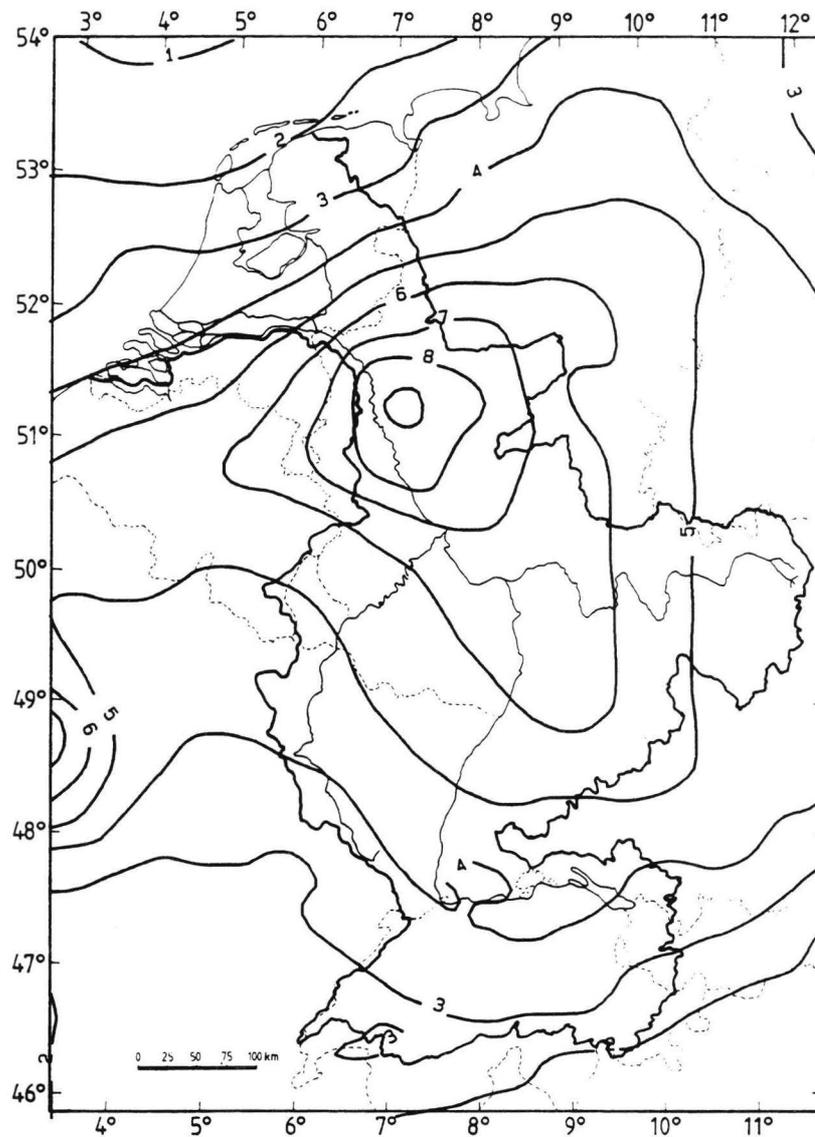


Figure D10 Calculated deposition of chloroform in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



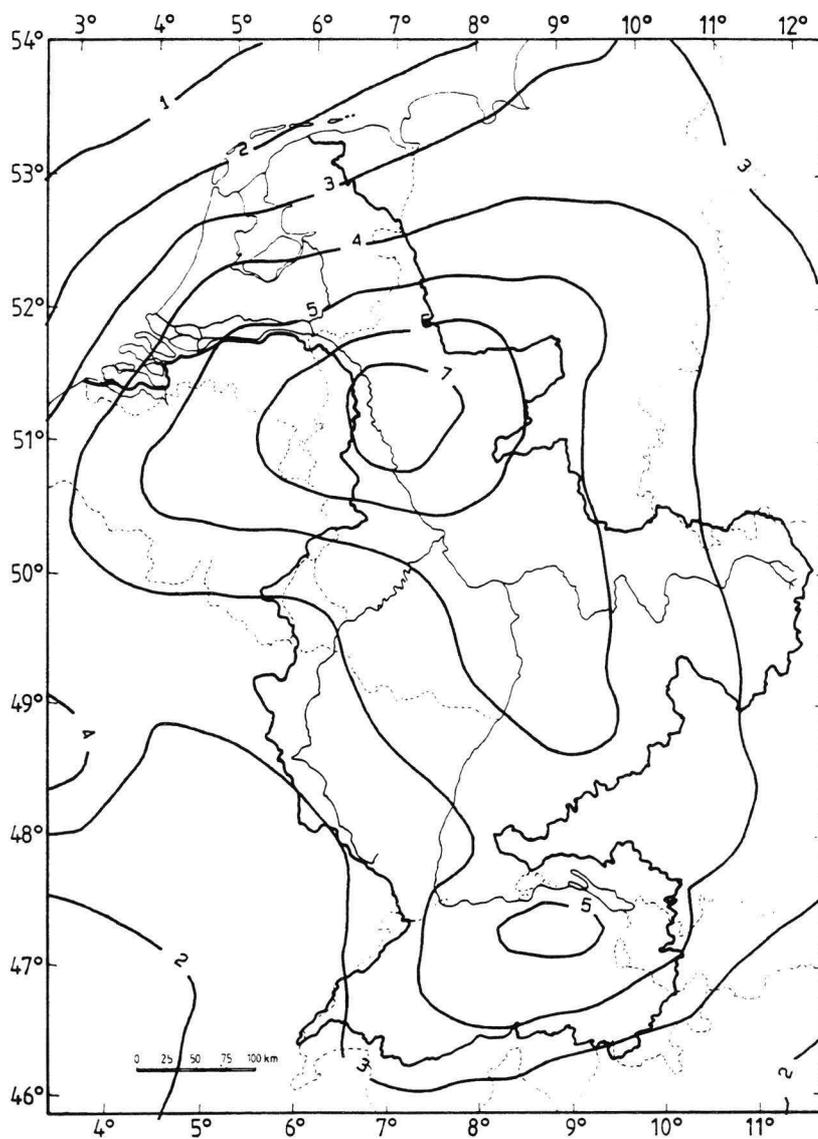
- 1 = .2000E-03
- 2 = .3000E-03
- 3 = .4000E-03
- 4 = .5000E-03
- 5 = .6000E-03
- 6 = .7000E-03
- 7 = .8000E-03

*Figure D11* Calculated deposition of tetrachloromethane in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



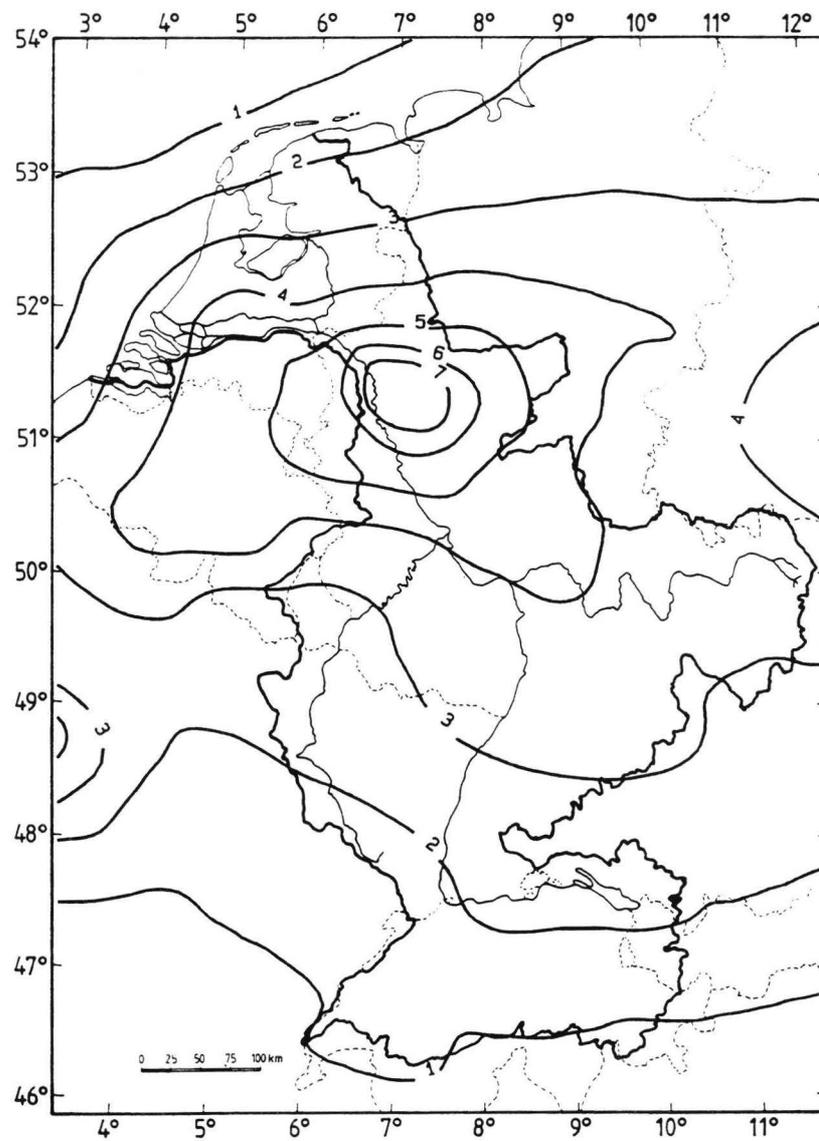
1	=	.8000E-02
2	=	.1000E-01
3	=	.1200E-01
4	=	.1400E-01
5	=	.1600E-01
6	=	.1800E-01
7	=	.2000E-01
8	=	.2200E-01
9	=	.2400E-01

Figure D12 Calculated deposition of trichloroethene in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



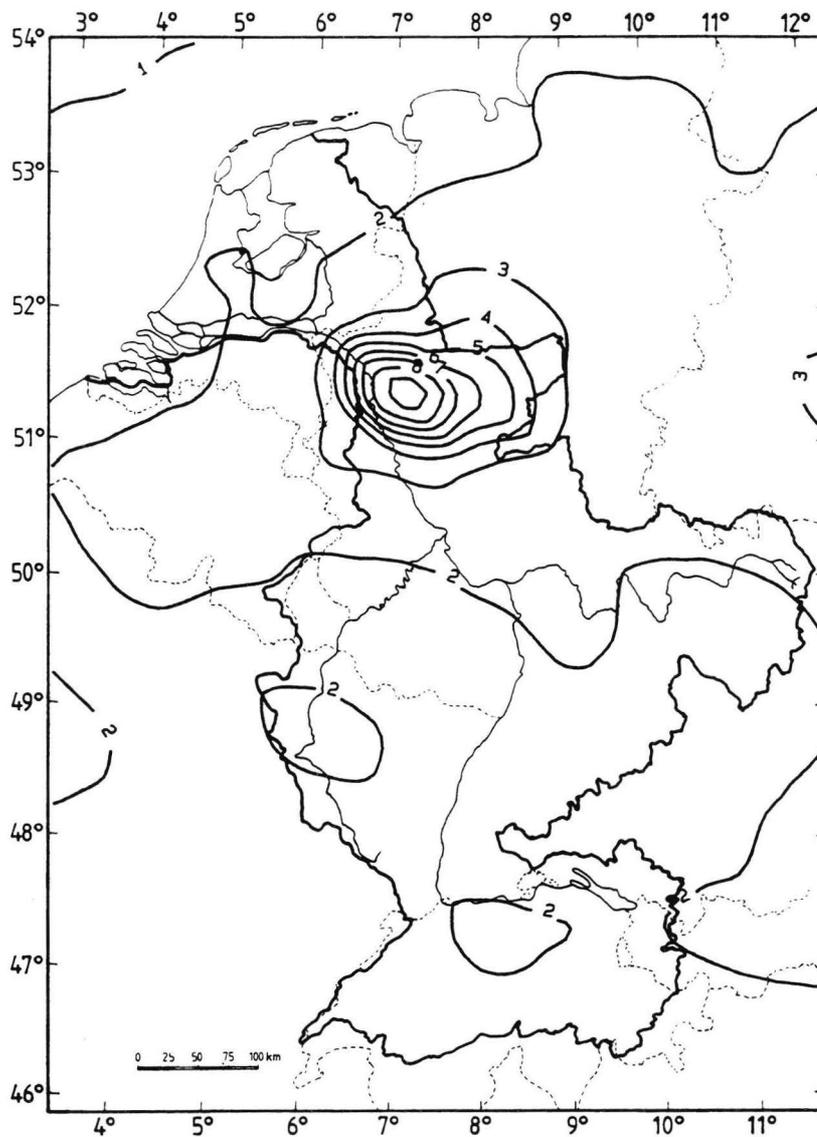
- 1 = .3000E-02
- 2 = .4000E-02
- 3 = .5000E-02
- 4 = .6000E-02
- 5 = .7000E-02
- 6 = .8000E-02
- 7 = .9000E-02

*Figure D13* Calculated deposition of tetrachloroethene in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



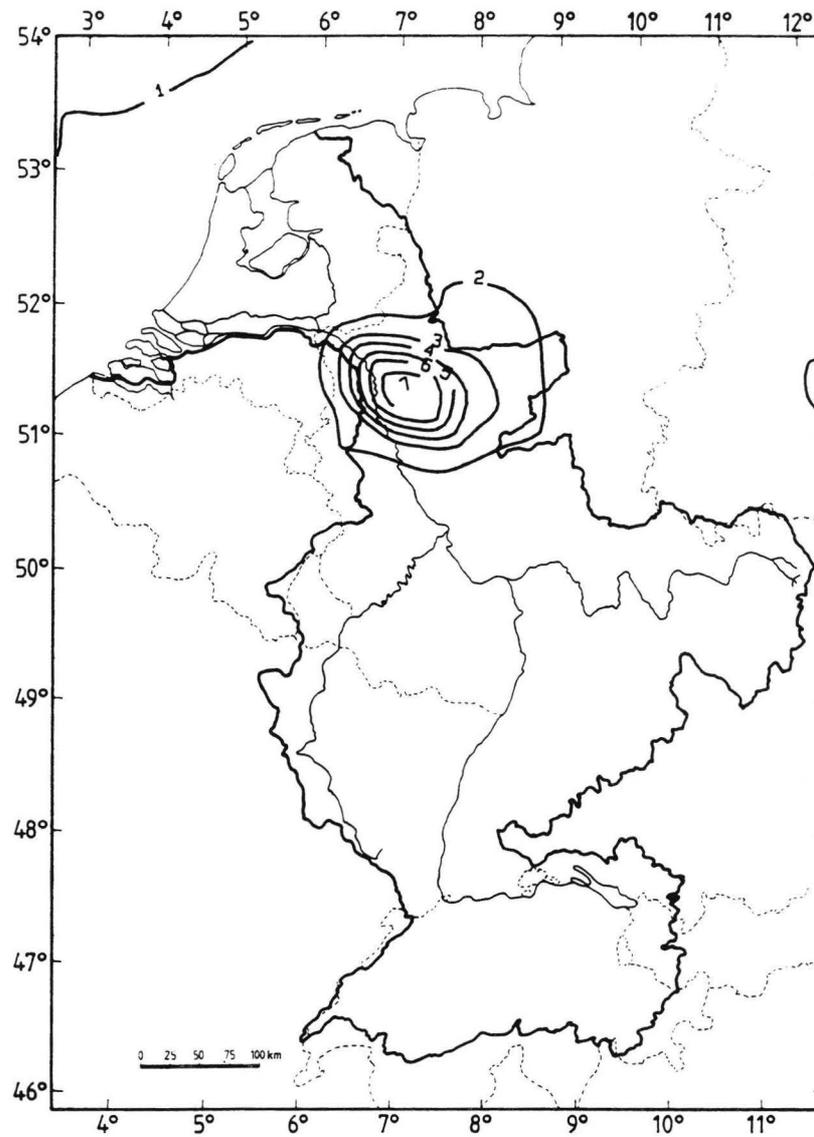
1	=	.2000E-01
2	=	.2500E-01
3	=	.3000E-01
4	=	.3500E-01
5	=	.4000E-01
6	=	.4500E-01
7	=	.5000E-01

Figure D14 Calculated deposition of benzene in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



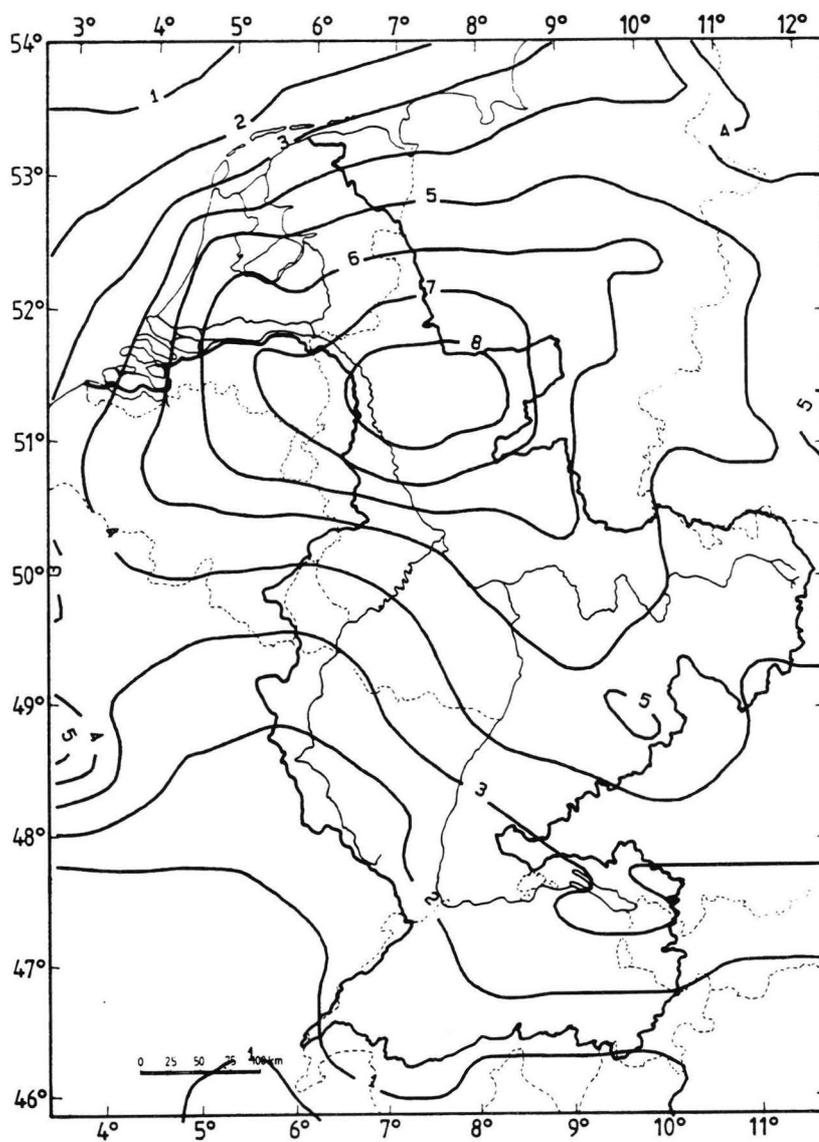
1	=	.9000E-03
2	=	.1900E-02
3	=	.2900E-02
4	=	.3900E-02
5	=	.4900E-02
6	=	.5900E-02
7	=	.6900E-02
8	=	.7900E-02
9	=	.8900E-02

*Figure D15* Calculated deposition of aerosol PAH in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1 = .1000E-03  
2 = .1100E-02  
3 = .2100E-02  
4 = .3100E-02  
5 = .4100E-02  
6 = .5100E-02  
7 = .6100E-02

**Figure D16** Calculated deposition of gaseous PAH in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.1000E-02
2	=	.1200E-02
3	=	.1400E-02
4	=	.1600E-02
5	=	.1800E-02
6	=	.2000E-02
7	=	.2200E-02
8	=	.2400E-02

Figure D17 Calculated deposition of PCB in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

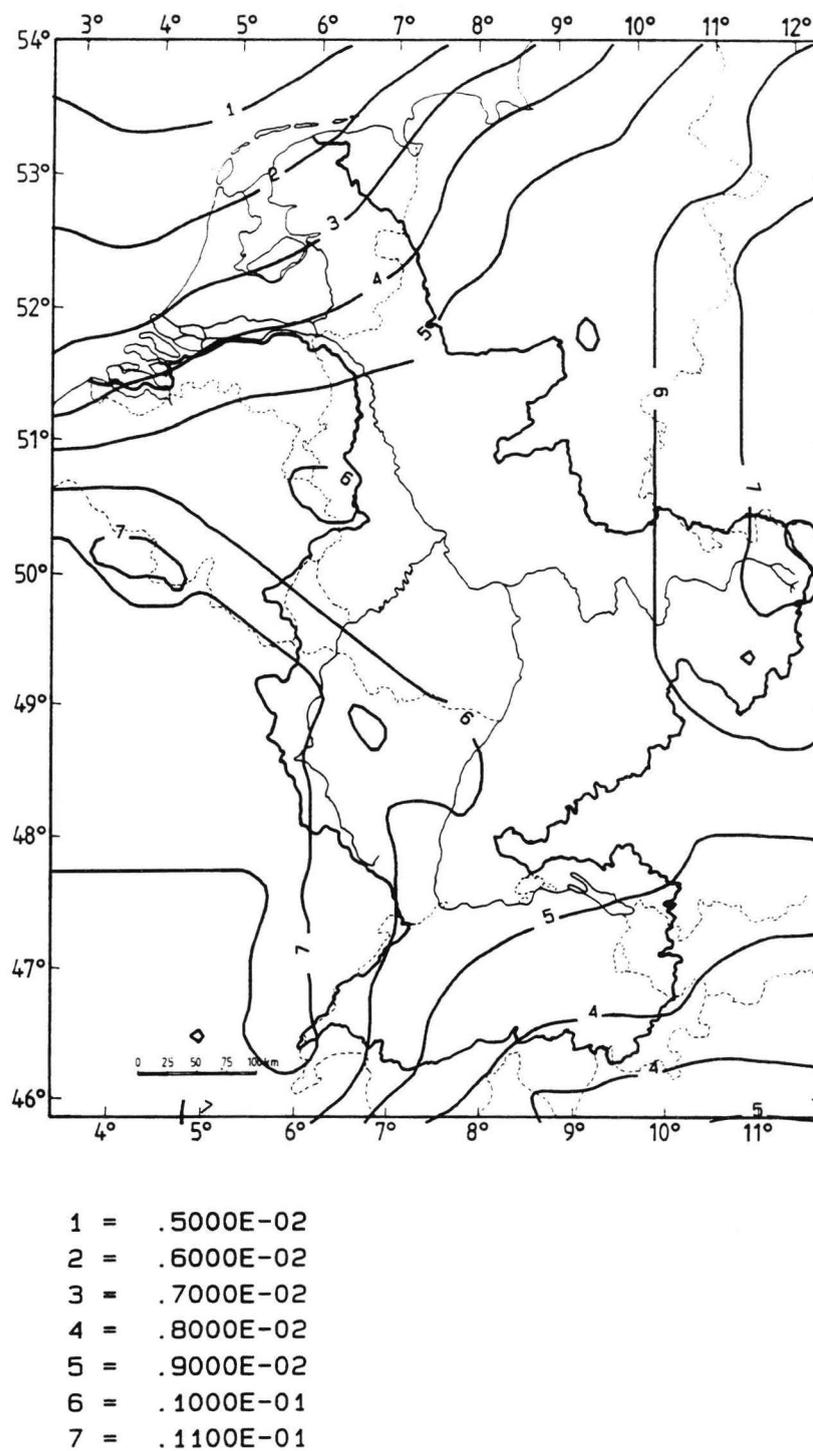
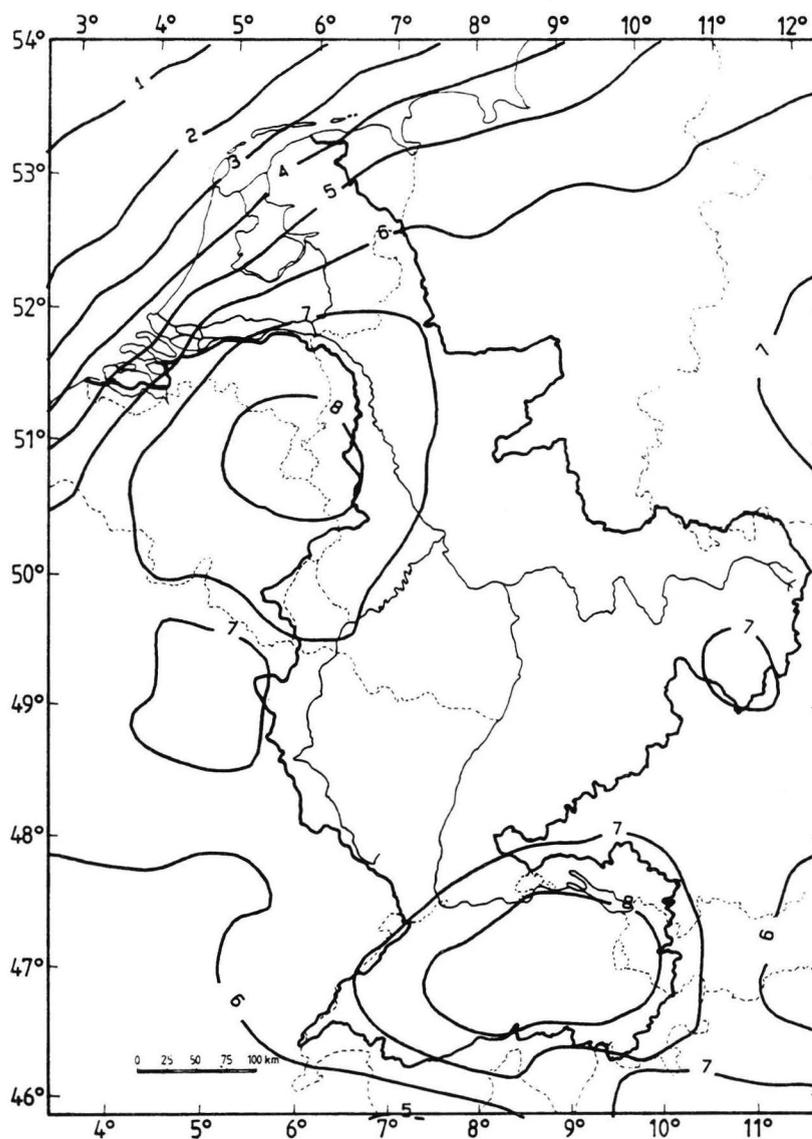
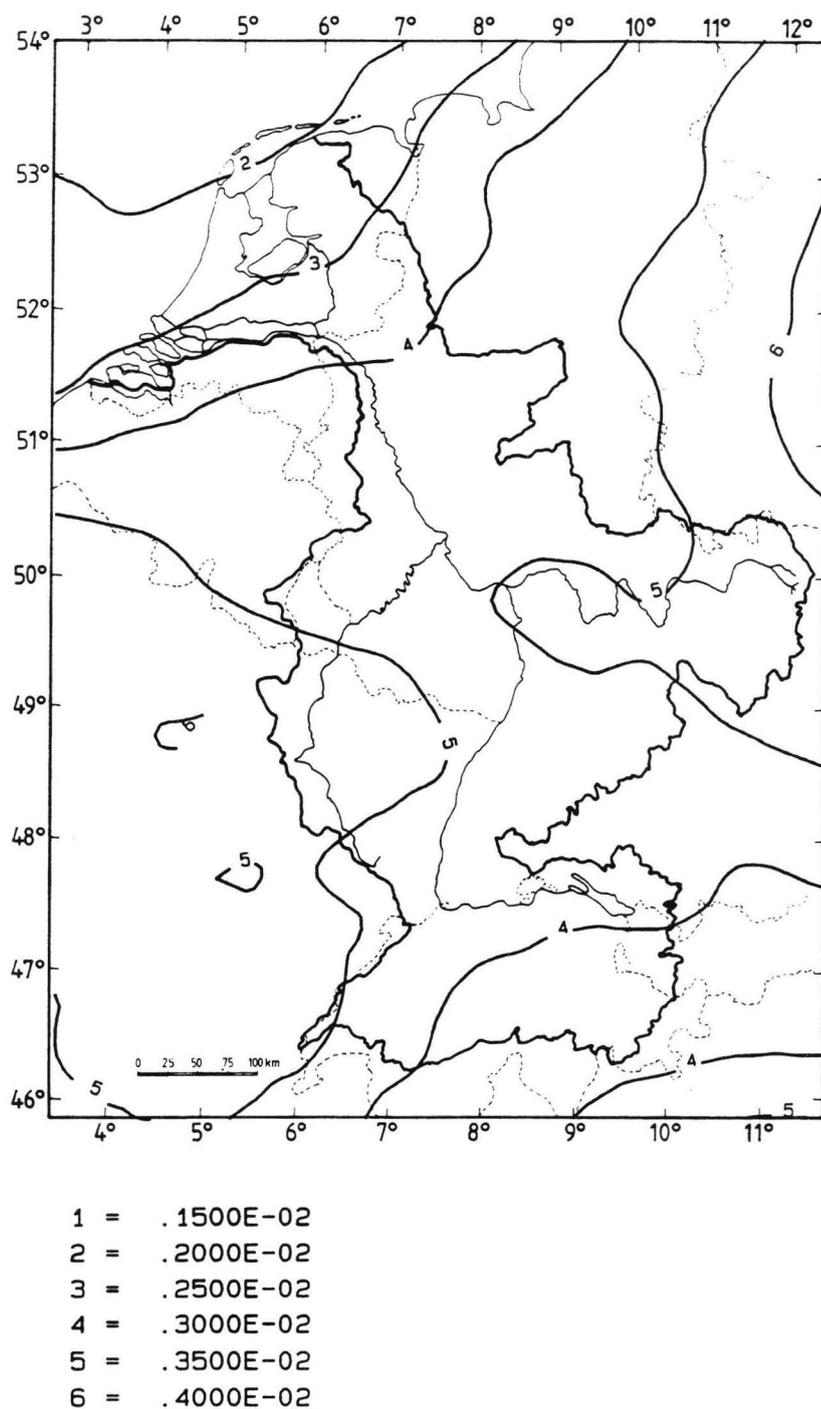


Figure D18 Calculated deposition of atrazine in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

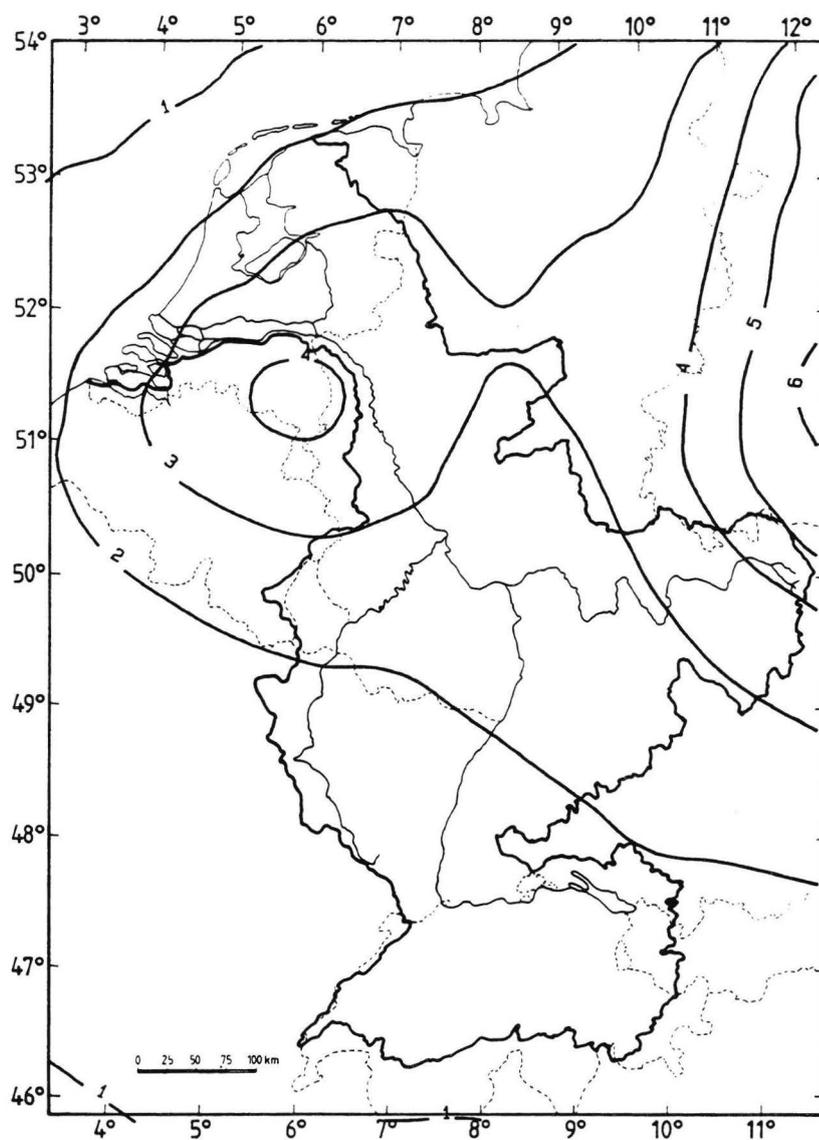


1	=	.3000E-04
2	=	.4000E-04
3	=	.5000E-04
4	=	.6000E-04
5	=	.7000E-04
6	=	.8000E-04
7	=	.9000E-04
8	=	.1000E-03

Figure D19 Calculated deposition of azinphos-methyl in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



**Figure D20** Calculated deposition of bentazone in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



- 1 = .2000E-02
- 2 = .4000E-02
- 3 = .6000E-02
- 4 = .8000E-02
- 5 = .1000E-01
- 6 = .1200E-01

**Figure D21** Calculated deposition of dichloropropene in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

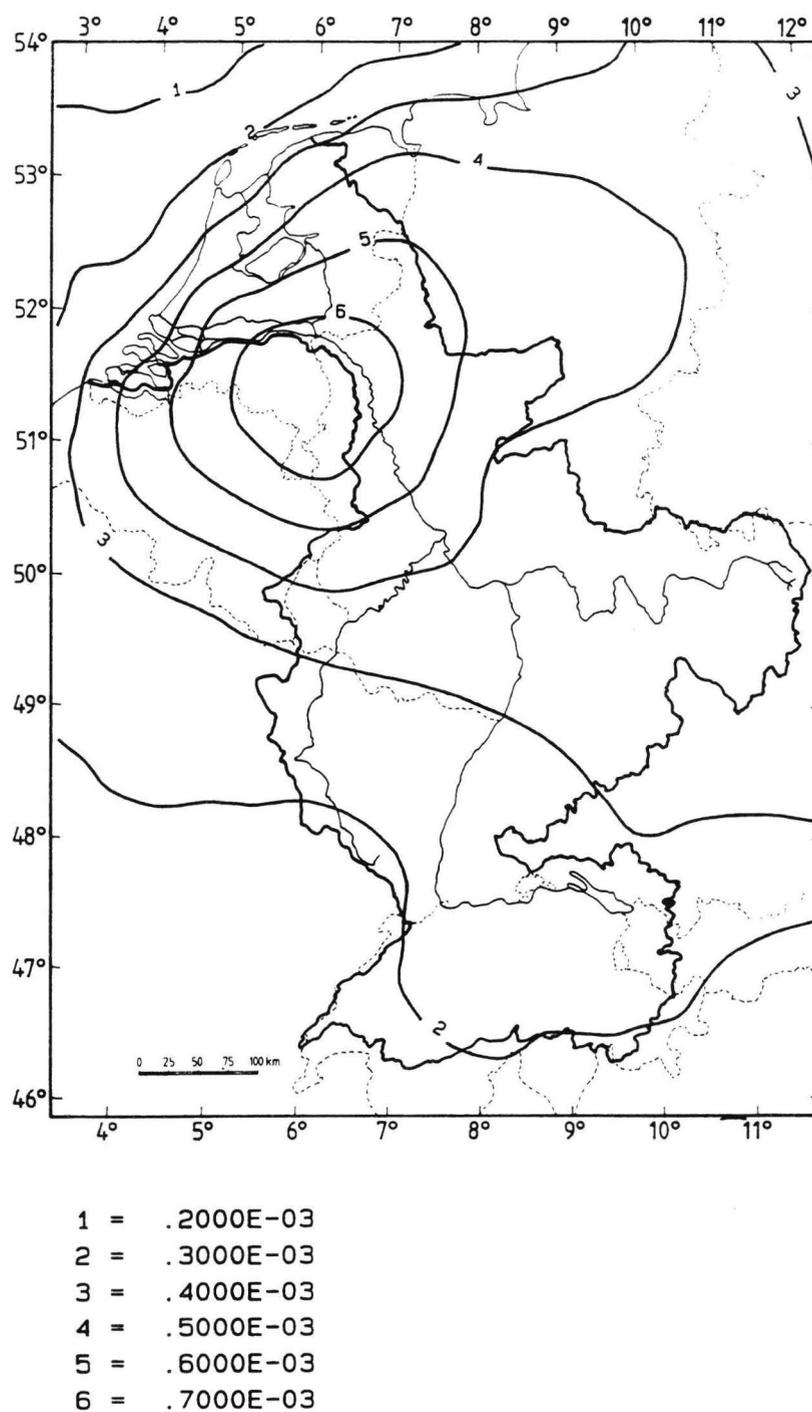
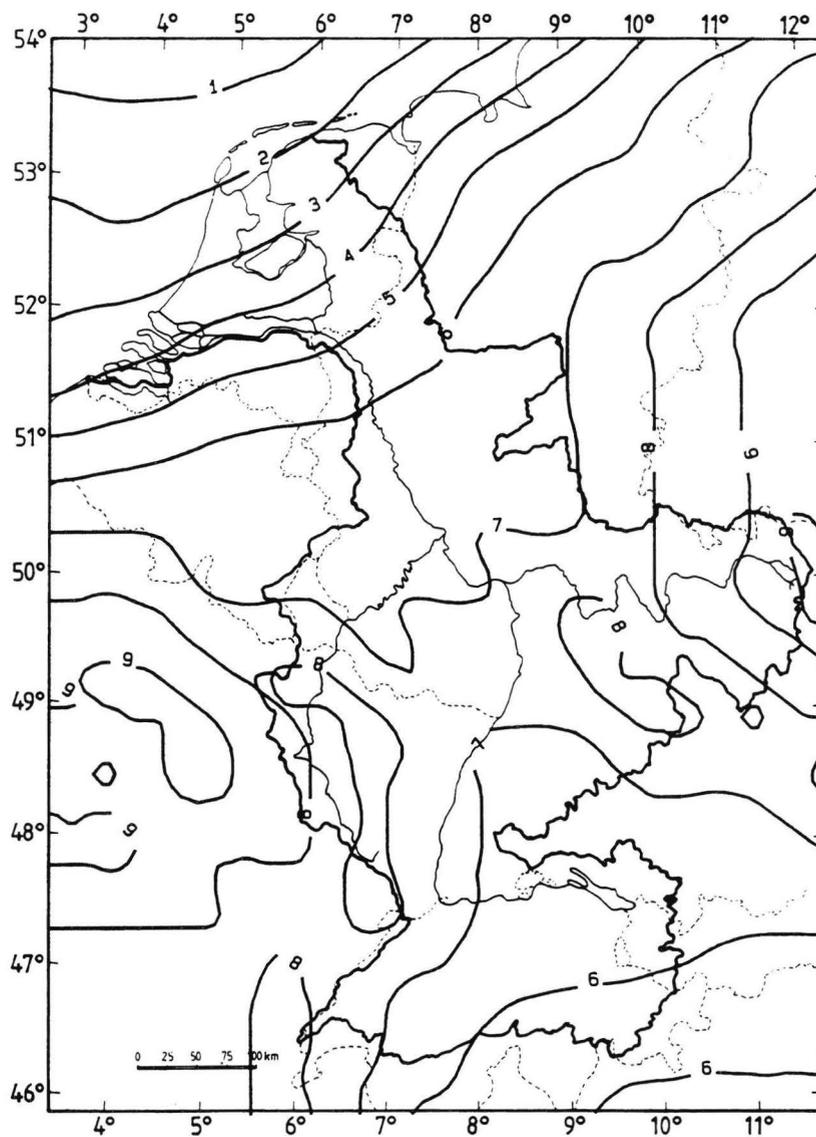


Figure D22 Calculated deposition of dichlorvos in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



- 1 = .4000E-05
- 2 = .5000E-05
- 3 = .6000E-05
- 4 = .7000E-05
- 5 = .8000E-05
- 6 = .9000E-05
- 7 = .1000E-04
- 8 = .1100E-04
- 9 = .1200E-04

Figure D23 Calculated deposition of endosulfan in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

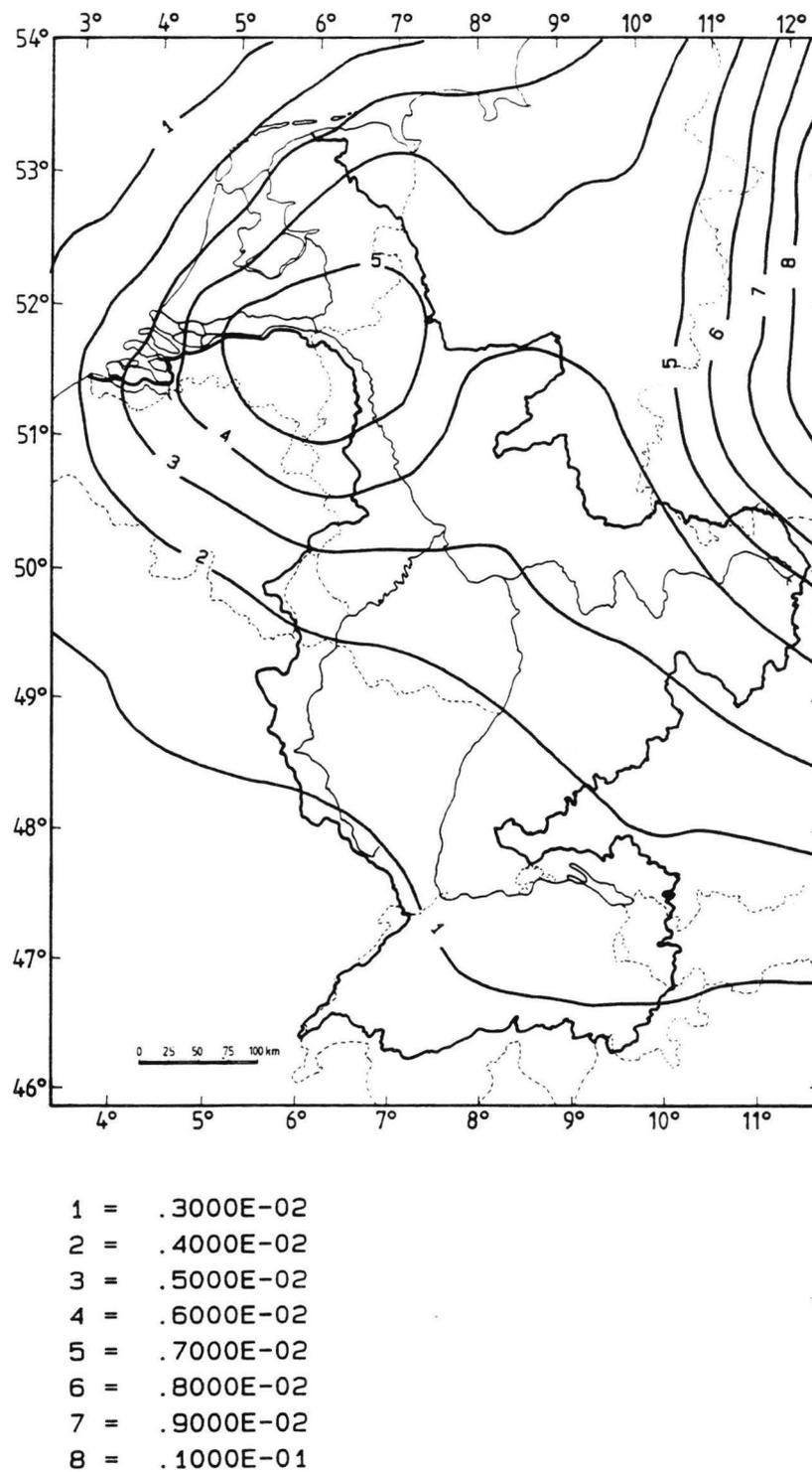


Figure D24 Calculated deposition of fentin in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

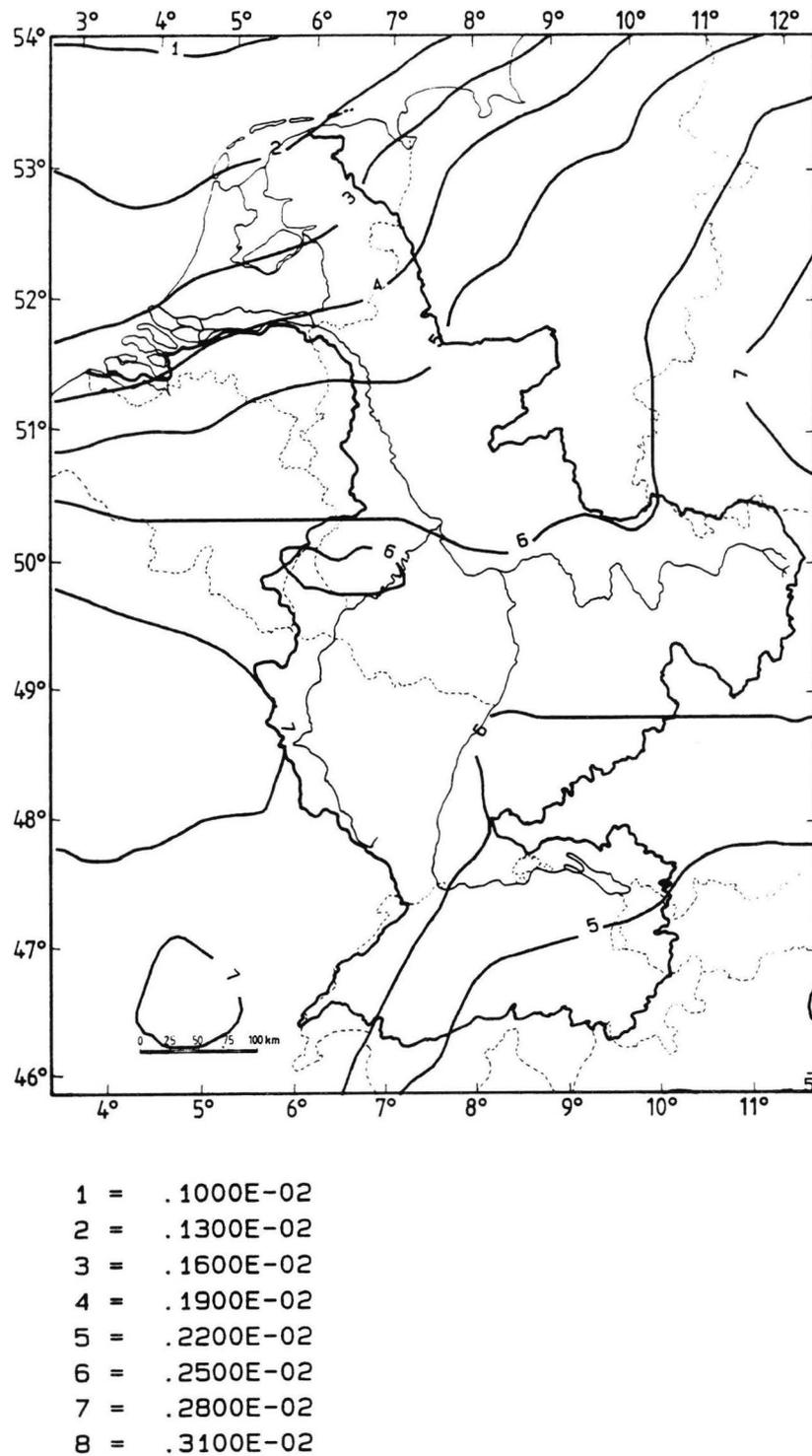
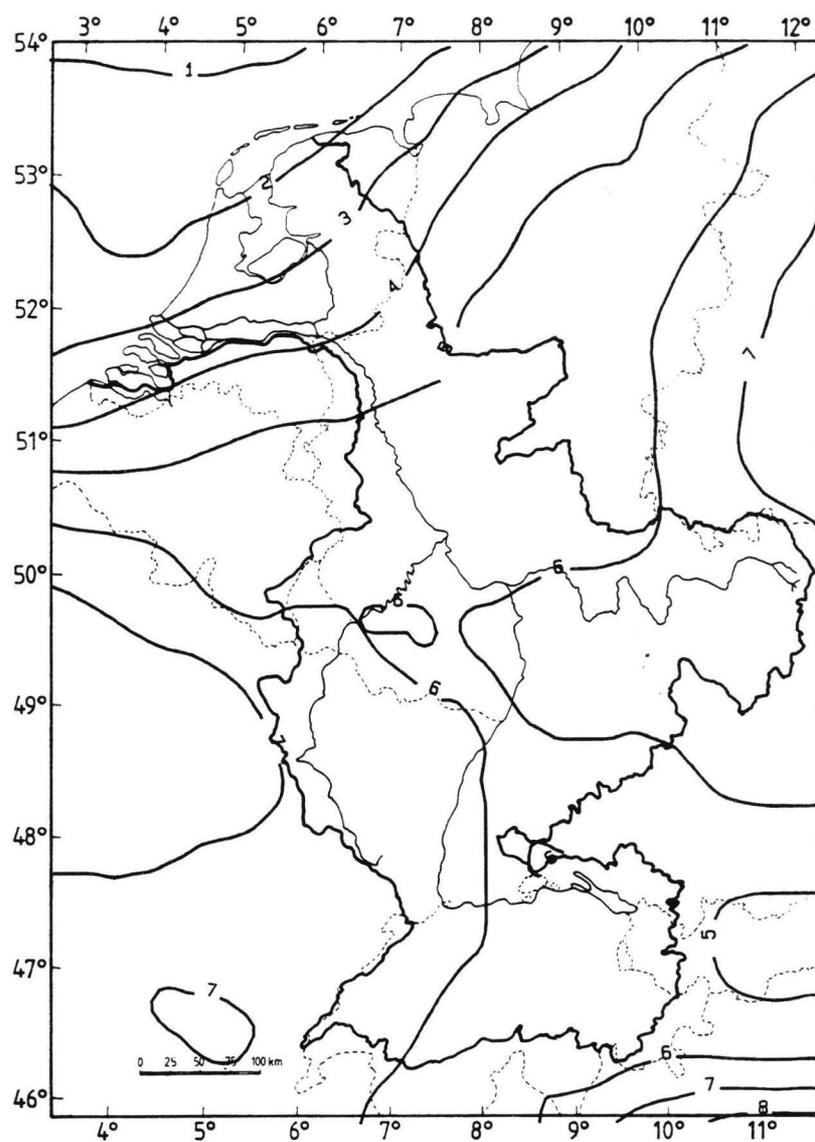
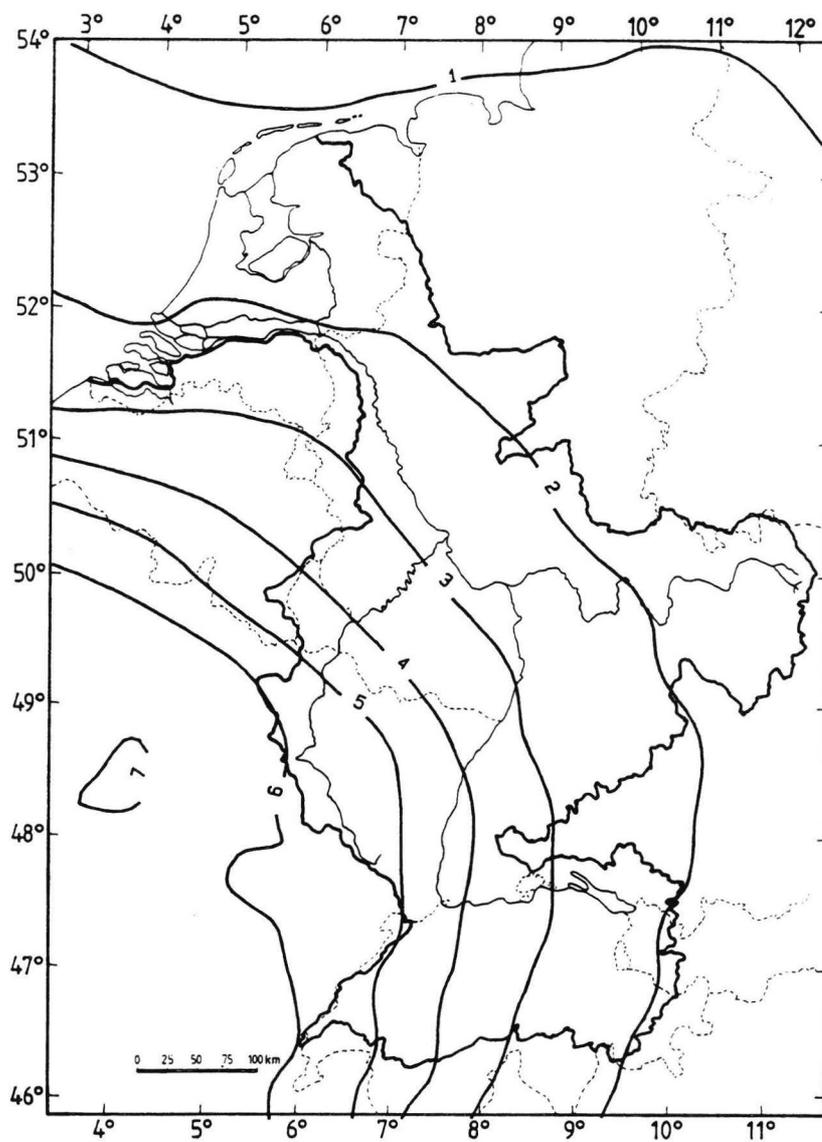


Figure D25 Calculated deposition of lindane in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



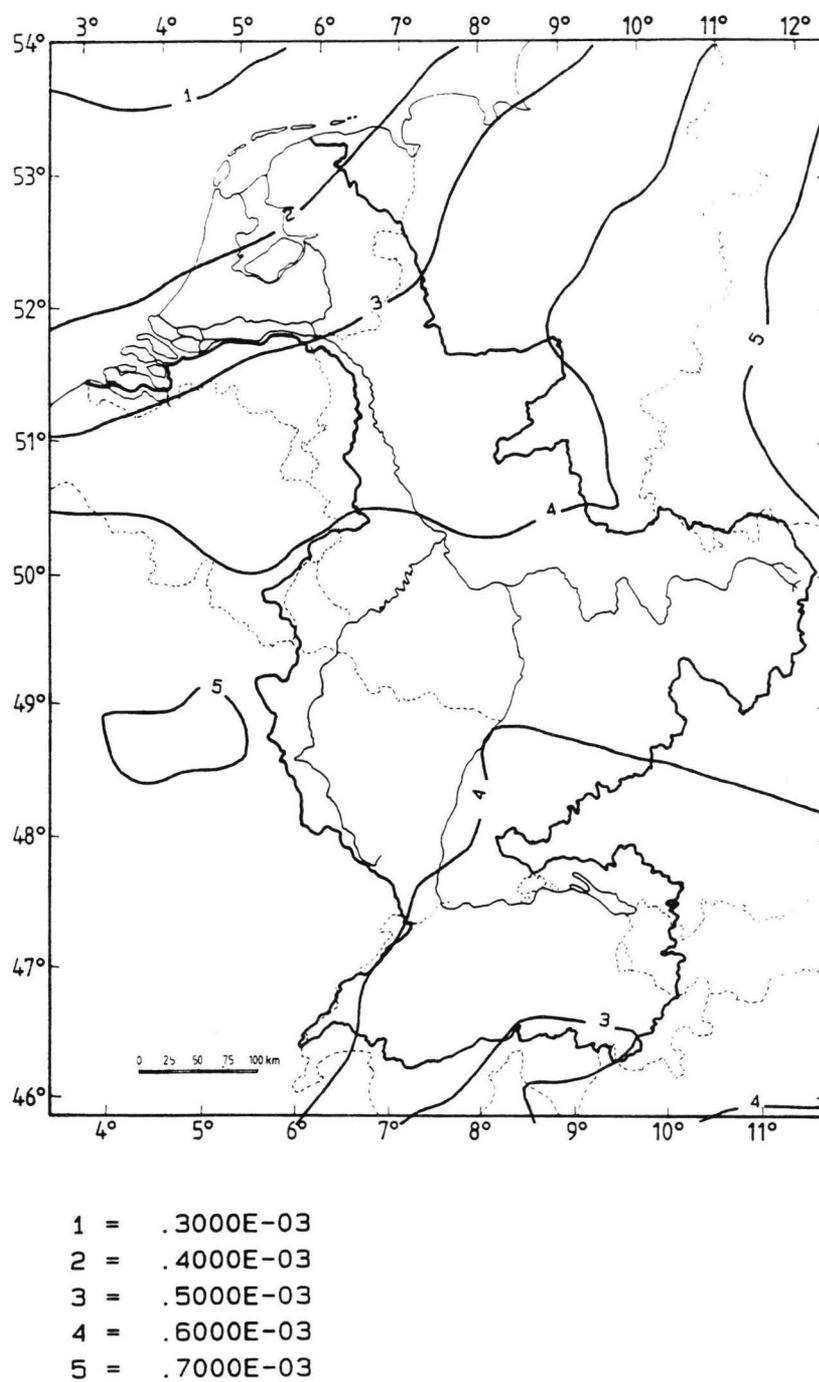
1	=	.1000E-02
2	=	.1400E-02
3	=	.1800E-02
4	=	.2200E-02
5	=	.2600E-02
6	=	.3000E-02
7	=	.3400E-02
8	=	.3800E-02

**Figure D26** Calculated deposition of parathion in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.

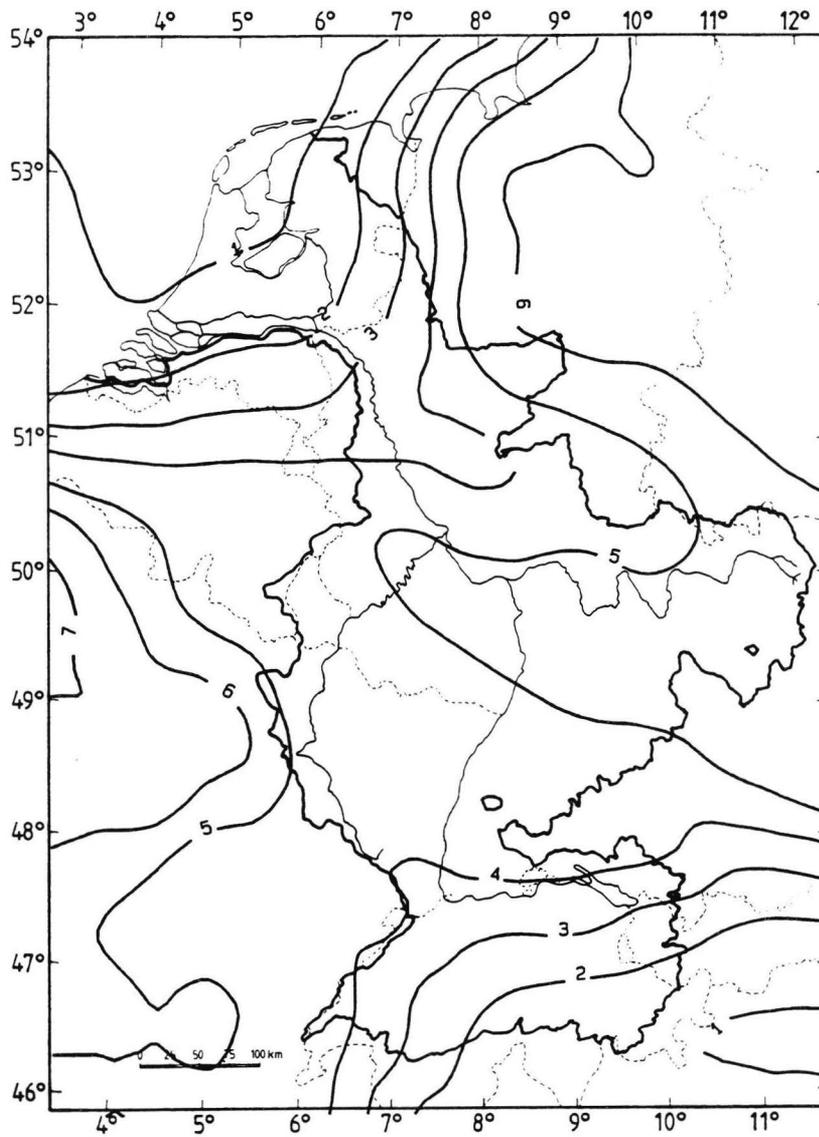


- 1 = .5000E-02
- 2 = .1000E-01
- 3 = .1500E-01
- 4 = .2000E-01
- 5 = .2500E-01
- 6 = .3000E-01
- 7 = .3500E-01

Figure D27 Calculated deposition of pentachlorophenol in  $\text{kg.ha}^{-1}.\text{y}^{-1}$  on the Rhine catchment area.



**Figure D28** Calculated deposition of simazine in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  on the Rhine catchment area.



1	=	.5000E-04
2	=	.1000E-03
3	=	.1500E-03
4	=	.2000E-03
5	=	.2500E-03
6	=	.3000E-03
7	=	.3500E-03

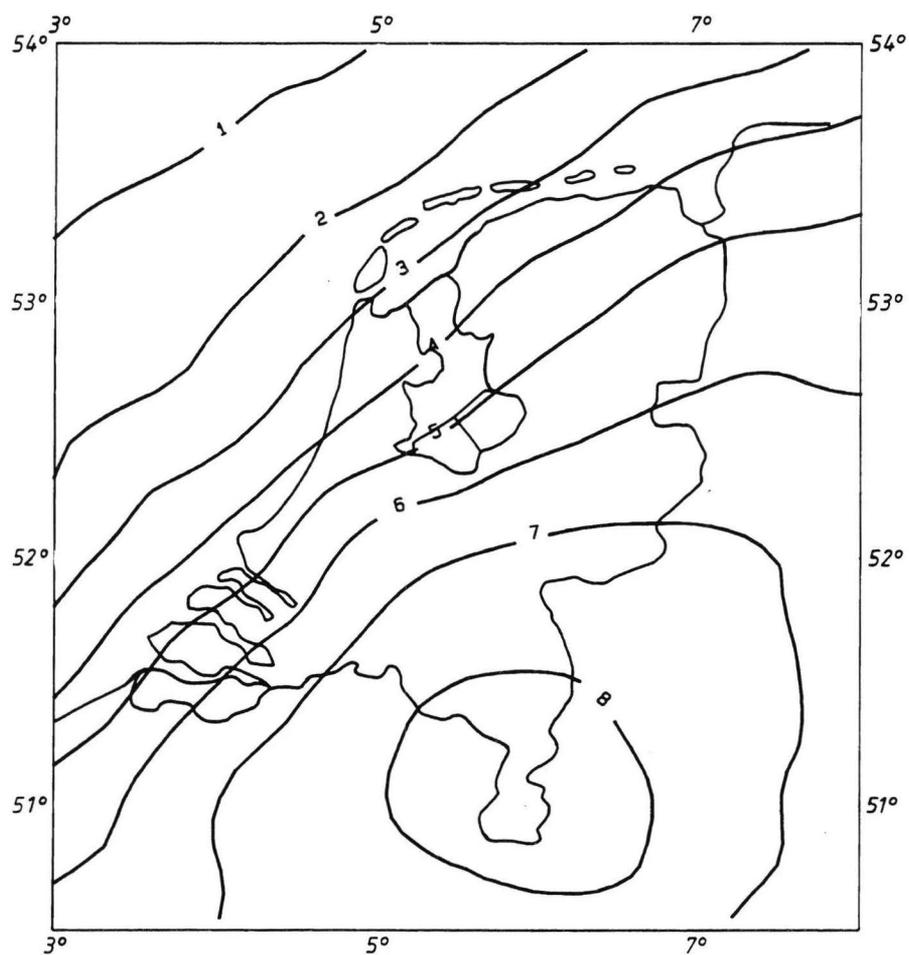
Figure D29 Calculated deposition of trifluralin in  $\text{kg.ha}^{-1}.\text{y}^{-1}$  on the Rhine catchment area.

**Table D1** Averaged depositionfluxes on the Dutch part of the Rhine catchment area.

	kg/ha/y
Cadmium	$1.3 \cdot 10^{-3}$
Chromium	$5.5 \cdot 10^{-3}$
Copper	$9.6 \cdot 10^{-3}$
Lead	$1.6 \cdot 10^{-1}$
Mercury	$1.4 \cdot 10^{-3}$
Nickel	$8.5 \cdot 10^{-3}$
Zinc	$8.4 \cdot 10^{-2}$
Benzene	$3.6 \cdot 10^{-2}$
PAH aer.	$2.4 \cdot 10^{-3}$
PAH gas	$8.0 \cdot 10^{-4}$
PCB	$2.0 \cdot 10^{-3}$
1,2-Dichloroethane	$6.6 \cdot 10^{-3}$
1,1,1-trichloroethane	$4.7 \cdot 10^{-2}$
Tetrachloromethane	$2.8 \cdot 10^{-4}$
Chloroform	$8.5 \cdot 10^{-4}$
Trichloroethene	$1.6 \cdot 10^{-2}$
Tetrachloroethene	$6.9 \cdot 10^{-3}$
Attrazine	$8.1 \cdot 10^{-3}$
Azinphos-methyl	$8.5 \cdot 10^{-5}$
Bentazone	$2.7 \cdot 10^{-3}$
Dichlorvos	$6.4 \cdot 10^{-4}$
Dichloropropene	$6.8 \cdot 10^{-3}$
Endosulfan	$5.1 \cdot 10^{-4}$
Fentin	$6.7 \cdot 10^{-3}$
Lindane	$1.9 \cdot 10^{-3}$
Parathion	$2.1 \cdot 10^{-3}$
Pentachlorophenol	$1.1 \cdot 10^{-2}$
Simazine	$4.8 \cdot 10^{-4}$
Trifluralin	$1.1 \cdot 10^{-4}$

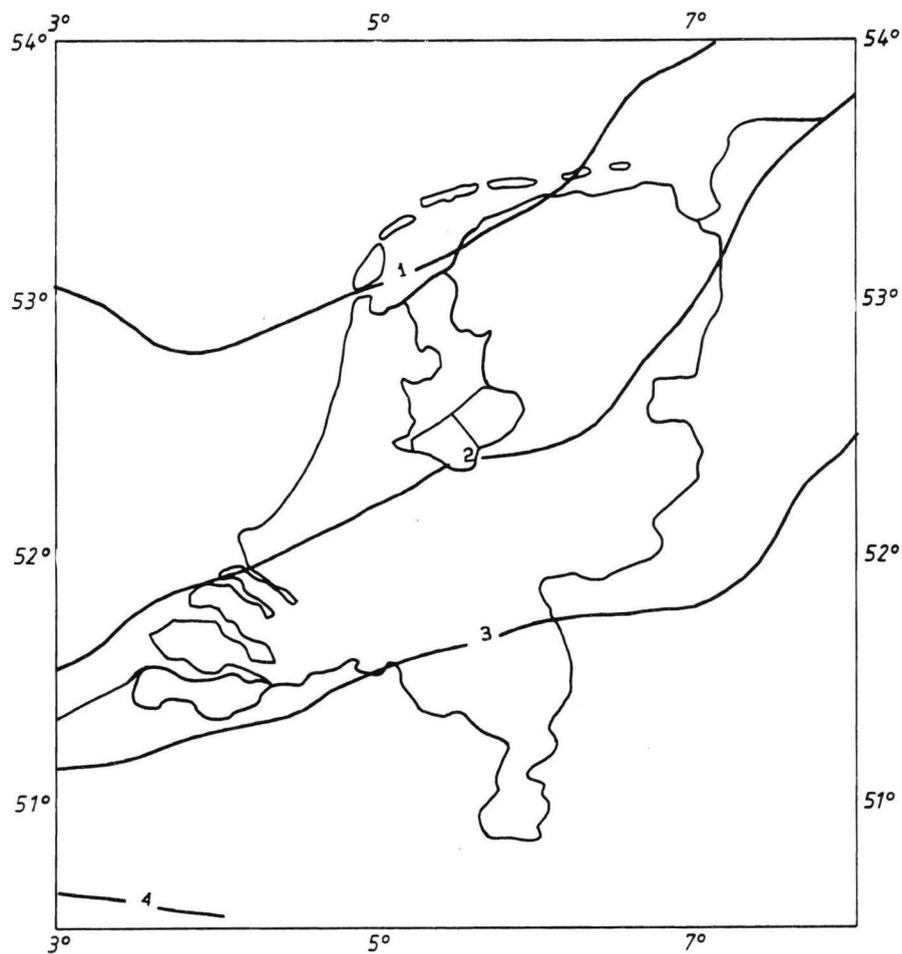
## APPENDIX E





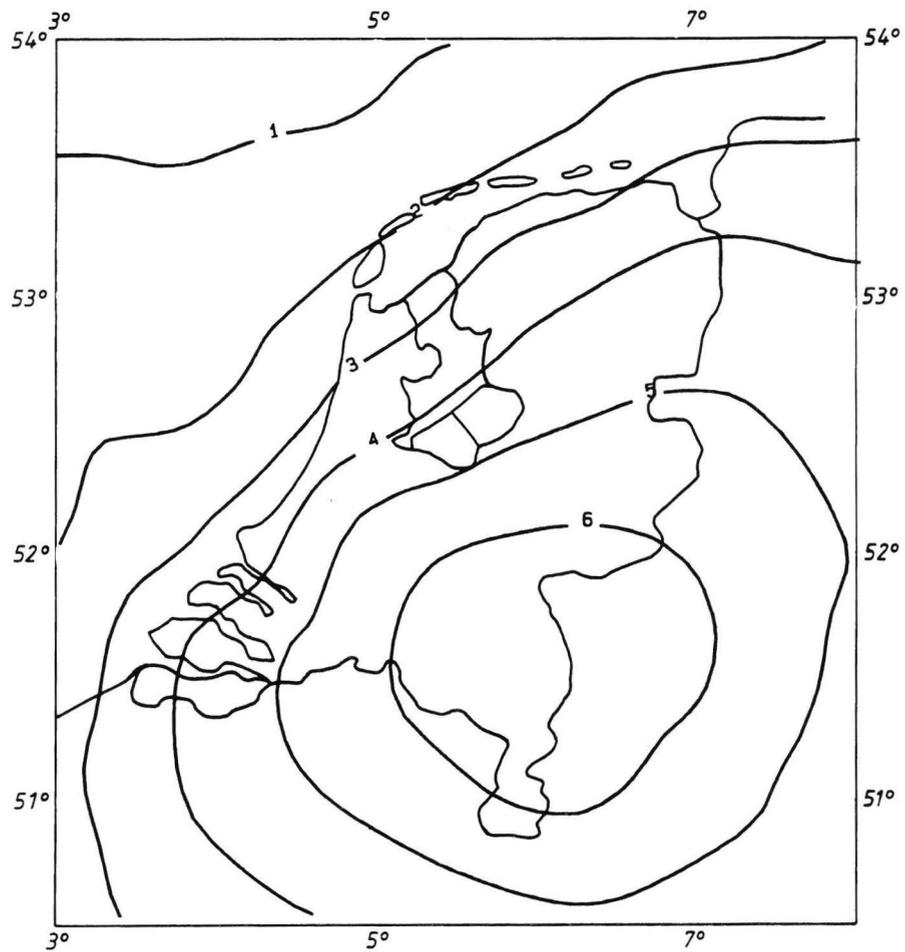
1	=	.3000E-04
2	=	.4000E-04
3	=	.5000E-04
4	=	.6000E-04
5	=	.7000E-04
6	=	.8000E-04
7	=	.9000E-04
8	=	.1000E-03

**Figure E1** Calculated total deposition of azinphosmethyl in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.



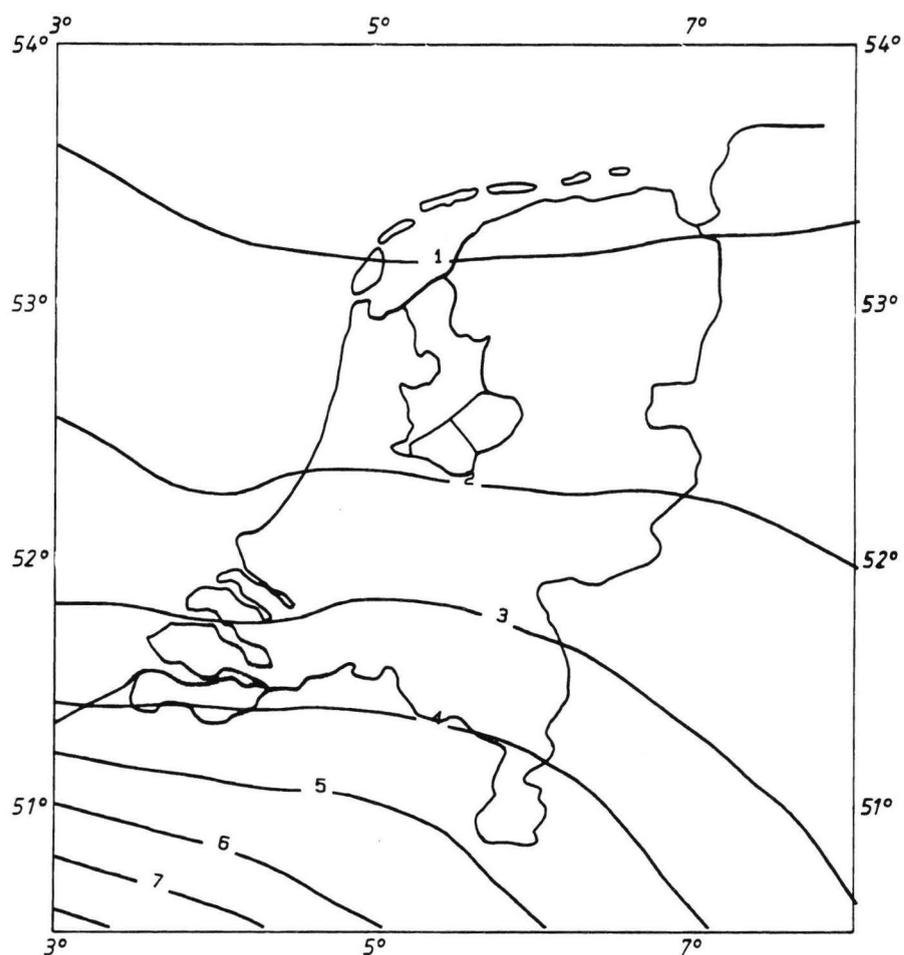
- 1 = .2000E-02
- 2 = .2500E-02
- 3 = .3000E-02
- 4 = .3500E-02

**Figure E2** Calculated total deposition of bentazone in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.



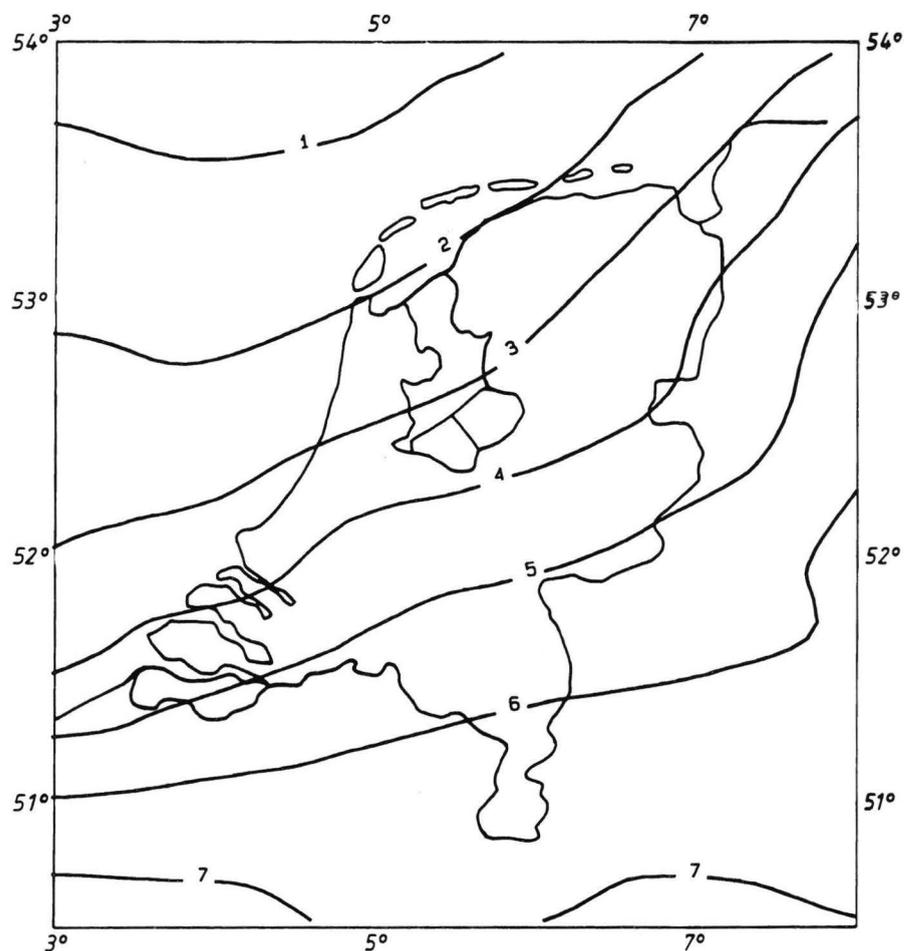
- 1 = .2000E-03
- 2 = .3000E-03
- 3 = .4000E-03
- 4 = .5000E-03
- 5 = .6000E-03
- 6 = .7000E-03

**Figure E3** Calculated total deposition of dichlorvos in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.



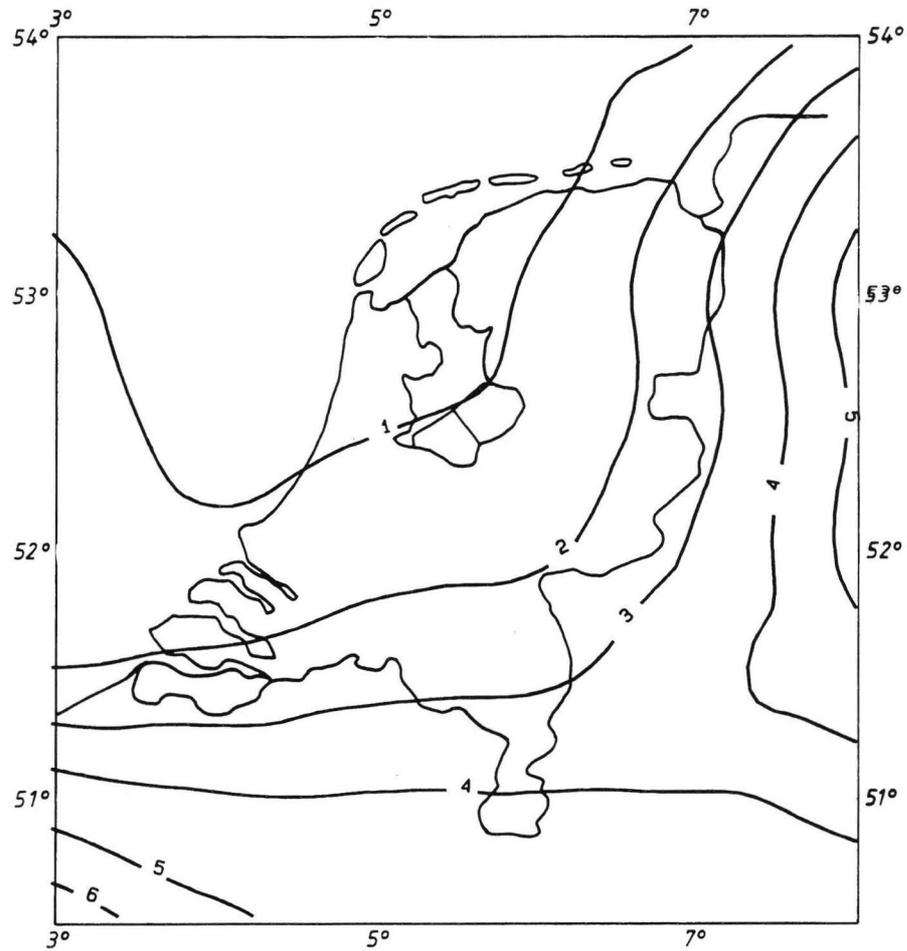
1	=	.6000E-02
2	=	.9000E-02
3	=	.1200E-01
4	=	.1500E-01
5	=	.1800E-01
6	=	.2100E-01
7	=	.2400E-01
8	=	.2700E-01

**Figure E4** Calculated total deposition of pentachlorophenol in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.



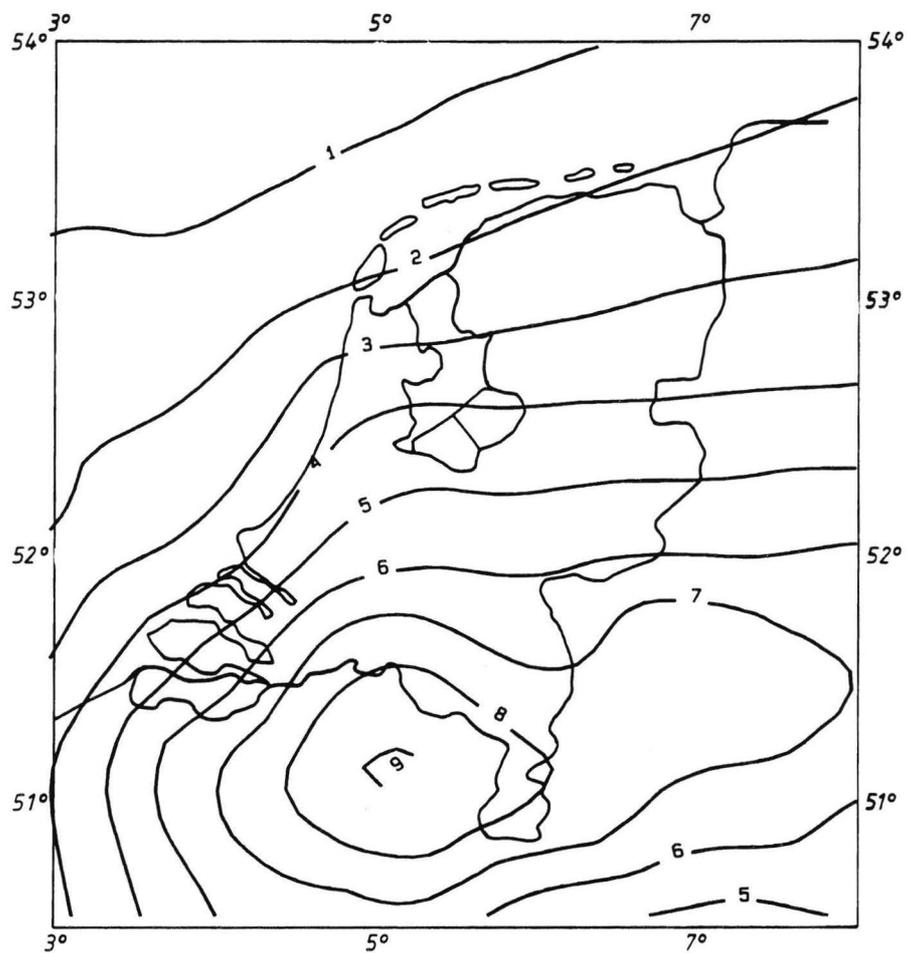
- 1 = .3000E-03
- 2 = .3500E-03
- 3 = .4000E-03
- 4 = .4500E-03
- 5 = .5000E-03
- 6 = .5500E-03
- 7 = .6000E-03

Figure E5 Calculated total deposition of simazine in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.



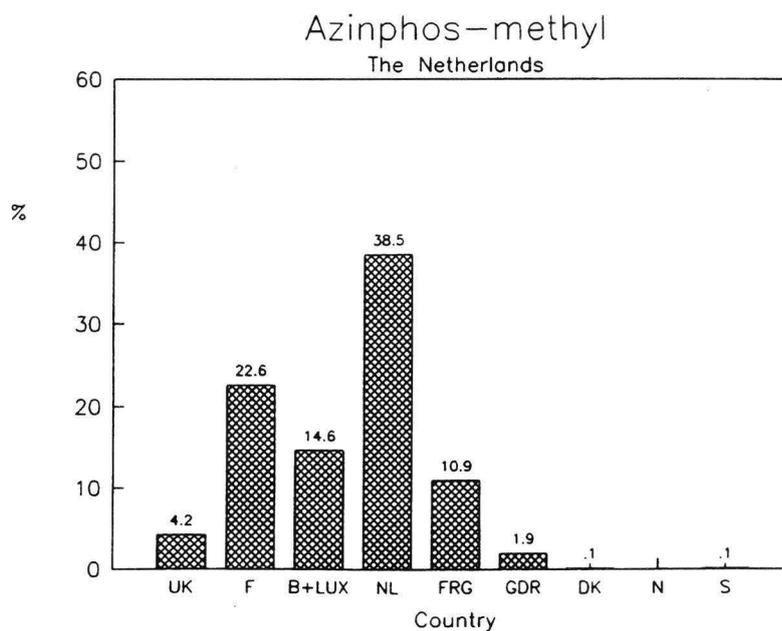
1	=	.5000E-04
2	=	.1000E-03
3	=	.1500E-03
4	=	.2000E-03
5	=	.2500E-03
6	=	.3000E-03

**Figure E6** Calculated total deposition of trifluralin in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  in the Netherlands.

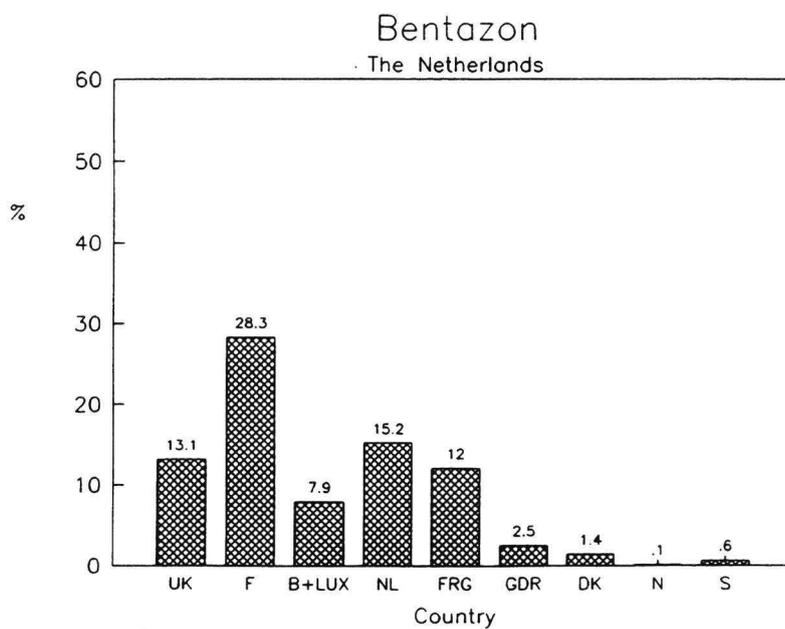


1	=	.4000E-02
2	=	.5000E-02
3	=	.6000E-02
4	=	.7000E-02
5	=	.8000E-02
6	=	.9000E-02
7	=	.1000E-01
8	=	.1100E-01
9	=	.1200E-01

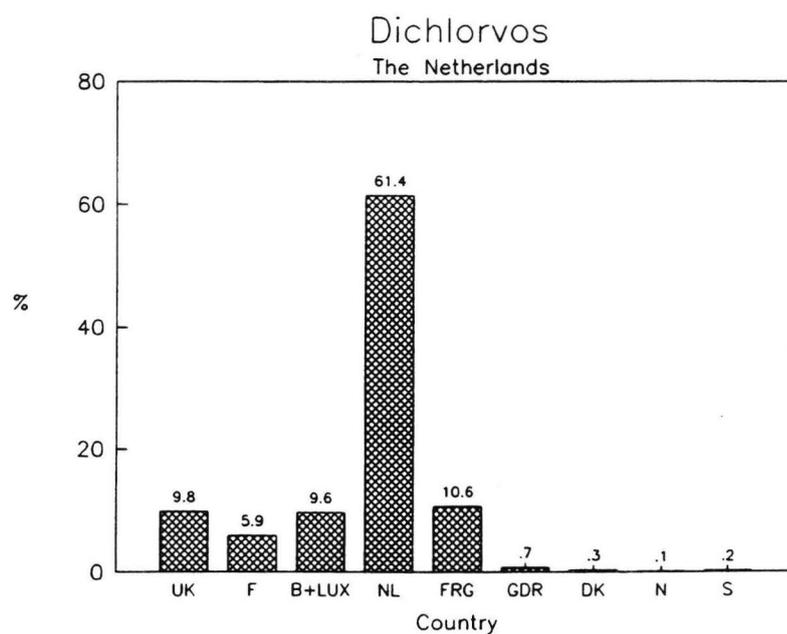
**Figure E7** Calculated total deposition of nickel in in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  the Netherlands.



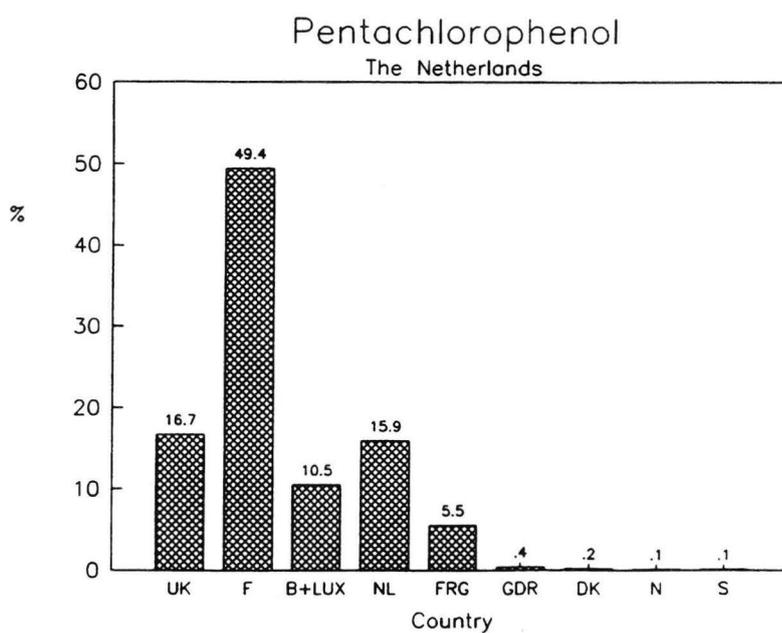
**Figure E8** Relative contributions of the surrounding countries to the total deposition of azinphos-methyl on the Netherlands. Total deposition 0.33 ton/y.



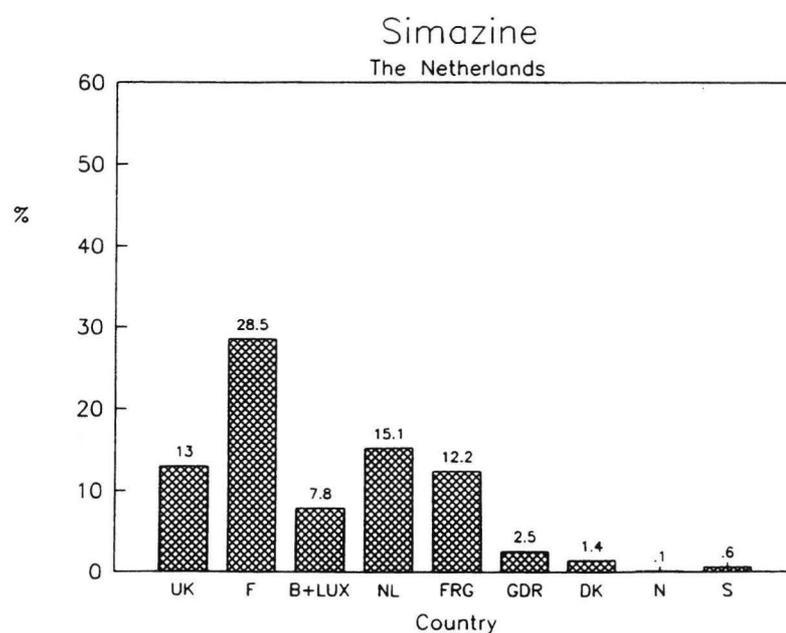
**Figure E9** Relative contributions of the surrounding countries to the total deposition of bentazone on the Netherlands. Total deposition 11.6 ton/y.



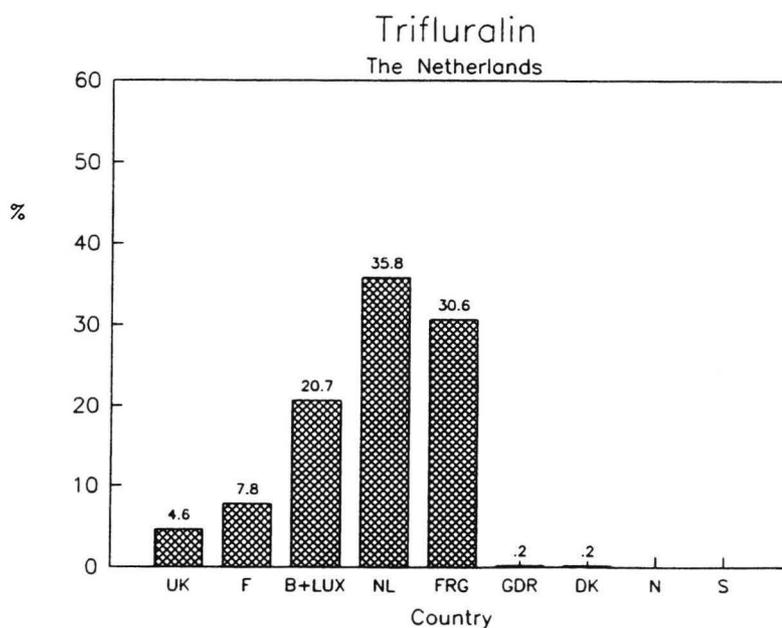
**Figure E10** Relative contributions of the surrounding countries to the total deposition of dichlorvos on the Netherlands. Total deposition 2.4 ton/y.



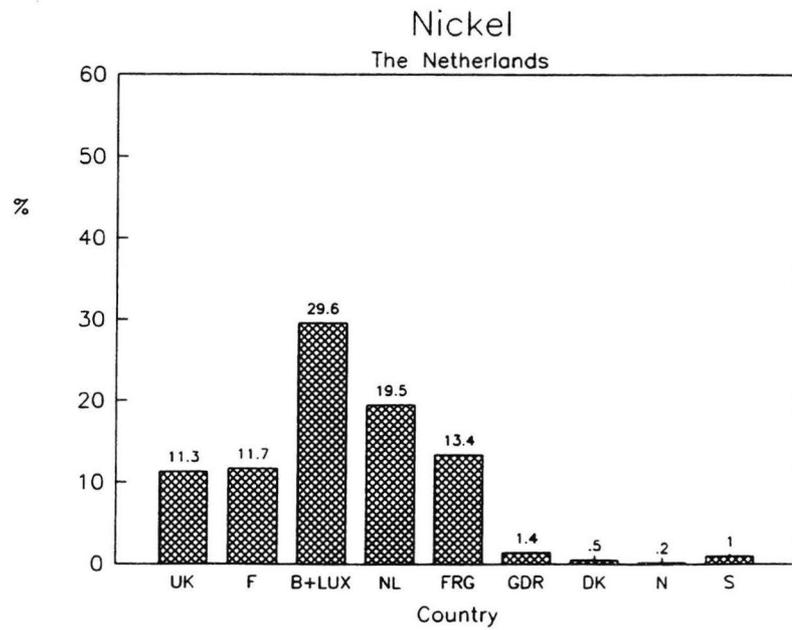
**Figure E11** Relative contributions of the surrounding countries to the total deposition of pentachlorophenol on the Netherlands. Total deposition 44.2 ton/y.



**Figure E12** Relative contributions of the surrounding countries to the total deposition of simazine on the Netherlands. Total deposition 2.1 ton/y.



**Figure E13** Relative contributions of the surrounding countries to the total deposition of trifluralin on the Netherlands. Total deposition 0.37 ton/y.



**Figure E14** Relative contributions of the surrounding countries to the total deposition of nickel on the Netherlands. Total deposition 33.5 ton/y.

## APPENDIX F

Deposition on the Netherlands specified to the deposition on different provinces and different categories of land uses

abbreviations:

- depo : deposition flux density
- recr : area used for recreation
- natu : nature reserves
- fore : forest
- gras : grassland
- arab : arable land
- wat : water
- gard : garden allotments
- tot : total area, not including coastal waters

**Table F1** Areas of the different provinces, specified to different categories of land use.

	recr <sup>1)</sup> ha	natu <sup>1)</sup> ha	fore <sup>1)</sup> ha	gras <sup>2)</sup> ha	arab <sup>2)</sup> ha	wat <sup>3)</sup> ha	gard <sup>1)</sup> ha	tot <sup>1)</sup> ha
Groningen	2925	4645	1923	63553	109211	5943	191	259585
Friesland	4219	25498	7453	204452	2473	39348	158	380838
Drenthe	4136	12475	24811	85481	82442	6209	62	268066
Overijssel	5451	12782	33957	170915	65845	16010	221	392498
Gelderland	11076	24964	84726	196091	49420	18637	215	512930
Utrecht	4080	3077	17106	62214	3241	8391	219	139641
N-Holland	11179	20100	6857	81660	40239	16070	829	293294
Z-Holland	11093	16569	2546	88373	45288	39739	1067	334398
Zeeland	3205	8665	1949	15068	97286	78535	78	301669
N-Brabant	12940	13759	62083	154799	100210	17182	290	510578
Limburg	6349	4892	26192	48002	5105	6593	74	220919
IJss-polder	2749	12896	9037	7926	46565	15858	101	113462

1) CBS 1979

2) CBS 1985

3) CBS 1979 and CUWVO 1986

**Table F2** Deposition of azinphos-methyl on the Netherlands.

	Depo kg.ha <sup>-1</sup> .y <sup>-1</sup>	recr kg/y	natu kg/y	fore kg/y	gras kg/y	arab kg/y	wat kg/y	gard kg/y	tot kg/y
Groningen	0.00006225	0.2	0.3	0.1	4.0	6.8	0.4	0.0	16.2
Friesland	0.00005783	0.2	1.5	0.4	11.8	1.4	2.3	0.0	22.0
Drenthe	0.00001728	0.3	0.9	1.8	6.1	5.9	0.4	0.0	19.1
Overijssel	0.00007765	0.4	1.0	2.6	13.3	5.1	1.2	0.0	30.5
Gelderland	0.00007756	1.0	2.2	7.3	17.0	4.3	1.6	0.0	44.5
Utrecht	0.00007682	0.3	0.2	1.3	4.8	0.2	0.6	0.0	10.7
N-Holland	0.00005775	0.6	1.2	0.4	4.7	2.3	0.9	0.0	16.9
Z-Holland	0.00007506	0.8	1.2	0.2	6.6	3.4	3.0	0.1	25.1
Zeeland	0.00007366	0.2	0.6	0.1	1.1	7.2	5.8	0.0	22.2
N-Brabant	0.00000911	1.2	1.3	5.7	14.1	9.1	1.6	0.0	46.5
Limburg	0.00009885	0.6	0.5	2.6	4.7	5.1	0.7	0.0	21.8
IJss-polder	0.00007476	0.2	1.0	0.7	0.6	3.5	1.2	0.0	8.5
Total		6.1	11.8	23.3	88.8	54.3	19.7	0.3	284.1

**Table F3** *Deposition of bentazone on the Netherlands.*

	Depo kg.ha <sup>-1</sup> .y <sup>-1</sup>	recr kg/y	natu kg/y	fore kg/y	gras kg/y	arab kg/y	wat kg/y	gard kg/y	tot kg/y
Groningen	0.002241	6.6	10.4	4.3	142.4	244.7	13.3	0.4	581.7
Friesland	0.002129	9.0	54.3	15.9	435.3	52.7	83.8	0.3	810.8
Drenthe	0.002409	10.0	30.1	59.8	205.9	198.4	15.0	1.0	645.8
Overijssel	0.002539	13.8	32.5	86.2	434.0	167.2	40.6	0.6	996.6
Gelderland	0.002729	30.2	68.1	231.2	535.1	134.9	50.9	0.6	1399.8
Utrecht	0.002517	10.3	7.7	43.1	156.6	8.2	21.1	0.6	351.5
N-Holland	0.002185	24.4	43.9	15.0	178.4	87.9	35.1	1.8	640.8
Z-Holland	0.002576	28.6	42.7	6.6	227.6	116.7	102.4	2.7	861.4
Zeeland	0.002767	8.9	24.0	5.4	41.7	269.2	217.3	0.2	834.7
N-Brabant	0.00289	37.4	39.8	179.4	447.4	289.6	49.7	0.8	1475.6
Limburg	0.003163	20.1	15.5	82.8	151.8	162.9	20.9	0.2	698.8
IJs-polder	0.002443	6.7	31.5	22.1	19.4	113.8	38.7	0.2	277.2
Total		205.9	400.4	751.7	2975.6	1846.0	688.7	8.7	9574.6

**Table F4** *Deposition of dichlorvos on the Netherlands*

	Depo kg.ha <sup>-1</sup> .y <sup>-1</sup>	recr kg/y	natu kg/y	fore kg/y	gras kg/y	arab kg/y	wat kg/y	gard kg/y	tot kg/y
Groningen	0.0004382	1.3	2.0	0.8	27.8	47.9	2.6	0.1	113.8
Friesland	0.0004078	1.7	10.4	3.0	83.4	10.1	16.0	0.1	155.3
Drenthe	0.0005271	2.2	6.6	13.1	45.1	43.4	3.3	0.0	141.3
Overijssel	0.000585	3.2	7.5	19.9	100.0	38.5	9.4	0.1	229.6
Gelderland	0.0006609	7.3	16.5	56.0	129.6	32.7	12.3	0.1	339.0
Utrecht	0.0005812	2.4	1.8	9.9	36.2	1.9	4.9	0.1	81.2
N-Holland	0.0004142	4.6	8.3	2.8	33.8	16.7	6.7	0.3	121.5
Z-Holland	0.0005481	6.1	9.1	1.4	48.4	24.8	21.8	0.6	183.3
Zeeland	0.0004817	1.5	4.2	0.9	7.3	46.9	37.8	0.0	145.3
N-Brabant	0.0006672	8.6	9.2	41.4	103.3	66.9	11.5	0.2	340.7
Limburg	0.0006858	4.4	3.4	18.0	32.9	35.3	4.5	0.1	151.5
IJs-polder	0.0005671	1.6	7.3	5.1	4.5	26.4	9.0	0.1	64.3
Total		44.9	86.2	172.4	652.2	391.4	139.7	1.8	2066.7

**Table F5** *Deposition of pentachlorophenol on the Netherlands*

	Depo kg.ha <sup>-1</sup> .y <sup>-1</sup>	recr kg/y	natu kg/y	fore kg/y	gras kg/y	arab kg/y	wat kg/y	gard kg/y	tot kg/y
Groningen	0.005939	17.4	27.6	11.4	377.4	648.6	35.3	1.1	1541.7
Friesland	0.006227	26.3	158.8	46.4	1273.1	154.0	245.0	1.0	2371.5
Drenthe	0.007014	29.0	87.5	174.0	599.6	577.5	43.5	0.4	1880.2
Overijssel	0.008232	44.9	105.2	279.5	1407.0	542.0	131.8	1.8	3231.0
Gelderland	0.01032	114.3	257.6	874.4	2023.7	510.0	192.3	2.2	5293.4
Utrecht	0.009763	39.8	30.0	167.0	607.4	31.6	81.9	2.1	1363.3
N-Holland	0.00797	89.1	160.2	54.7	650.8	320.7	128.1	6.6	2337.6
Z-Holland	0.01142	126.7	189.2	29.1	1009.2	517.2	453.8	12.2	3818.8
Zeeland	0.01503	48.2	130.2	29.3	226.5	1462.2	1180.4	1.2	4534.1
N-Brabant	0.01326	171.6	182.4	823.2	2052.6	1328.8	227.8	3.8	6770.3
Limburg	0.01497	95.0	73.2	392.1	718.6	771.0	98.7	1.1	3307.2
IJs-polder	0.008848	24.3	114.1	80.0	70.1	412.0	140.3	0.9	1003.9
Total		826.6	1516.2	2961.1	11016.0	7275.8	2959.0	34.5	37453.0

**Table F6** *Deposition of simazine on the Netherlands*

	Depo kg.ha <sup>-1</sup> .y <sup>-1</sup>	recr kg/y	natu kg/y	fore kg/y	gras kg/y	arab kg/y	wat kg/y	gard kg/y	tot kg/y
Groningen	0.0003959	1.2	1.8	0.8	25.2	43.2	2.4	0.1	102.8
Friesland	0.0003762	1.6	9.6	2.8	76.9	9.3	14.8	0.1	143.3
Drenthe	0.0004256	1.8	5.3	10.6	36.4	35.0	2.6	0.0	114.1
Overijssel	0.0004485	2.4	5.7	15.2	76.7	29.5	7.2	0.1	176.0
Gelderland	0.0004817	5.3	12.0	40.8	94.5	23.8	9.0	0.1	247.1
Utrecht	0.0004441	1.8	1.4	7.6	27.6	1.4	3.7	0.1	62.0
N-Holland	0.0003858	4.3	7.8	2.6	31.5	15.5	6.2	0.3	113.2
Z-Holland	0.0004545	5.0	7.5	1.2	40.2	20.6	18.1	0.5	152.0
Zeeland	0.0004887	1.6	4.2	1.0	7.4	47.5	38.4	0.0	147.4
N-Brabant	0.0005098	6.6	7.0	31.6	78.9	51.1	8.8	0.1	260.3
Limburg	0.0005585	3.5	2.7	14.6	26.8	28.8	3.7	0.0	123.4
IJs-polder	0.0004312	1.2	5.6	3.9	3.4	20.1	6.8	0.0	48.9
Total		36.3	70.7	132.7	525.4	325.9	121.6	1.5	1690.4

**Table F7** *Deposition of trifluralin on the Netherlands*

	<b>Depo</b> <b>kg.ha<sup>-1</sup>.y<sup>-1</sup></b>	<b>recr</b> <b>kg/y</b>	<b>natu</b> <b>kg/y</b>	<b>fore</b> <b>kg/y</b>	<b>gras</b> <b>kg/y</b>	<b>arab</b> <b>kg/y</b>	<b>wat</b> <b>kg/y</b>	<b>gard</b> <b>kg/y</b>	<b>tot</b> <b>kg/y</b>
Groningen	0.00008803	0.3	0.4	0.2	5.6	9.6	0.5	0.0	22.9
Friesland	0.00005676	0.2	1.4	0.4	11.6	1.4	2.2	0.0	21.6
Drenthe	0.00009961	0.4	1.2	2.5	8.5	8.2	0.6	0.0	26.7
Overijssel	0.00009808	0.5	1.3	3.3	16.8	6.5	1.6	0.0	38.5
Gelderland	0.0001046	1.2	2.6	8.9	20.5	5.2	1.9	0.0	53.7
Utrecht	0.0007202	0.3	0.2	1.2	4.5	0.2	0.6	0.0	10.1
N-Holland	0.00004483	0.5	0.9	0.3	3.7	1.8	0.7	0.0	13.1
Z-Holland	0.00008357	0.9	1.4	0.2	7.4	3.8	3.3	0.1	27.9
Zeeland	0.0001304	0.4	1.1	0.3	2.0	12.7	10.2	0.0	39.3
N-Brabant	0.0001249	1.6	1.7	7.8	19.3	12.5	2.1	0.0	63.8
Limburg	0.0001763	1.1	0.9	4.6	8.5	9.1	1.2	0.0	38.9
IJs-polder	0.00006541	0.2	0.8	0.6	0.5	3.0	1.0	0.0	7.4
<b>Total</b>		<b>7.7</b>	<b>14.0</b>	<b>30.2</b>	<b>108.8</b>	<b>74.0</b>	<b>26.1</b>	<b>0.3</b>	<b>363.9</b>

**Table F8** *Deposition of nickel on the Netherlands*

	<b>Depo</b> <b>kg.ha<sup>-1</sup>.y<sup>-1</sup></b>	<b>recr</b> <b>kg/y</b>	<b>natu</b> <b>kg/y</b>	<b>fore</b> <b>kg/y</b>	<b>gras</b> <b>kg/y</b>	<b>arab</b> <b>kg/y</b>	<b>wat</b> <b>kg/y</b>	<b>gard</b> <b>kg/y</b>	<b>tot</b> <b>kg/y</b>
Groningen	0.005413	15.8	25.1	10.4	344.0	591.2	32.2	1.0	1405.1
Friesland	0.005431	22.9	138.5	40.5	1110.4	134.3	213.7	0.9	2068.3
Drenthe	0.006255	25.9	78.0	155.2	534.7	515.0	38.8	0.4	1676.8
Overijssel	0.007201	39.3	92.0	244.5	1230.8	474.1	115.3	1.6	2826.4
Gelderland	0.008566	94.9	213.8	725.8	1679.7	423.3	159.6	1.8	4393.8
Utrecht	0.00776	31.7	23.9	132.7	482.8	25.2	65.1	1.7	1083.6
N-Holland	0.006089	68.1	122.4	41.8	497.2	245.0	97.9	5.0	1785.9
Z-Holland	0.007979	88.5	132.2	20.3	705.1	361.4	317.1	8.5	2668.2
Zeeland	0.007971	25.5	69.1	15.5	120.1	775.5	626.0	0.6	2404.6
N-Brabant	0.009634	124.7	132.6	598.1	1491.3	965.4	165.5	2.8	4918.9
Limburg	0.01035	65.7	50.6	271.1	496.8	533.1	68.2	0.8	2286.5
IJs-polder	0.007389	20.3	95.3	66.8	58.6	344.1	117.2	0.7	838.4
<b>Total</b>		<b>623.2</b>	<b>1173.6</b>	<b>2322.7</b>	<b>8751.5</b>	<b>5387.6</b>	<b>2016.6</b>	<b>25.9</b>	<b>28356.4</b>

## APPENDIX G

**Table G1** Total deposition and relative contributions of the surrounding countries to the total deposition on the Rhine catchment area, including the area of effluent rivers in the Netherlands (total area 186915 km<sup>2</sup>).

	Relative contributions									total ton/y
	UK %	F %	B+Lux %	NL %	FRG %	GDR %	AU %	CH %	I %	
Cadmium	1.9	12.3	11.5	2.3	40.9	0.6	10.9	3.4	5.9	23
Chromium	2.4	9	12.5	0.7	33.8	1.2	3.7	7	10.5	110
Copper	3.2	9	21.3	1.8	41.5	2.1	1.8	2.2	3.1	140
Lead	5.7	21.1	13.6	8.5	31.4	1.3	1.7	5.4	4.9	2100
Mercury	3.4	6.6	9.5	8.1	58.1	4.1	0.1	6.8	0.5	19
Nickel	4.5	18.3	11	5	25.9	2.5	2.5	6.3	10.5	140
Zinc	2.6	15.8	8.1	1.9	51.7	0.7	5	6.6	3	1600
Benzene	6.2	20	4.7	7.7	38.2	4.9	1.5	4.6	2.6	570
PAH aer.	3.2	25.3	4.3	3.8	36.6	3.3	3.9	6.8	1.8	39
PAH gas	0.6	18.1	3.6	4.3	58.7	1.6	1.7	10.1	0.5	10
PCB	7.5	22.6	6.3	8.9	35.2	2	0.8	5.2	4.1	30
1,2-dichloroethane	1.2	8	11.5	16.9	38.8	2.5	0	0	1.6	69
1,1,1-trichloroethane	7.3	22.3	6.7	4.4	43.4	1.4	1.1	7.1	3.4	790
Tetrachloromethane	5.6	15.8	6	7.3	39.2	2.7	0.8	9.2	4.7	4.6
Chloroform	7.7	14.4	4.8	7.6	48.8	3.3	0.7	3.4	3.4	13
Trichloroethene	7.2	23.3	3.8	2.7	45.7	2.2	0.3	5.9	3.2	300
Tetrachloroethane	3	18.7	5.3	6.8	43.3	1.6	0.7	12.2	4.1	120
Atrazine	4.2	39.6	3.5	3.8	24.8	3.5	0.7	2.2	4.7	180
Azinphos-methyl	1.3	31.4	6.9	9.5	23.1	2.6	0.7	12	6.9	1.6
Bentazone	3.9	36.4	3.4	3.5	22.8	3.2	0.6	2	5.6	60
Dichlorvos	4.2	15.3	7.5	23	36.4	2	0.4	5.6	2.7	8.2
Dichloropropene	2.4	9.8	5.5	25	29.1	13.8	0.4	2.8	1.2	88
Endosulfan	4.3	33.8	3.6	4.2	29.9	5.4	0.7	1.9	4.8	13
Fentin	3.2	12.4	5.3	21.1	22.8	9.6	0.5	3.1	2	86
Lindane	4.9	37.9	3.6	4.1	27.7	5	0.5	2.1	4.2	44
Parathion	3.7	35.7	3.7	4.5	30.2	4.7	0.1	3.9	6.9	53
Pentachlorophenol	3.8	73.4	4.6	3.4	10.2	0.7	0.2	1.9	0.5	270
Simazine	3.8	36.6	3.3	3.4	23	3.2	0.6	2	5.6	11
Trifluralin	0.4	20.4	4.6	3.7	63.8	2.5	0.3	3.7	0.4	3.7

**Table G2** Total deposition and relative contributions of the surrounding countries to the total deposition on the Dutch part of the Rhine catchment area, including the area of effluent rivers in the Netherlands (total area 22601 km<sup>2</sup>).

	Relative contributions									total ton/y
	UK %	F %	B+Lux %	NL %	FRG %	GDR %	AU %	CH %	I %	
Cadmium	6.5	9.1	32.5	12.3	25	0.4	3.4	0.3	1.8	2.3
Chromium	8.9	6.9	38.6	4	21.6	0.9	1.1	0.5	3.3	10.0
Copper	8.3	5.3	47.5	7.5	20	1.1	0.4	0.1	0.8	17.3
Mercury	9.9	3.3	21.3	35.6	26.3	1.7	0	0.3	0.1	2.6
Lead	13.1	10.7	26.2	30.7	13.1	0.6	0.4	0.3	1	310.1
nickel	12.5	11.4	26	22	13.2	1.4	0.6	0.4	2.7	16.5
Zinc	9.5	12.7	24.7	10.7	34.2	0.5	1.7	0.6	1	151.6
Benzene	14.3	12.2	9.3	30.1	22.7	2.7	0.4	0.5	0.9	72.0
PAH aer.	9.3	15.6	10	19.3	32.4	2	1.1	0.5	0.5	4.4
PAH gas	3.5	8.1	11.3	27.7	48.8	0.3	0	0.1	0	1.1
PCB	17	13.5	12.9	31.7	17.3	1.1	0.2	0.5	1.1	4.1
1,2-dichloroethane	2	1.6	17.6	49	24.6	0.9	0	0	0.6	10.8
1,1,1-trichloroethane	17.6	15.5	14.6	18.3	27.9	0.9	0.3	0.9	1.4	9.4
Tetrachloromethane	12.9	9.8	11.4	28.3	25.9	1.6	0.3	1.1	1.8	0.5
Chloroform	17.3	8.5	8.9	27	30.2	1.9	0.2	0.4	1.2	1.7
Trichloroethene	19.8	17.4	9.2	12.8	31.9	1.5	0.1	0.7	1.3	31.1
Tetrachloroethane	7.4	13.5	12	29.5	29.2	1	0.2	1.6	1.8	13.4
Atrazine	15.9	29.7	7.6	17.4	12.7	2.8	0.3	0.2	1.4	16.5
Azinphos-methyl	4.6	22	12.5	40.7	10.7	1.9	0.3	1	1.8	0.2
Bentazone	14.5	27.3	6.8	16	11.7	2.5	0.3	0.2	1.6	5.6
Dichlorvos	10.9	5.6	7.6	63.2	10.2	0.7	0.1	0.2	0.3	1.2
Dichloropropene	6.5	3.5	5.6	67.9	9	3.9	0	0.1	0.1	12.9
Endosulfan	17.5	23.7	6.5	19.3	18.1	3.1	0.2	0.2	1.3	1.0
Fentin	7.1	5.5	6.7	57.6	6.9	4.5	0.1	0.2	0.3	13.4
Lindane	18.3	27	6.6	18.2	15	3.2	0.2	0.2	1.3	3.8
Parathion	17.9	25	7.4	22.9	16.4	2.9	0	0.3	1.4	4.2
Pentachlorophenol	19.3	47.4	8.8	17.1	5.5	0.5	0	0.1	0.1	21.0
Simazine	14.3	27.5	6.7	15.8	11.8	2.6	0.3	0.2	1.7	1.0
Trifluralin	6.6	6.7	13.5	42.1	30.6	0.2	0	0	0	0.2