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Lindane:
use, emissions and fate in the Rhine Basin

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Abstract

The objective of this study was to estimate the use, emissions and aquatic fate of lindane in the Rhine Basin from 1985 to 2000. The use of lindane in the Rhine Basin is based on its agricultural use in the five most important bordering countries: Germany, Switzerland, France, Luxembourg and the Netherlands for 1985 and 1990. Based on anticipative measurements on the different uses in these countries, hardly any change was to be expected in the period 1990 - 2000. Monitored data up to 1993 more-or-less confirm this assumption. Six major emission pathways are distinguished: 1) agricultural applications, 2) erosion, 3) domestic use, 4) atmospheric deposition directly onto surfacewaters, 5) atmospheric deposition via non-paved areas and 6) runoff from urban areas. In 1985 agriculture and atmospheric deposition together comprised over 70% of all emissions whereas in 1990 households and agriculture were calculated to be responsible for almost 80% of all emissions inside the Rhine Basin.

The aquatic fate in the Rhine Basin was calculated with the water quality model DELTAWAT. Comparison of the calculated with the observed water quality shows in general an overestimation of the emissions in 1985 by a factor ranging from 1 to 2, whereas the estimates for 1990 looked fairly accurate. Since the monitored discharges showed unexplainable discrepancies, further analysis of the emission estimates was not very useful. Assuming an overestimation of the sources by a factor of 1 to 2 in 1985 and of the 1990 emission estimates within a range of 50%, the 50% emission reduction objective of the International Commission for the Protection of the Rhine (ICPR) in 1995 in comparison with 1985 has most likely already been met. The water quality objective for the year 2000 however will most certainly not be met or even be approached in most parts of the Rhine Basin. The ICPR objectives for emissions and water quality seem to be in conflict.

Introduction

The River Rhine water quality has strongly deteriorated during this century due to emissions from @culture, and industrial and municipal wastewater. Water quality became a particularly acute problem in the 1960's and 1970's. After the Sandoz accident in Basel in November 1986, the states bordering the River Rhine agreed on the Rhine Action Programme for ecological rehabilitation of this river. The Rhine Action Programme was initially focused on the improvement of water quality. The Rhine states agreed on a target reduction of at least 50% of the pollution caused by priority compounds by the year 1995 (compared to the situation in 1985). Furthermore, water quality targets were set for about 50 priority compounds. In 1993, Rhine water quality from 1990 was measured against the targets set for the priority compounds. An overall comparison showed that for approximately two-thirds of these compounds, the targets had been reached or the concentrations were below the analytical detection limit. However, in 1990 the targets for mercury, cadmium, copper, zinc, lindane, chloroform, hexachlorobenzene, PCBs, and ammonium had not been reached anywhere along the entire course of the Rhine (ICPR, 1994). Apparently, additional measures were required to achieve the water quality targets for these substances. In formulating such measures, insight into the relationship between sources and concentrations in the water is considered very helpful. In this study, aimed at providing insight into the contribution of different lindane sources, pathways, fate in the water, and resulting lindane concentrations in the river, we performed an analysis on riverbasin scale by combining estimates of emission and of aquatic fate of the substance. Both estimates can not be separated simply because only the result of the combined emission and fate can be related to monitored water quality. If the monitoring takes place close to the sources the ultimate calibration will mainly concern the emission, but only on a local scale. This would need an unrealistically large account of water quality data for large riverbasins. The obvious method then is the use of a generic emission model which can be applied to a large number of situations. This method also needs considerable data but more general data compared with the water quality data. Number of inhabitants or information on land use is more common and therefore in general much more accessible than specific waterquality measurements. Yet the estimates rely largely on the genericity of the model on the one hand and need less common and therefore less accessible substance-specific data on the other hand.

This report will present analyses of estimates of the use and the consequent emissions of lindane for the period 1985 - 2000. The aquatic fate was calculated with the water quality model DELTAWAT. Since 1985, 1995 and 2000 are target years of the ICPR, this study used the period 1985 - 1993 to compare the combination of emissions and aquatic fate with water quality data. The results were compared with the objectives of the ICPR on emission reduction and water quality.

This report has been carried out on behalf of the Directorate General of Environmental Protection Directorate for Drinking Water, Water and Agriculture of the Ministry of Housing, Spatial Planning and Environment and in close co-operation with the Institute for Water Management and Waste Water Treatment.

Discussion and conclusions

The objective of this study was to estimate use, emissions and fate of lindane and to perform an uncalibrated run. This integrated approach also provides the opportunity to analyze whether reliable statements can be made on the realizability of the ICPR objectives.

Calculated water quality is always a combination of estimates of use, emissions and aquatic fate. Yet more detailed analysis provides possibilities to separate at least part of these components. The method however needs at least reliable monitoring data. As median values are most robust, they are chosen for comparison (Figure 5 and Figure 6). The overall impression then could be that the 1985 emissions are overestimated, whereas the 1993 emissions are estimated fairly accurately on average.

Figure 12 and Figure 13 present the calculated and observed discharges at monitoring stations in the basin upstream from Lobith. The minimum and maximum values of the observed loads are calculated taking into account possible ranges in water quality if values lie below the detection limit, and the relative error of the load calculation method (Klaver and De Vries, 1993). For both years, the observations show a positive trend from Village-Neuf to Koblenz and a sharp decline between Koblenz and Lobith. This effect cannot be caused by dilution of Rhine water with clean water from the Mosel since the observed water quality of the Mosel is even worse than that of the Rhine water quality at the same location.

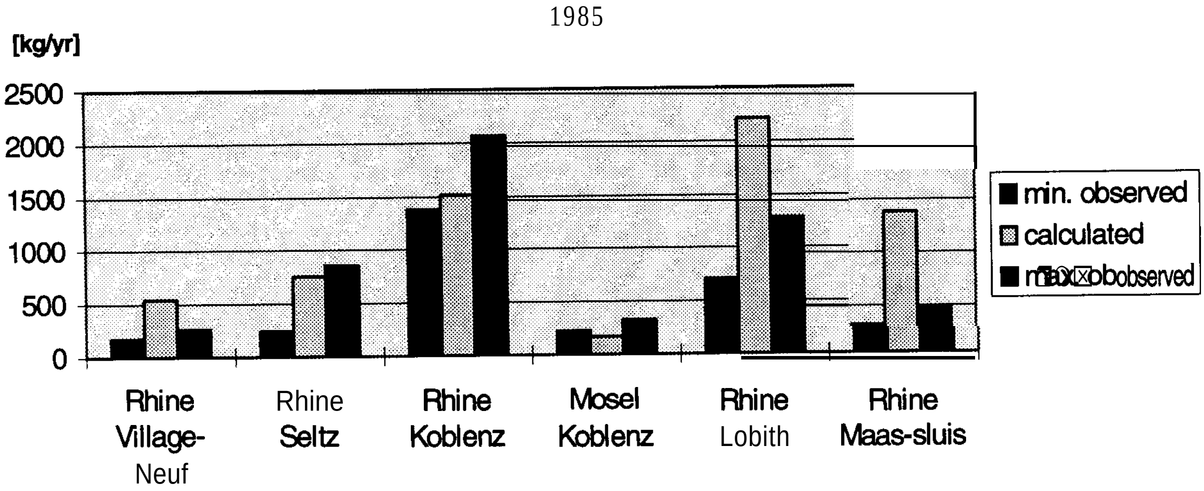

Figure 12: Observed and calculated discharges in 1985.

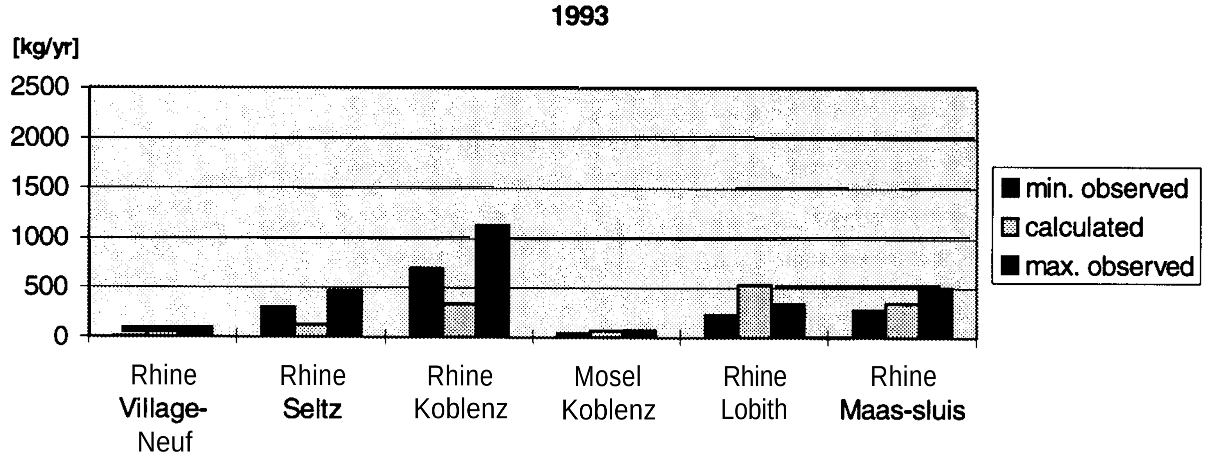

Figure 13: Observed and calculated discharges in 1993.

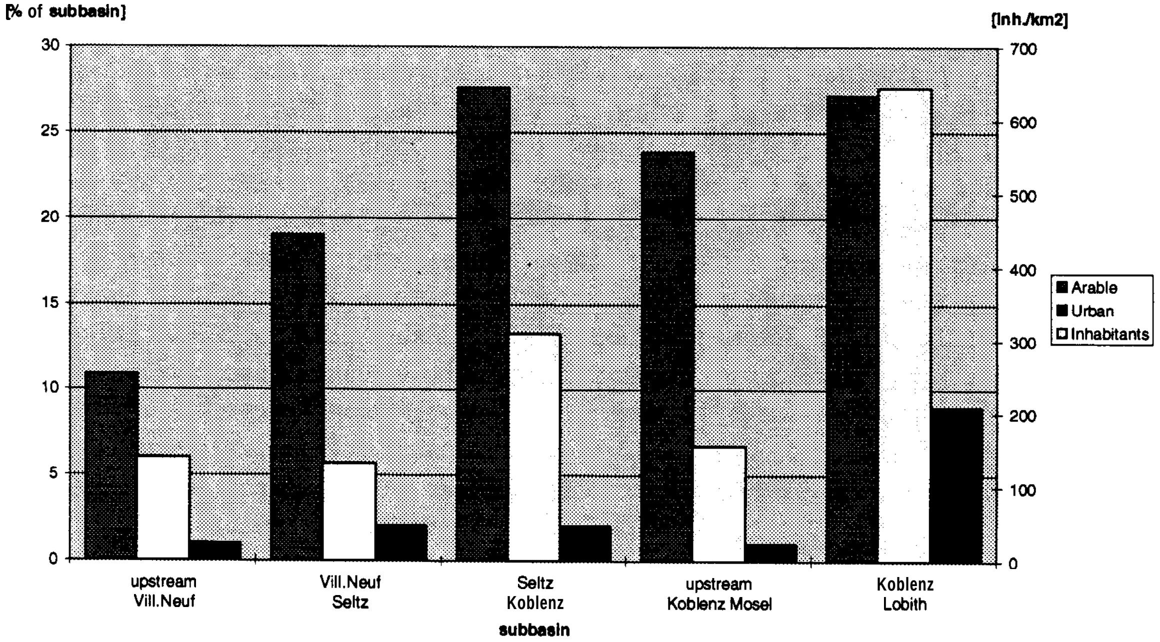

Figure 14: Subbasin properties.

Figure 14 shows the most important subbasin properties relevant to the emissions. These numbers suggest a relatively high lindane input at the Koblenz - Lobith stretch with no reason at all why the discharge should accumulate upstream from Koblenz and decline downstream. With an overall loss rate of approximately 0.05 day^{-1} and travelling times of less than 10 days, the mass balances will be dominated by inputs, with accumulation as a result. So the increasing discharge from Village-Neuf to Koblenz is anticipated but the decline between Koblenz and Lobith must most presumably be attributed to the monitoring itself. Four out of 5 gauging stations use different analytical techniques (ICPR, 1985 and 1993c) and may therefore cause systematic errors in the estimation of the discharge. Nevertheless, our presumption is that all data combined contain some information. At least the yearly averages between observations and calculations must be close. Hence it can be concluded that the emissions for 1985 in general are overestimated by a factor of 1 to 2, whereas the estimates for 1993 are close to the observed concentrations and the resulting calculated discharges.

Since all Dutch locations are analyzed by the same laboratory, a more reliable comparison can be made between Lobith and Maassluis and between Lake IJsselmeer on the other hand. The predictions for the Rotterdam harbour water quality are a little too high, whereas the predictions for the water quality of Lake IJsselmeer are good or even too low. For both locations one has to bear in mind however that the predictions for Lobith are most likely to high. Lake IJsselmeer is the only part of the basin where processes play a dominating role in determining the fate of lindane. But since processes do not change over time, the difference between observations and calculations for Lobith and Lake IJsselmeer for both time slices show an unambiguousness which cannot be explained by processes alone.

Predicting the fate of a chemical as a function of use, emissions and water quality processes, leads to uncertainties induced by every step of this chain. The first errors originate from the estimated use of lindane in the different countries. Table 1 shows large gaps. Only for 1985 and 1990 does there seem to be a consistent set of information. For both years the use in all countries was either calibrated or verified with data on lindane deposition. For 1990 the uncertainty is estimated at 2 - 5 but this is mainly based on the uncertainty in the emission factor for agricultural use (ESQUAD, 1994). The assumption that the use and therefore the consequent emissions remain practically the same from 1990 onwards seems to be in line with the observed water quality (Figure 4). The assumption was made that lindane is used equally on arable land in all the different countries. There is no evidence to assume otherwise, especially for Germany, the major contributor, where geographical differences must be very extreme since the Rhine Basin comprises a large part of the country. Hence it can be concluded that the negative trend in the use of lindane is well estimated, whereas the margins in the use itself could be up to 100% for France and Switzerland but far lower for Germany and the Netherlands.

For 1985 the discharge of lindane at Lobith was concluded to be overestimated by a factor of 2 at most. As mentioned before, this could be the result of combined errors in the estimates of emissions and aquatic processes. Still, the mass balance of the upstream section gives reason to assume that the major source of errors is the emission estimation. The loss of lindane in the aquatic system amounts to approximately 20% of the emissions. Although no calibration has been performed a simple first-order decay approach would need a decay rate of at least one order of magnitude greater than the 0.05 per day used in the model. This is believed unrealistic. The chosen decay rate is calibrated in a water system quality mode1 representing the Dutch main surfacewater systems (De Nijs and Burns, 1990). The residence time is much higher than in the upstream part hence the ‘ ‘calibration space’’ is much greater. Furthermore, the 0.05 per day value is partly based on generally accepted chemical properties and mode1 formulations. So the uncertainty must to a large extend be caused by the estimation of the sources. Qualitative remarks on the different pathways are given below:

- atmospheric deposition
  The deposition is based on the measured lindane concentrations in air. The estimation of the largest share, namely the runoff from paved areas is very reliable, since the numbers on paved areas and sewage systems are fairly accurate. The only important factor which is not taken into account is the loss of lindane in the sewer system, but since the major part of the lindane deposition is wet or caused by wet deposition, the local residence times will be low.
- erosion
  Estimating the contribution of this source is very uncertain. The estimate is based on scarce soil quality data in The Netherlands applied to the rest of the basin. The estimation of the erosion and the enrichment is also uncertain, yet the contribution from this source, especially in 1985 will never be very substantial.
- agriculture
  Most of this source (approximately 2/3) is assumed to originate in the cleaning of equipment. No information on the reliability of this assumption is found, but it is likely to be large, especially when this Dutch factor is applied to other countries.
- households
  Large uncertainties are linked to households as a source. Without an acceptable explanation for the presence of the 12 to 13 grams of lindane per inhabitant per year this Dutch factor was applied to all Rhine Basin inhabitants. In total, the estimated contribution of households is 0.36 tonnes in 1990, whereas the ICPR estimates a contribution of only 0.07 tonnes (ICPR, 1993d).
- Meuse river
  The contribution of the Meuse river to the loading of the Rhine-Meuse delta is based on the monitored discharge at Eysden. Eysden is located at the Dutch-Belgium border, almost 200 kilometres upstream from the point where the Meuse enters the delta. The Dutch contribution to this source is therefore not included. The residence time in this part of the Meuse, on the other hand, can be up to 10 days (WL, 1995). During these low flow periods more than 50% of the discharge at Eysden will presumably disappear before it reaches the delta.

The ICPR indicates an additional industrial source of 30 kg in 1992 (ICPR, 1993d). This can only result from formulation since lindane is not produced inside the basin. Still the apparently limited number of industrial sources is neglected.

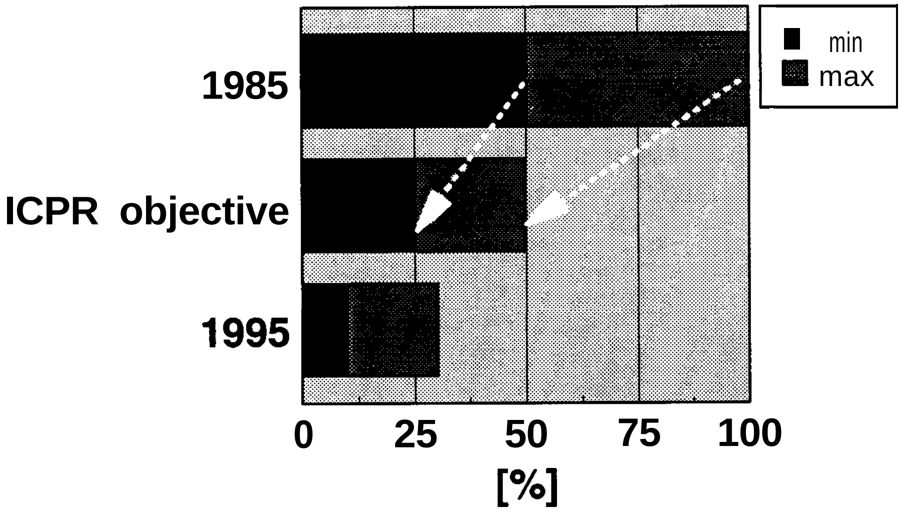

Figure 15: calculated ranges of emissions in 1995 with respect to 1985 (= 100%).

The first ICPR objective is to reduce the emissions in 1995 by 50% with respect to the situation in 1985. Assuming an overestimation of the sources in 1985 by a factor of 1 to 2 and estimates of the 1990 emissions to be within a range of 50%, the 50% emission reduction objective of the ICPR in 1995 in comparison with 1985 has most likely already been met (Figure 15). The water quality

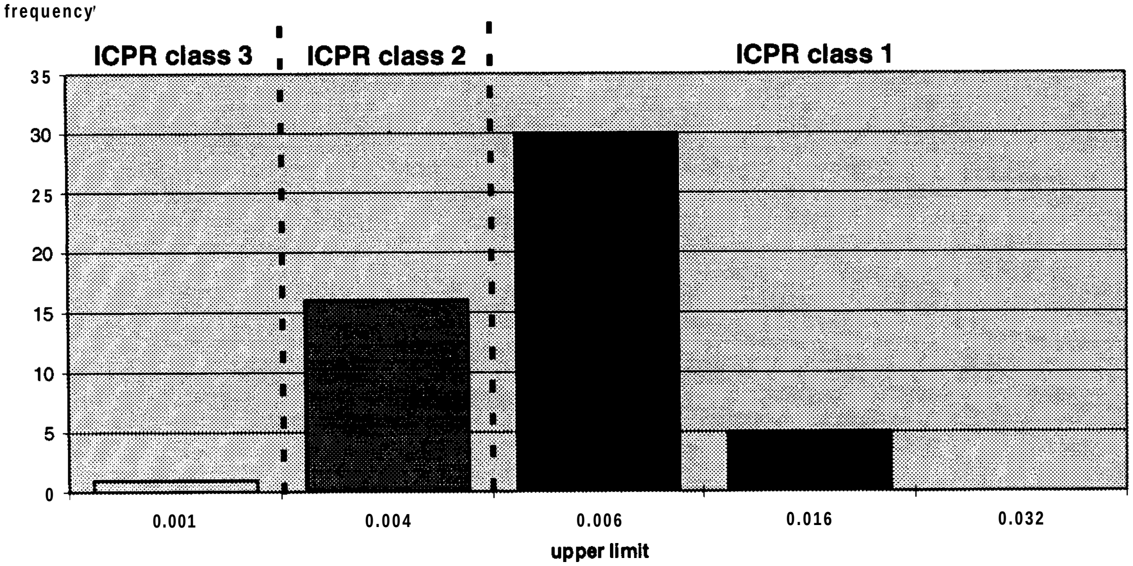

*Figure 16: frequency distribution **of** the calculated 90 percentile values in 2000 **for** the water quality model segments, assuming a 50% reduction **of** all sources (see text; **for** the ICPR classification see page 16).*

data at Lobith confirm this conclusion, bearing in mind that water quality processes influence the Lobith discharge only to a limited extent and even so, presumably almost linear. The 2000 water quality objective on the other hand will most certainly not be met or even be approached in most parts of the basin. The overall error in the estimation of the emissions from 1990 onwards is a factor of around 2 at maximum. Assuming 50% reduction of all sources compared to these estimated, being an almost absolute minimum value, would still lead to a water quality which in most cases is classified as ICPR category 1, at least two times higher than the objective of a P-90 of 0.002 ug/l (Figure 16). Therefore the two ICPR objectives seem to be in conflict with each other.