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Mapping the Potentially Affected Fraction (PAF) of species as an indicator of generic toxic stress

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Preface

KEES program

The work reported here is part of the RIVM research program "Kartering Ecotoxische Effecten Stoffen" (KEES; Geographic Representation of Ecotoxicological Effects of Substances). The KEES program comprises a number of related projects, a.o.:

1. Calculation of toxic stress on generic sets of organisms
2. Calculation of toxic stress on target species
3. Indicator toxic stress
4. Measurement of toxic potency of fresh waters in The Netherlands

These four projects have now produced four technical reports, describing how "toxic stress on ecosystems" can be calculated or measured. The first two projects start from measured concentrations of chemicals in soil and water, and calculate toxic stress for (a limited number of) chemicals for which measured concentrations are available. Project 1 focuses at the potential for toxic effects on all possible species (the generic set of species), disregarding the actual occurrence of species at the locations for which toxic stress is calculated. In contrast, project 2 focuses at the species that are thought to occur naturally at the locations of study (sets of target species). Project 3 contrasts to the first two in that it starts from model-calculated concentrations. This way, toxic stress can be calculated for a larger group of chemicals for which emissions and physical-chemical properties are available, but for which measured concentrations are scarce or absent. In project 4 the toxicity of natural waters is assessed by experimental means. Water is concentrated and tested toxicologically. The number of times a given water sample needs to be concentrated before toxic effects are observed is used as a measure of the toxic potency of the water sampled.

Potentially Affected Fraction

The four projects have in common that they use the concept of Potentially Affected Fraction of species (PAF). Projects 1-3 calculate toxic stress from known concentrations of chemicals in the environment and laboratory-measured toxicities of these chemicals. This is done for pre-defined sets of chemicals. Project 4 measures the toxicity of water. This is done for unknown mixtures of chemicals. In each case the results are reported in terms of the fraction of species for which the concentration in the environment exceeds the No Observed Effect Concentration (NOEC). We define this fraction as the Potentially Affected Fraction of species (PAF). PAF expresses a potential for adverse effects; no indication is given of the sort of effect or the extent of it.

The PAF concept can best be described as the inverse operation of the well-known "Van Straalen procedure" for deriving "safe" concentrations in the environment. Van Straalen's procedure uses the cumulative NOEC distribution to find the exposure concentration at which a given fraction (usually 5%) of the species suffers from "above-NOEC exposure". Given a concentration in the environment, the PAF concept finds -- using the same NOEC distribution-- the fraction of species that is exposed above NOEC. Both ways of use of the NOEC distribution have been mentioned by Van Straalen (1990), who has pointed out that finding a safe concentration ought to be regarded as "forward use"; reading potentially affected fractions is "inverse use".

At the start of this work, there were --to the best of our knowledge-- no reports of PAF-like procedures of assessment of toxic stress on ecosystems. The potential value of "forward use" of Van Straalen's procedure to yield PAF was first mentioned to us in

1989 by our colleagues T. Aldenberg and W. Slooff in 1989, during the preparation of the "Streven naar waarden" document. Recently, while working on this program, we learned that similar work had been started at RIKZ (Kater and Lefèvre, 1996[1]) and RIZA (Knoben and Beek, 1997).

Goal of the KEES program

The long-term goal of the KEES program is to quantitatively relate concentrations of toxic substances in the environment to species diversity of ecosystems. Toxic stress to ecosystems will eventually be reported as the fraction of species with (too) low probability to occur or survive, given the exposure to toxic substances. Trends of toxic stress in space and/or time can be used to evaluate or develop environmental management policies. Quantification of toxic stress in terms of species diversity will allow comparison of toxic stress with other forms of stress to ecosystems (dehydration, acidification, eutrophication, etc.), for which presently probabilities of occurrence are reported.

The KEES program thus aims at providing rational support for environmental decision making. The results are meant to be used also in the annual RIVM reports on the State of the Environment, and in the four-yearly National Environmental Outlooks.

Present work

The long-term goal of relating concentrations to species diversity is not within immediate reach. The realistic short-term objective of the four above-mentioned projects is to deliver operational procedures to compute and measure Potentially Affected Fractions of species as an indication of toxic stress. It is assumed that spatial and temporal trends in PAF are indicative of trends in toxic effects on ecosystems. However, the indicative value of PAF, its relationship with species diversity, and its potential for environmental decision making are beyond the scope of the present work. The scope is limited to the technical aspects of PAF-assessment.

Future work

On-going work in the KEES program addresses the above-mentioned left-outs. Taking the technical status of the PAF concept as it is reported here as a starting point, the following items are investigated

- Comparison and analysis of the results of the four types of toxic stress assessment. What are the differences and similarities; can this be explained/understood? Is adjustment of the methods necessary/possible?
- Relationship of the Potentially Affected Fraction with ecosystem health. Is there an understandable and predictable relationship between PAF and species diversity? Are the results of PAF assessment useful starting points for assessing the extent of ecosystem damage?
- The possibilities of using PAF as toxic stress indicator in environmental management practice. Do maps of toxic stress provide a meaningful basis for focusing on hot spots? Are trends of toxic stress in time meaningful as indicators of progress in environmental management policy?

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[1] Perhaps somewhat confusing in this context, these authors name their risk assessment reading of the NOEC distribution "inverse Van Staalen procedure"!

Acknowledgments

This report is the output of project 1. Several RIVM-laboratories, and other research institutes have cooperated in this work. Geographical information on concentrations of heavy metals in soil, and of soil properties, were obtained from the Laboratory of Soil and Groundwater Research. The Institute of Inland Water Management (RIZA) provided measured concentrations of heavy metals and pesticides in the major water systems. The Commission Integral Water Management (CIW) provided measured concentrations in regional waters. Estimates of pesticide concentrations in natural soil were made through cooperation of the several RIVM laboratories with the Winand Staring Center.

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Table of contents

Samenvatting

De No Observed Effect Concentration (NOEC) speelt een belangrijke rol in het Nederlandse systeem van ecotoxicologische risicobeoordeling. In dit rapport wordt een methode beschreven om te berekenen wat, gegeven een bepaalde concentratie van een toxische stof in het milieu, de fractie van soorten is die blootgesteld is boven de NOEC van de soort. Deze fractie wordt gedefinieerd als de Potentieel Aangetaste Fractie (PAF). Uitgangspunt voor de PAF berekeningen zijn kaartbeelden van gehalten van toxische stoffen in de bodem en verschillende typen oppervlaktewater. Voor water is rechtstreeks met de metingen gewerkt, voor zware metalen in de bodem is gewerkt met ruimtelijk geïnterpoleerde metingen; voor een selectie van pesticiden in niet-landbouwgebieden zijn eigen schattingen gemaakt. Deze gehalten worden vervolgens gecombineerd met laboratoriumgegevens van NOEC's en een berekening van de biologische beschikbaarheid in respectievelijk laboratorium en veld. Voor zware metalen moet ook rekening worden gehouden met een natuurlijk achtergrondsgehalte. De (aanzienlijke) onzekerheden in de methode worden gekwantificeerd. Hieruit blijkt dat de resultaten betrekkelijk robuust zijn t.o.v. deze onzekerheden. Een uitzondering vormen de pesticiden in niet-landbouwgronden: hier is de onzekerheid groter dan de ruimtelijke spreiding in resultaten, zodat een kartering weinig zinvol lijkt. Het belangrijkste voordeel van de PAF-methodiek is de vergelijkbaarheid van deze maat voor toxische druk tussen verschillende stoffen: PAF's kunnen worden vergeleken en zelfs gecombineerd om tot een totaalbeeld te komen. Tegelijkertijd is de methode eenvoudig genoeg om een praktische rol te kunnen spelen in karteringen, risicobeoordelingssystemen en modelstudies.

Summary

The No Observed Effect Concentration (NOEC) plays an important role in the Dutch system of ecotoxicological risk assessment. In this report a method is described to calculate the fraction of species exposed above its NOEC for a given environmental concentration of a toxicant. This fraction is defined as the Potentially Affected Fraction (PAF). Starting point for the PAF calculations are maps of concentrations of toxic compounds in soil and several types of surface water. For water PAF's were based directly on measurements, for heavy metals in soils interpolated measurements were used, for a selection of pesticides own estimates were made. These concentrations were subsequently combined with laboratory data on NOECs and a calculation of biological availability in laboratory and field, respectively. For heavy metals a natural background level has to be taken into account. The (considerable) uncertainties were quantified. It appears that the results are fairly robust for these uncertainties. An exception are pesticides in non-agricultural areas: here uncertainty is larger than spatial variability, so that mapping is not meaningful. The main advantage of the PAF-methodology is the possibility to compare this measure of toxic stress between species and compounds: PAF's can be compared and even combined to obtain a comprehensive view. At the same time, the method is simple enough to be practically useable for purposes of mapping, risk assessment schemes and model studies.

1. Introduction

The No Observed Effect Concentration (NOEC) plays a central role in the Dutch system of risk assessment for hazardous substances as one of the methods to derive a maximum permissible environmental concentration. Basically, a logistic distribution[2] is fitted through literature NOEC data. The 5th percentile of the distribution (i.e. the concentration at which ≤ 5% of all tested species shows an effect of a particular substance) is used as a threshold to ascertain the healthy functioning of the ecosystem (Kooijman, 1987; Van Straalen and Denneman, 1989; Aldenberg and Slob, 1993). In this report we will use essentially the same approach to arrive at an assessment of the inverse. For a given environmental concentration, what is the fraction of species exposed above its NOEC? We will define this fraction as the Potentially Affected Fraction (PAF).

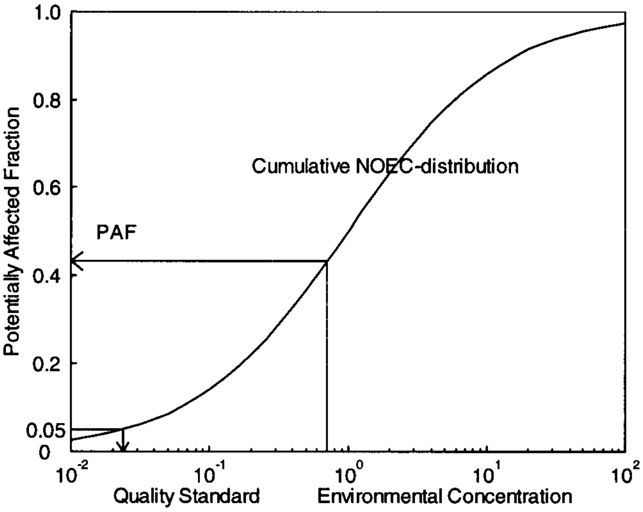

Figure 1. The smooth curve gives the cumulative distribution fitted through NOEC data. The curve is used to derive an environmental quality standard by finding the concentration at which the cumulative fraction of NOEC's reaches 5%; it is here used to obtain a Potentially Affected Fraction at a certain environmental concentration (fictitious data).

Although conceptually simple, the method to derive a PAF needs to take into account several points:

- *What are environmental concentrations*? The NOECs have been obtained for chronic exposure to chemicals; therefore we should consider only long-term average concentrations. Maps of metals in soils (cadmium, copper, lead and zinc) have been derived from interpolated measurements by Tiktak et al. (1997). Because of the long residence time of metals in the soil, these are directly usable for our purpose. Concentrations of metals and pesticides in major surface waters (i.e., those under state control: major rivers, lakes, canals) were obtained from RIZA (data

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[2] According to Aldenberg and Slob (1993) "The logistic distribution is very much like the well-known normal distribution The logistic has more extended tails, and therefore can be regarded as a more conservative assumption in comparison to the normal distribution". In practice, differences become notable only for fractions < 0.001 and > 0.999, which implies that (1) thousands of observations would be required to make a statistically significant distinction between the two (which data are unlikely to be ever collected) and (2) the difference does not play a role in practical policy as a PAF < 0.001 is negligible anyway.

from Watersysteemverkenningen, RWS, 1996). Concentrations in regional surface water (i.e., those under control of regional authorities) were obtained from RIZA and CIW (Geenen and Van der Geest, 1995). These are much more variable, and a long-term average or median is needed for comparison with chronic NOEC data. The calculation of a mean value is complicated by the large fraction of measurements below the detection limit; a method to derive a median value under these conditions was applied (Appendix V). For pesticides in soils virtually no data are available; in this case concentrations were estimated by models (Appendix III).

- *How much is biologically available?* The total amount of a substance may not be toxicologically meaningful: it may partly be non-available. This would not be important as long as availability would be a constant fraction, but particular care should be taken to define this fraction in case of systematic differences between laboratory and field.
- *How to take into account background levels?* Many organic chemicals are man-made, but for metals there has always been a certain amount present in the environment. Whether this amount is toxic is hardly relevant[3]: naturally occurring concentrations are evidently not subject of environmental policy, and should not be considered here. We will therefore define an *anthropogenic PAF* which relates to the *added* effect of anthropogenic substances.
- *How to deal with uncertainties?* There is a substantial uncertainty in all calculations: it is not clear how this would affect the results. The effect of individual uncertain factors depends on the overall uncertainty of the results, in which some factors may be more important than others. It also depends on the results themselves: if the uncertainty range is ± a factor 10, this would not be important if the median is PAF 0.001: the upper limit (0.01) would still be negligible. However, if median PAF were 0.1, the results would range from negligible to extremely high (0.01-1) so that no firm conclusions could be drawn. We will try to quantify uncertainties, and indicate which factors are most important in this respect.

This report addresses these questions, illustrating the issues for heavy metals and pesticides in water and soils of the Netherlands. The report is one in a series of reports, i.e., Luttik et al.(1997) who have calculated PAFs for a number of birds and mammals in the Netherlands, Roghair et al. (1997), who have used the PAF concept to a type of "whole effluent toxicity" measurements, and Bakker and Van de Meent (1997) who has calculated PAFs for a wide range of chemicals (but did not make a spatial distinction in concentrations).

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[3] Some ecosystems are stressed by naturally occurring metal concentrations. From a viewpoint of protecting biodiversity this should not be negatively interpreted: just as many ecosystems are nutrient-limited ("stressed"), metal stress may actually lead to specialized communities which may contribute to overall diversity.

2. Methods

Anthropogenic PAF for metals

Heavy metals in the environment may be partly or largely of natural origin. The importance of this distinction between natural and added amounts for environmental policy is discussed by Peijnenburg et al. (1996). Based on this, we can calculate both a PAF_{total} (for observed total) and PAF_{backgr} (for natural background level). We define an anthropogenic PAF by scaling the added effect to the not-affected fraction, i.e., we consider only those species *not* already affected by natural levels[4]:

$$PAF_{anthr.} = (PAF_{total} - PAF_{backgr.}) / (1 - PAF_{backgr}) \qquad (1)$$

This anthropogenic PAF depends both on added amount of toxicant *and* on natural background level. At high natural levels, the same added amount has much less effect than at low natural levels (figure 2).

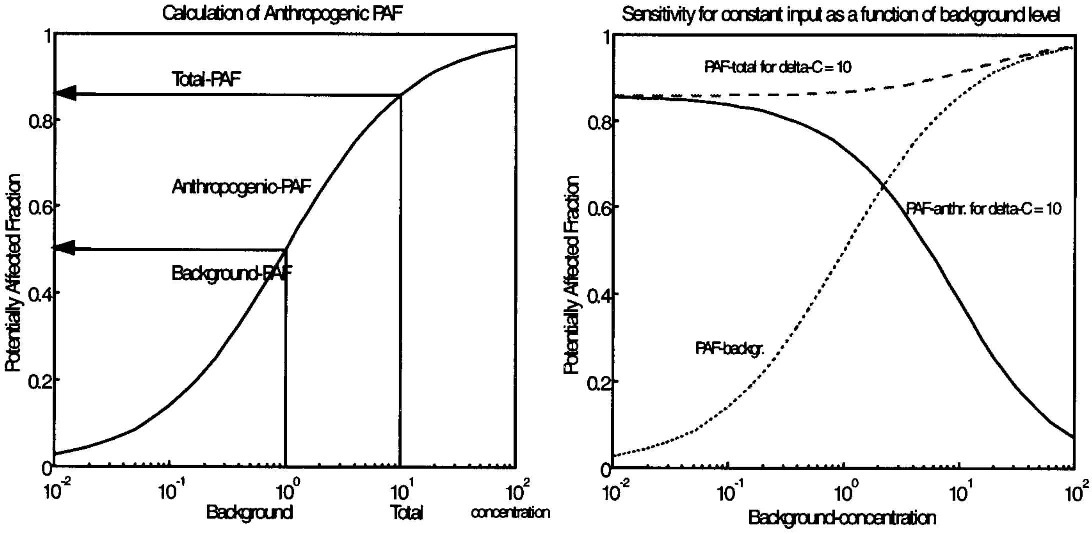

Figure 2 If we distinguish a total (natural + anthropogenic) and a background (natural) concentration of a toxicant we can split the PAF as well (left-hand panel). Because we are scaling the added PAF to the not-affected fraction at background levels (eq. 1), sensitivity for a fixed amount of toxicant added (in the example: 10 units) *decreases* (right-hand panel).

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[4] This approach is consistent with the argument that organisms which have a NOEC below the natural level for a specific location should be excluded from the analysis (Van Tilborg, 1996).

An estimate of natural background levels of metals in soil is given in Appendix IV. Due to a lack of data, an estimate of natural metal concentrations in water could not be made, and the following discussion will be restricted to soils. Briefly, we may distinguish an *immobile* or non-exchangeable amount of metal, which can be though of to be part of the soil matrix, plus a (mobile) part resulting from an equilibrium between natural (atmospheric) input and leaching to deeper soil layers.

Three independent methods were used to arrive at an estimate of the immobile or non-exchangeable amount ($M_{non\text{-}ex}$):

- geological properties of the parent material
- fractionation of Dutch soil samples into exchangeable and non-exchangeable
- statistical analysis of Dutch soil samples.

The three methods give fairly consistent results, which can be expressed as:

$$M_{non\text{-}ex} = a\ [\%\ \text{clay}] + b\ [\%\ \text{organic matter}] + c\ [\%\ \text{sand} + \text{silt}] \qquad (2)$$

The amount of metal in the soil from natural background input has been derived from estimates of natural input fluxes and leaching rates; these suggest that this flux would add a modest amount to the non-exchangeable amount (Appendix IV); however, since both input and leaching (which involves pore-water partitioning, see below) are uncertain, this amount is rather uncertain. We may put an upper bound to it using recent soil data, which are certainly not *lower* than natural levels. Lexmond and Edelman (1993) have surveyed relatively unpolluted sites in the Netherlands. These sites may have received an unknown amount of anthropogenic atmospheric input, but were removed from major atmospheric point sources or direct inputs. Regression equations to relate these *reference values* for metals to organic matter and clay content were derived by Lexmond and Edelman (1993) and are given in Appendix IV[5]. How conservative this upper bound is remains uncertain: the metal concentrations in the Dutch reference sites could differ little from natural background levels, but they probably include an appreciable anthropogenic contribution (Lexmond and Edelman, 1993).

A lower bound for natural background levels is provided by zero atmospheric input and/or high leaching, leading to a level identical to $M_{non\text{-}ex}$. With the upper bound provided by the reference values, our model for natural background levels in soils is now:

$$M_{background} = (1 - f)\ M_{non\text{-}ex} + f\ M_{reference} \qquad (3)$$

with f a value between 0 and 1

Biological availability

The total amount of toxicant in a compartment (water, soil) may not be very informative to predict biological effects. Major questions are how the organism is exposed and how environmental conditions may affect this exposure. Two major routes can be distinguished[6]:

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[5] These values should be distinguished from Dutch target values, which represent the 90% percentile of the observations by Lexmond and Edelman: here we use their mean results.

[6] Mixed exposure to both routes may occur for some species

1. direct exposure (via skin, gills)
2. indirect exposure via food uptake

It is thought that most organisms which live *in* a certain compartment (i.e. all aquatic species, soil organisms that live in the soil itself, plants) are primarily exposed via porewater (DiToro et al., 1991; Boesten, 1993; Allen, 1993). Organisms which live *on* the soil are exposed indirectly via their food. In the present NOEC database the first group dominates (for metals approximately 90% of tested species, for pesticides all species; see Appendix I); for higher organisms (Luttik and Traas, 1997) the second route.

Biological availability in water

Total dissolved concentration in water is taken as an estimate of bioavailability. In case measurements are reported as total (dissolved + particle-bound) concentrations, dissolved concentrations are calculated according to

$$C_{dissolved} = C_{total} / (1 + Kp.\ SM) \tag{4}$$

where SM represents the concentration of suspended particulate matter in water (in kg/L), and Kp is the suspended particle-water partition coefficient (L/kg).

Biological availability in soils

Toxicity data for pesticides were obtained from aquatic species. In this case only the field data (in fact, model results) needed to be converted to porewater concentrations, using (Brandes et al., 1996, see Appendix III):

$$C_{total\text{-}soil} = C_{porewater} \cdot Kp \tag{5}$$

with Kp estimated from K_{oc} and organic matter content of the soil (Appendix III).

In the case of metals, both field and toxicity data are reported as totals as $mg.kg^{-1}$ soil. For pore-water referencing of lab- and field data the following steps were taken:

- subtract a non-exchangeable amount (eq. 2) from the total
- because of the uncertainty in reported totals and estimated non-exchangeable amount, the difference may be negative. In this case we assume a minimum exchangeable amount:

$$M_{exchbl} = \max \{ M_{total} - M_{non\text{-}ex},\ fex_{min} \cdot M_{total} \} \tag{6}$$

- the porewater concentration is now obtained from exchangeable amount by

$$^{10}\log (M_{exchbl}) = a + b\ ^{10}\log (M_{porewater}) + c\ ^{10}\log (OM) + d\ ^{10}\log (clay) + e\ pH \tag{7}$$

with coefficients b..e listed in table II.1 (Appendix II).

- there is some evidence for systematic differences in availability between laboratory and field, presumably from time effects in the field ("aging", see Appendix II). A correction factor to account for this is applied to the field data, which has a value in the range of 0.2 - 1.0.

For food-referencing of metals the total was divided over organic matter ("food") and clay. The relative amounts bound to these two materials was estimated on the basis of models for cation exchange capacity and metal adsorption (Appendix II). We can then express the fraction bound to organic matter as

$$OM / (r\ clay + OM) \qquad (8)$$

with the coefficient r having a value of approximately 0.4 (range 0..2), see Appendix II.

Combination of PAFs

A major advantage of the PAF concept is that it provides a measure of toxic stress that is comparable between different substances. The combination of effects of different substances is discussed by Hamers et al (1995). In some cases where simultaneuous exposure to different substances occur, concentrations should be added to obtain a total effect, in other (most) cases, the individual effects. In their combined response, effects may be *more* than additive (toxic stress by substance A increases susceptibility to B), occasionally less than additive (for example, presence of zinc may reduce cadmium-toxicity -Alloway, 1990). Apart from direct interactions of the effects, additivity depends on the correlation between species sensitivities. It could be that the individual PAFs are *less* than additive, because the *same* species are affected by different substances: if 10% of species is exposed above its NOEC for substance A and 15% for B, the total fraction exposed above NOEC (i.e. the combi-PAF) could be anywhere between 15 (if the first 10% is completely included in the second 15%) and 25% (if the two percentages refer to completely separate groups of organisms). Generally, one would expect some positive correlation in sensitivities (i.e., a lower than additive effect).

For the metals and pesticides considered here, concentration addition can be ruled out (Hamers et al., 1995). Little is known about interaction of effects (combi-PAF higher than expected on the basis of individual PAFs) or correlations between sensitivities (combi-PAF lower than expected). An intermediate estimate can be obtained by assuming no interaction of effects and independence of sensitivities. This leads to the following combination rule (Hamers et al., 1995):

$$PAF_{total} = 1 - (1 - PAF_1)(1 - PAF_2)(1 - PAF_3) \ldots (1 - PAF_n) \qquad (9)^7$$

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[7] To illustrate this equation for the example above, 10% affected by A and 15% affected by B: we suppose that 15% of the 90% not-affected by A is affected by B, so we have 0.9*15 = 13.5% affected by B only, in total affected (affected by A or by A *and* B plus by B): 10 + 13.5 = 23.5%. The same results from starting with B (15%) and adding 0.85 10% =8.5%.

Uncertainty analysis for soil PAFs

At a number of points the calculations involve considerable uncertainties. These have been analysed for the soil PAFs. Quantifying uncertainties is important both for the interpretation of the results and as a guideline for further development of the method. It was thought that estimating worst- and best case bounds was both impractical[8] and unrealistic: the combination of a large number of upper bounds (each in themselves not unlikely) leads to a highly unlikely extreme result. For these reasons, a Monte Carlo method was followed: calculations were performed 1000 times, for each run parameters were sampled independently from given frequency distributions. The result is again a frequency distribution, from which median, 5th and 95th percentiles are shown.

For pesticides, not all uncertainties could be quantified in the present calculations. For example, considerable uncertainties in chemical and physical properties exist, which would have effects on results of deposition models (DEPASS/OPS) and on calculated soil concentrations (Simplebox). Including these in all model calculations proved to be impractical. However, these uncertainties were thought to be relatively modest in comparison with uncertainties in emission factors and toxicity which were taken into account (see appendices I and III, table 2). The calculated uncertainties therefore reflect only the latter factors but are thought to form most of the total uncertainty.

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[8] An increase in a particular parameter will not always lead to an overall increase- or decrease of PAF: it may *in*crease PAF for some soils or waters and *de*crease it for others.

Table 1. Description of parameters in calculation of PAF for heavy metals in soils [dimension in brackets] and frequency distribution used.

name	description	distribution
clnonx	non-exchangeable fraction associated with clay [(mg.kg^{-1}).(per cent)$^{-1}$]	three estimates in Appendix IV were assumed to represent 25, 50 and 75 percentiles of uniform distribution
omnonx	non-exchangeable fraction associated with organic matter [(mg.kg^{-1}).(per cent)$^{-1}$]	idem
sndnonx	non-exchangeable fraction associated with sand and silt [(mg.kg^{-1}).(per cent)$^{-1}$]	idem
backgr	factor to interpolate between extreme estimates of background content [-]	uniform over [0,1]
fexcmin	minimum exchangeable fraction [-]	log-normal with 95% of data in range [0.01,0.1]
concfac	1/n in Freundlich equation (factor b in equation 6) [-]	normal with 95% of data in range from table II.1 (Appendix II)
omfac	factor for log(OM) in Freundlich equation (factor c in equation 6) [OM in ^{10}log(%)]	idem
clayfac	factor for log(clay) in Freundlich equation (factor d in equation 6) [clay in ^{10}log(%)]	idem
phfac	factor for pH in Freundlich equation (factor e in equation 6) [pH KCl]	idem
fldavbl	fraction available in the field compared to the lab [-]	uniform over range [0.2,1]
clwgth	relative binding to clay relative to organic matter (factor r in eq. 7) [-]	log-normal with mean 0.4 and 95% at 2.0
fpore	fraction of organisms exposed via porewater [-]	beta-distribution around median estimate based on occurrence in NOEC data with range [0.75,1]
avgperr	the average of the porewater-exposed NOEC's was randomly disturbed by this coefficient [-]	normal distribution with mean zero, standard deviation = (std.dev. of observations)/√(no. of observations)
stdperr	the standard deviation of the porewater-exposed NOEC's was randomly disturbed by this coefficient [-]	standard deviation is $\sqrt{X^2}$ distributed around median estimate from data
avgferr	the average of the food-exposed NOEC's was randomly disturbed by this coefficient [-]	as avgperr
stdferr	the standard deviation of the food-exposed NOEC's was randomly disturbed by this coefficient [-]	as stdperr

Table 2. Description of parameters in calculation of PAF for pesticides in soils and frequency distribution used.

emisfac	factor to interpolate between two emission estimates in table III.6 (Appendix III)	uniform between the two estimates
stdnoec	standard-deviation of NOEC distribution	a power-normal distribution, see figure I.2 (Appendix I)
asfac	assessment-factor to extrapolate acute LC_{50} to chronic NOEC	a power-normal distribution, see figure I.1(Appendix I)

3. Results

Heavy metals in soils

The results are presented as cumulative distributions, with 5th, 50th (median) and 95th percentiles of the results[9]. The results indicate that most areas of the Netherlands are exposed to PAF values larger than 0.05 (which is used as an indicator for ecotoxicologically safe levels) and for copper and zinc sizable areas exceed a PAF level of 0.5, which is thought to indicate a level at which there is reason for concern. Uncertainty does affect these outcomes to some extent: the calculated PAFs are uncertain by approximately a factor 10. As a result, the conclusions may need some modification: the area with PAF > 0.05 could be smaller or larger, but as spatial differences are considerably larger than the uncertainty range, the areas involved would still be in the same order of magnitude (i.e., substantial). Uncertainty has a more pronounced effect on the area with PAF > 0.5 for copper and zinc: this are is highly uncertain and could range from zero to 20-40%.

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[9] Note that the percentiles resulting from the Monte Carlo sampling are valid *only* for one particular percentile of the spatial distribution. The graphs allow us to read the 5, 50 and 95 percentiles of calculated PAFs for the 20th, 30th etc. percentile of all soils. Although the three lines (5, 50 and 95%) are continuous, there need not be three parameter-combinations that actually represent the three lines as a single continuous distribution!

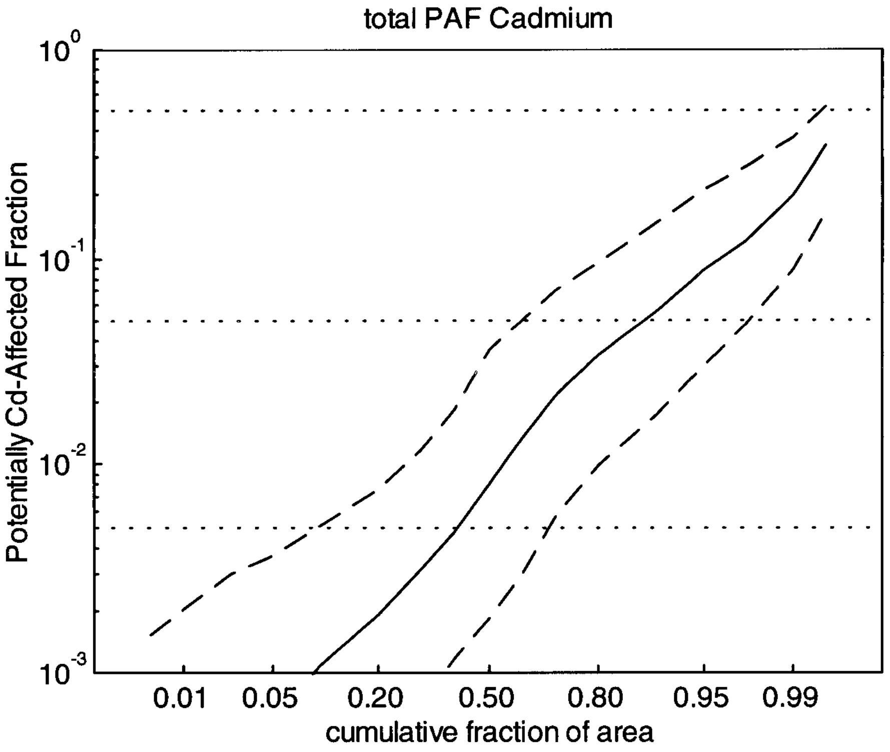

Figure 3 Cumulative spatial distribution of total PAF by cadmium with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes).

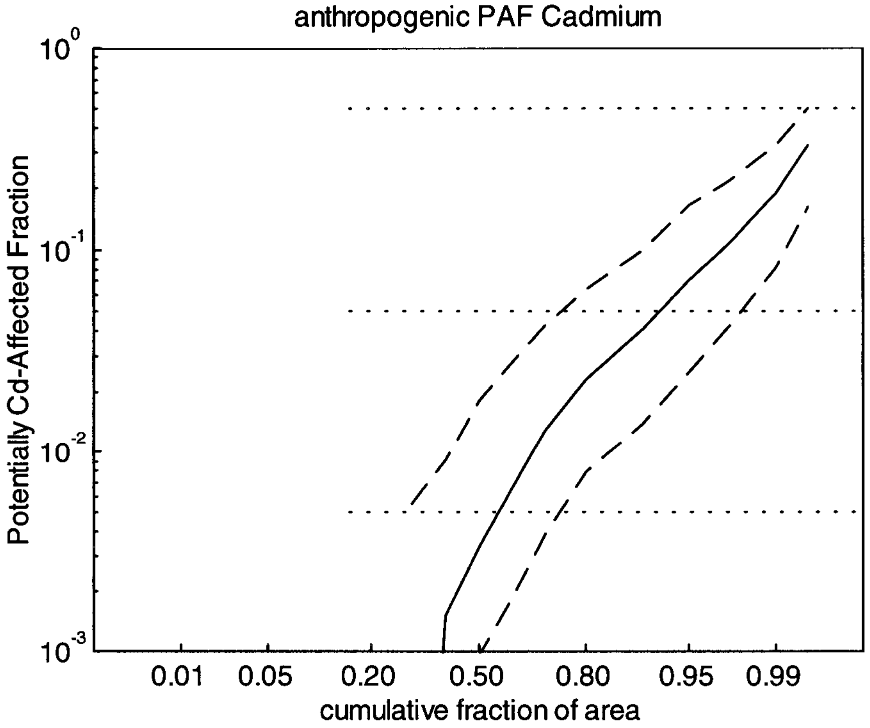

Figure 4 Cumulative spatial distribution of anthropogenic PAF by cadmium with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). The first (missing) part of the graph represents Cd-concentrations at or below estimated background levels.

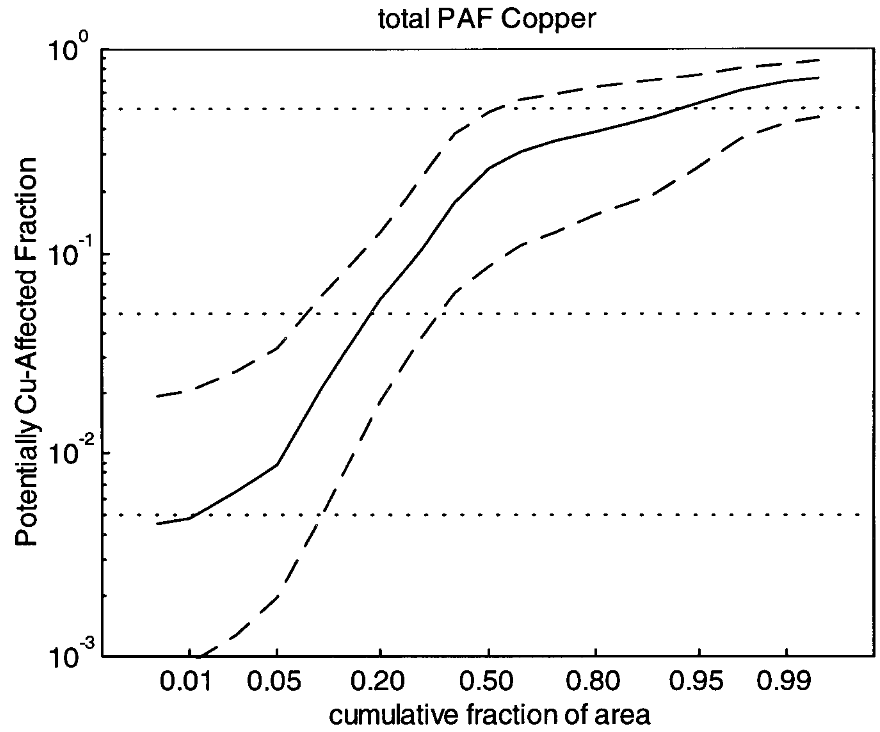

Figure 5 Cumulative spatial distribution of total PAF by copper with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes).

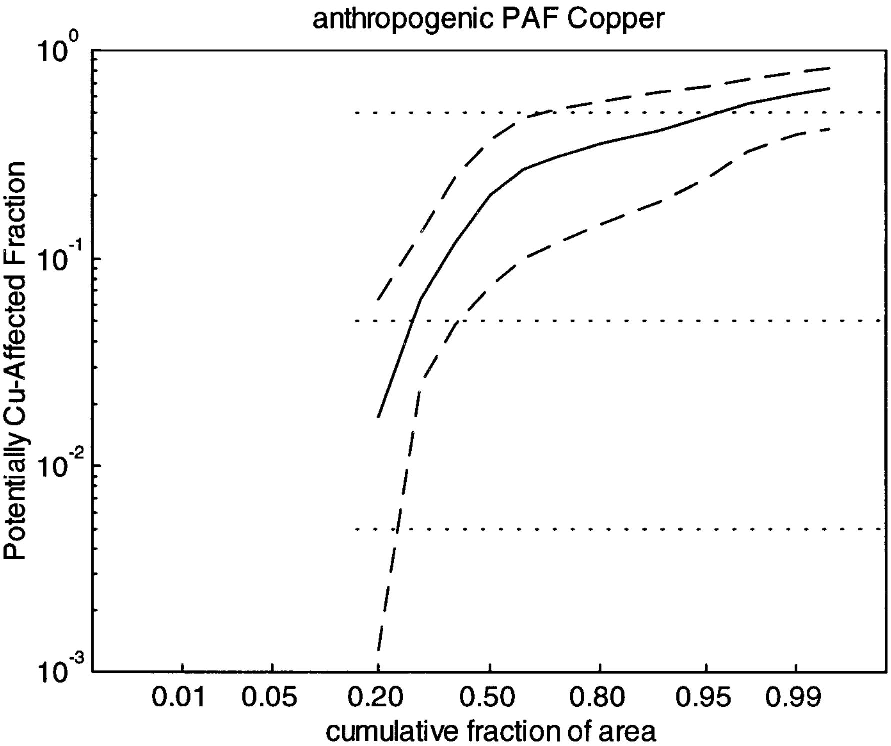

Figure 6 Cumulative spatial distribution of anthropogenic PAF by copper with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). The first (missing) part of the graph represents concentrations at or below estimated background levels.

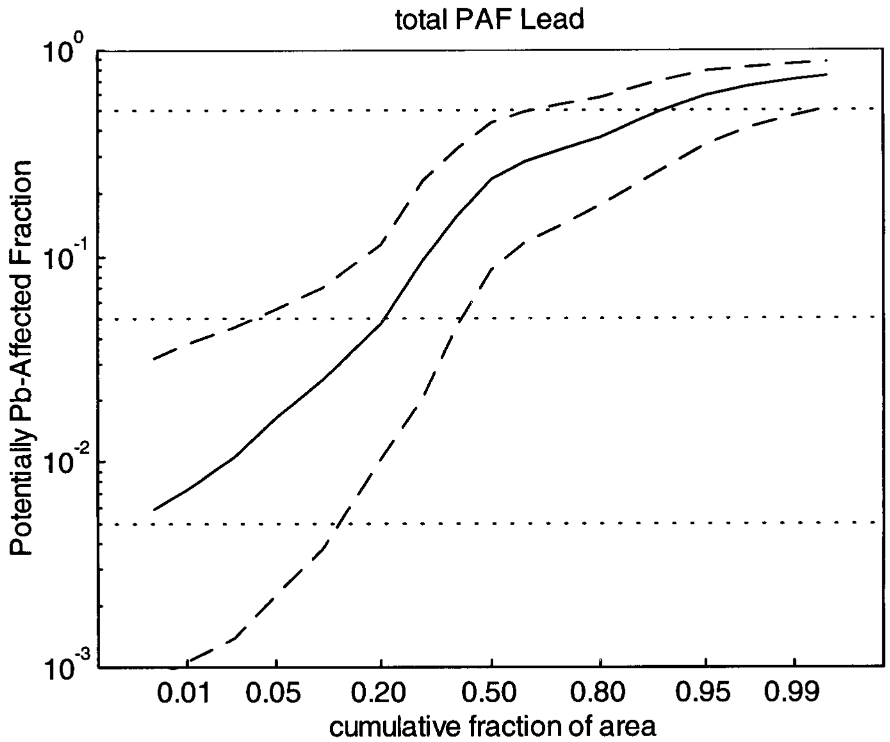

Figure 7 Cumulative spatial distribution of total PAF by lead with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes).

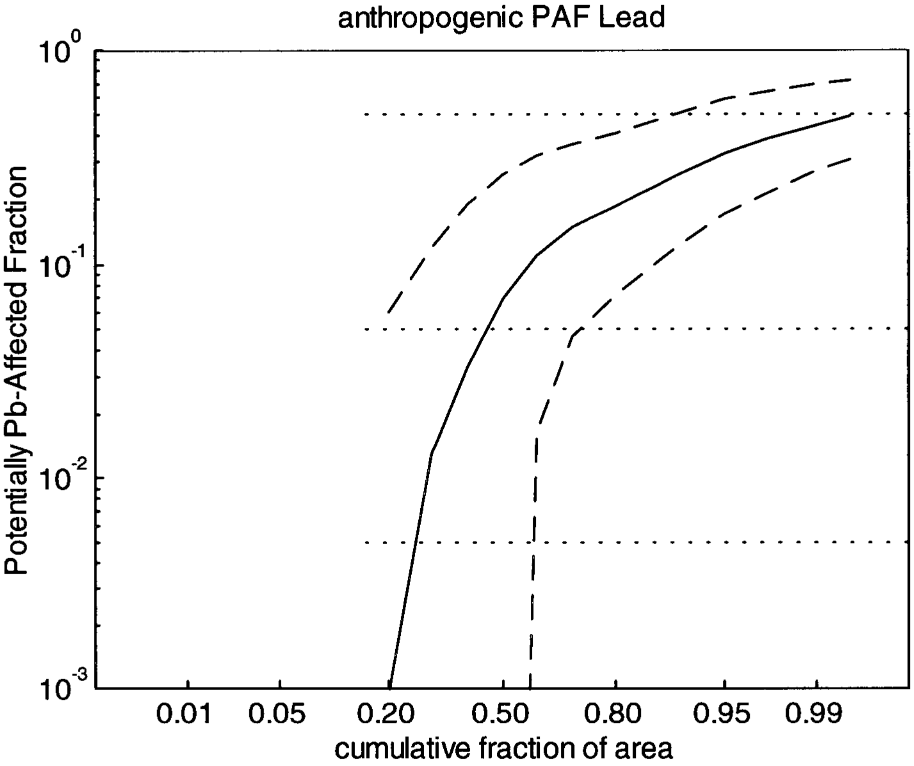

Figure 8 Cumulative spatial distribution of anthropogenic PAF by lead with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). The first (missing) part of the graph represents concentrations at or below estimated background levels.

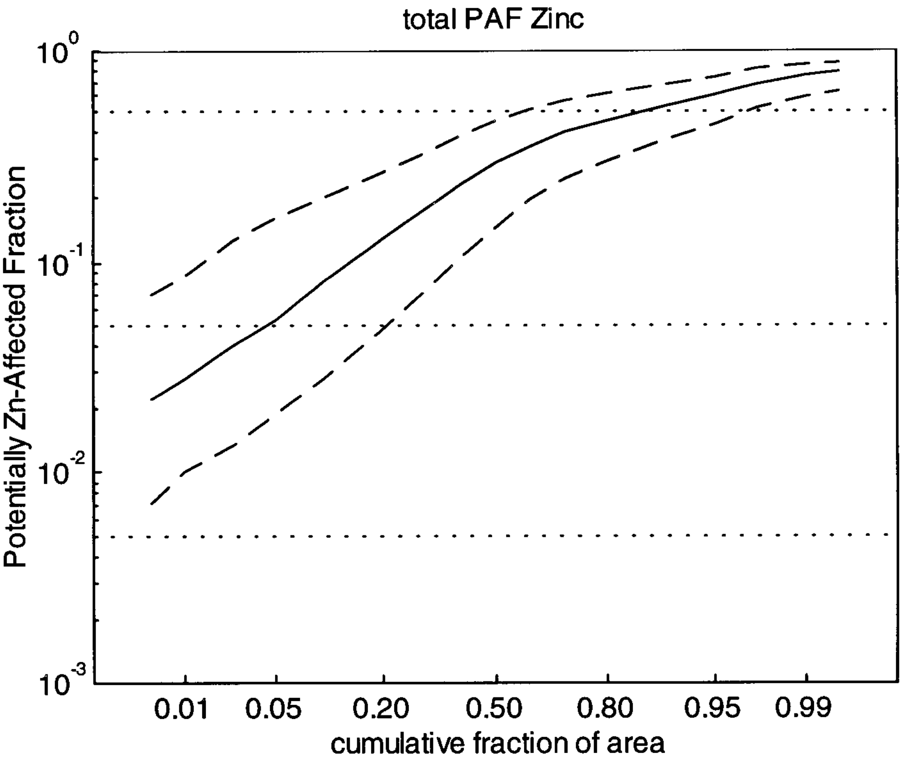

Figure 9 Cumulative spatial distribution of total PAF by zinc with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes).

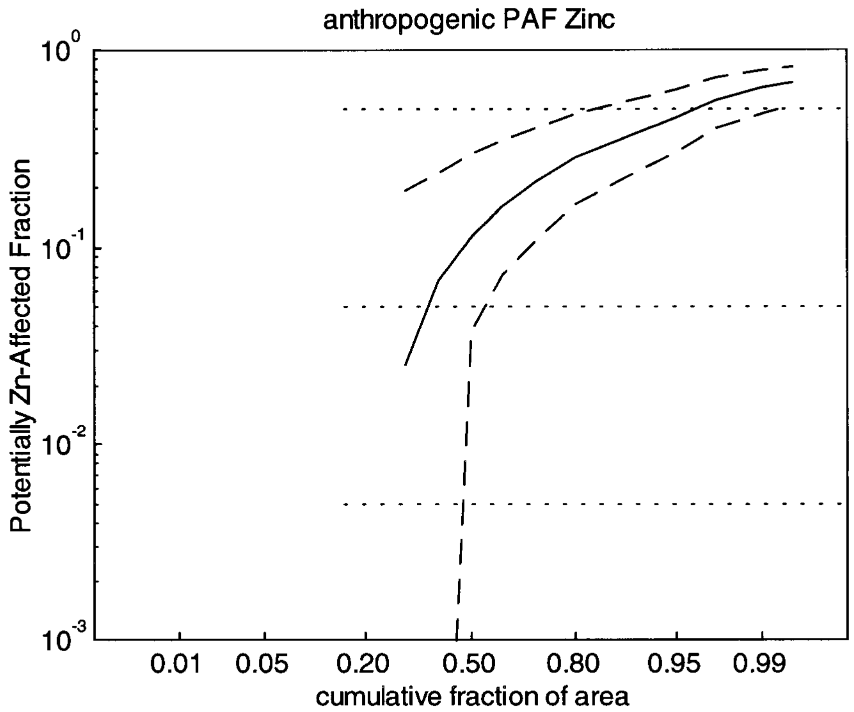

Figure 10 Cumulative spatial distribution of anthropogenic PAF by zinc with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). The first (missing) part of the graph represents concentrations at or below estimated background levels.

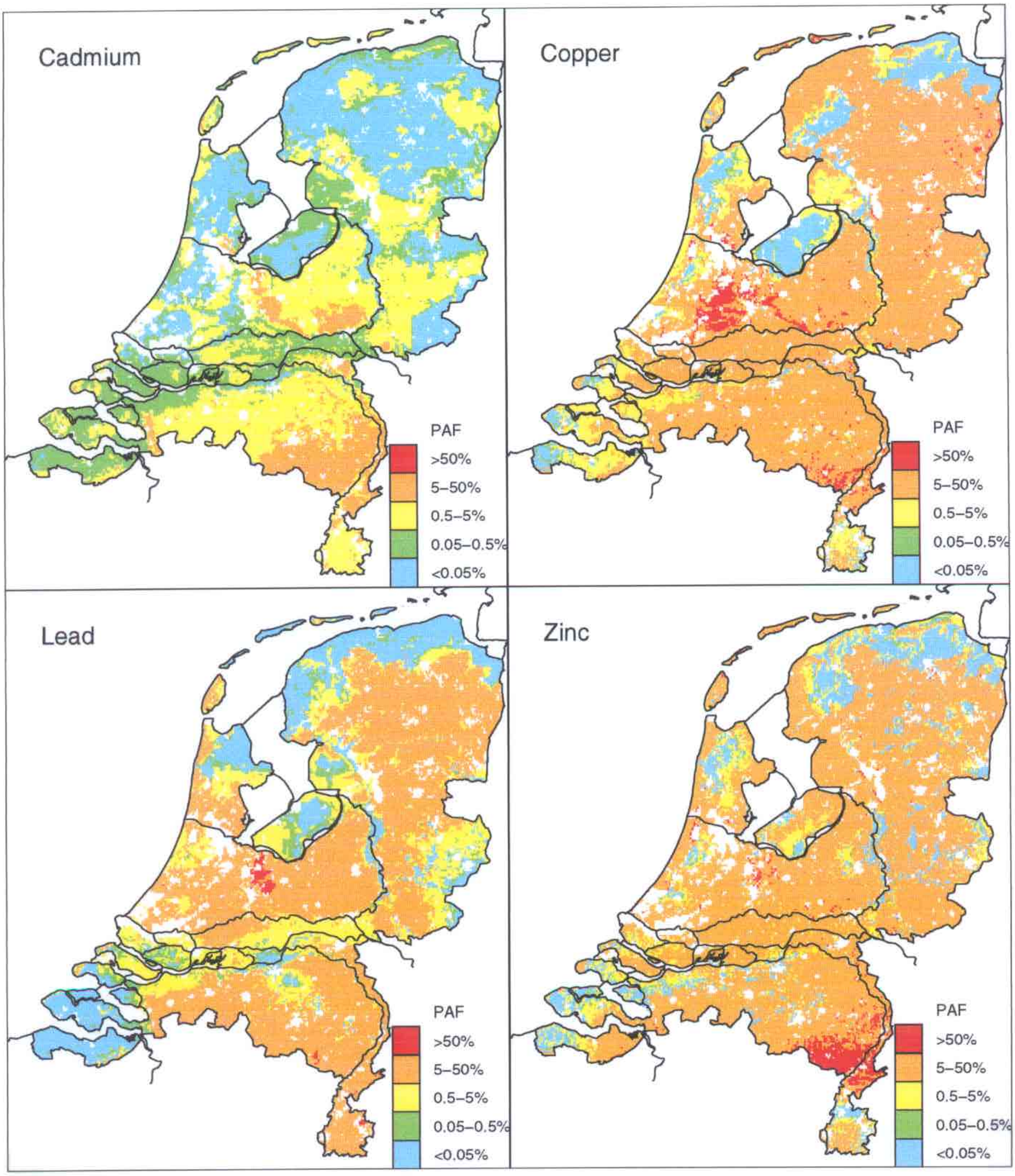

Figure 11 Maps representing anthropogenic PAFs by heavy metals for median parameter values[10]

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[10] As pointed out, there need to be no single parameter set corresponding to the overall median in figures 3-10. For map representation, the parameter set from the Monte Carlo sample that gives the spatial distribution closest to the overall median was chosen.

Pesticides in non-agricultural soils

The PAF by individual pesticides is highly uncertain (figs. 12-13) with values ranging several orders of magnitude. The resulting combination-PAF is less uncertain and comparable to those of metals. An approximate[11] analysis of the contribution by various pesticides (table 3) indicates that most of the toxic stress can be attributed to a few substances, notably Lindane.

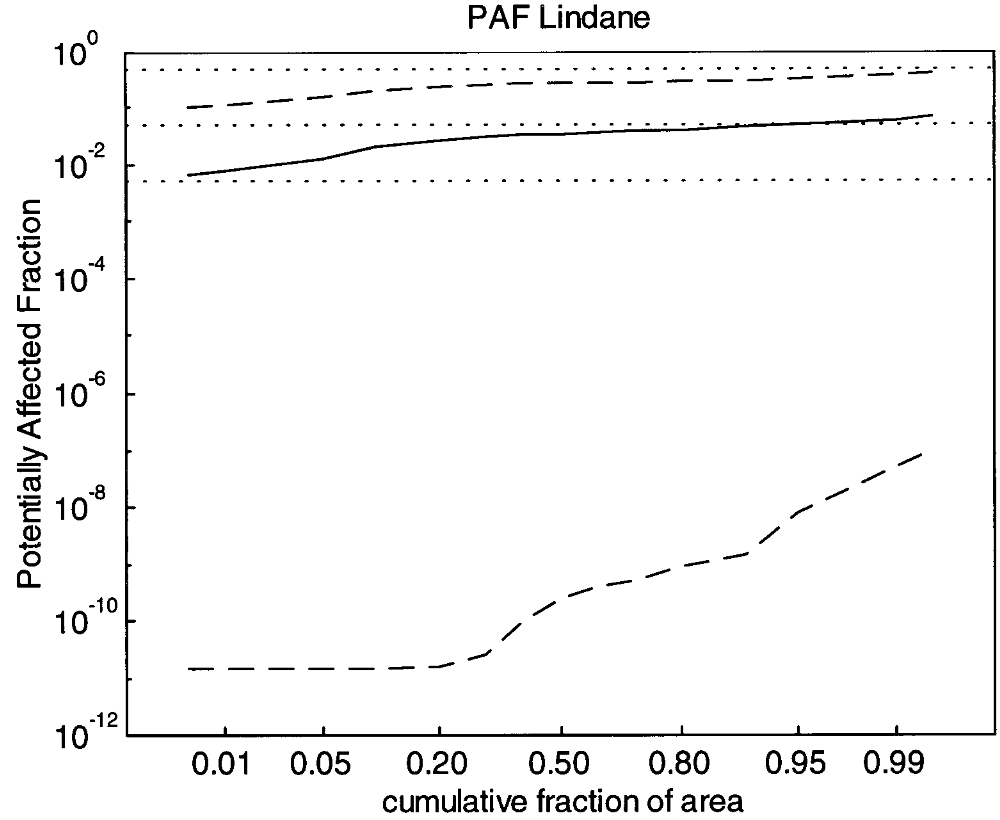

Figure 12 Cumulative spatial distribution of PAF by Lindane with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). Lowest values (1.5 10^{-11}) are arbitrarily set to prevent underflow and in fact represent PAF=0.

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[11] This analysis is based on median calculated values. However, the combination of PAFs as in equation 7 (for PAF << 1 they are in fact added) may lead to quite unexpected results. Suppose we have two substances, both with a PAF uncertainty as {0.001, 0.01, 0.1}. The median combi-PAF is now 0.101 and *not* 0.02, as can be seen from the table:

PAF_1 \ PAF_2	0.001	0.01	0.1
0.001	0.002	0.011	0.101
0.01	0.011	0.02	0.11
0.1	0.101	0.11	0.2

If we consider the three values to represent 25, 50 and 75% of possible PAF values, we can derive the same percentiles for the combi-PAF as {0.011, 0.101, 0.11}. Comparing this to the single PAF's, we see that addition of the second substance has resulted in a 10-fold increase in 25% and median PAF, but hardly in 75% PAF. These are fictitious data only, but they illustrate the point that individual PAF distributions and a combi-PAF distribution may not be easily derived from each other.

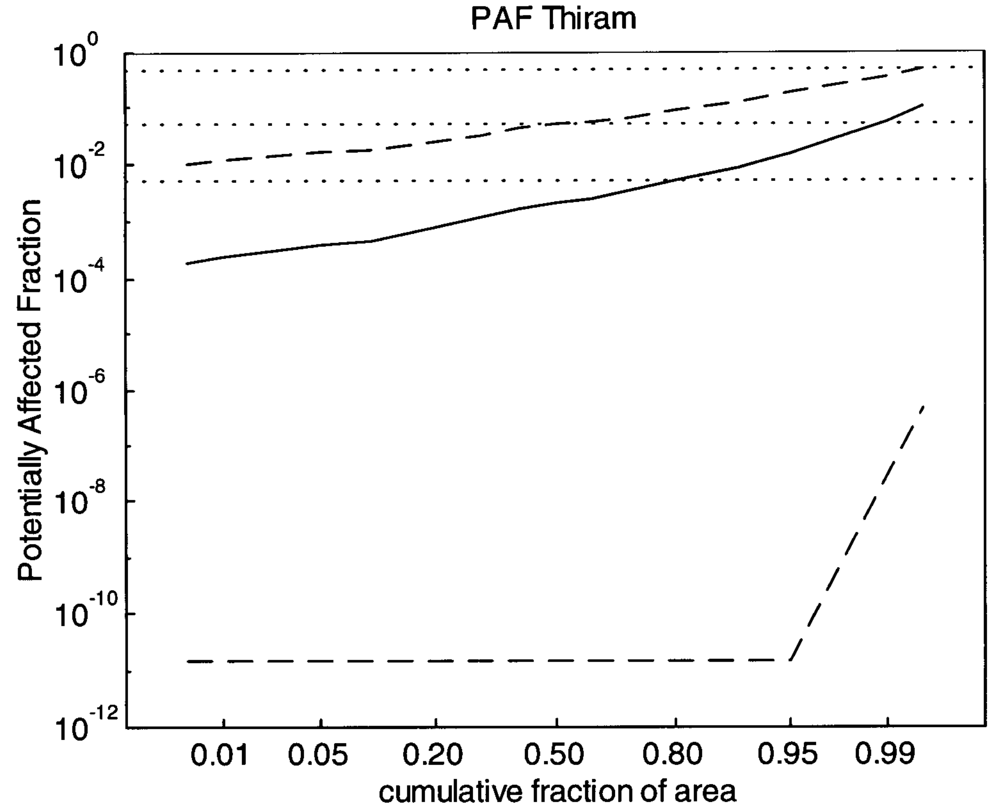


Figure 13 Cumulative spatial distribution of PAF by Mevinfos with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes). Lowest values (1.5 10^{-11}) are arbitrarily set to prevent underflow and in fact represent PAF=0.

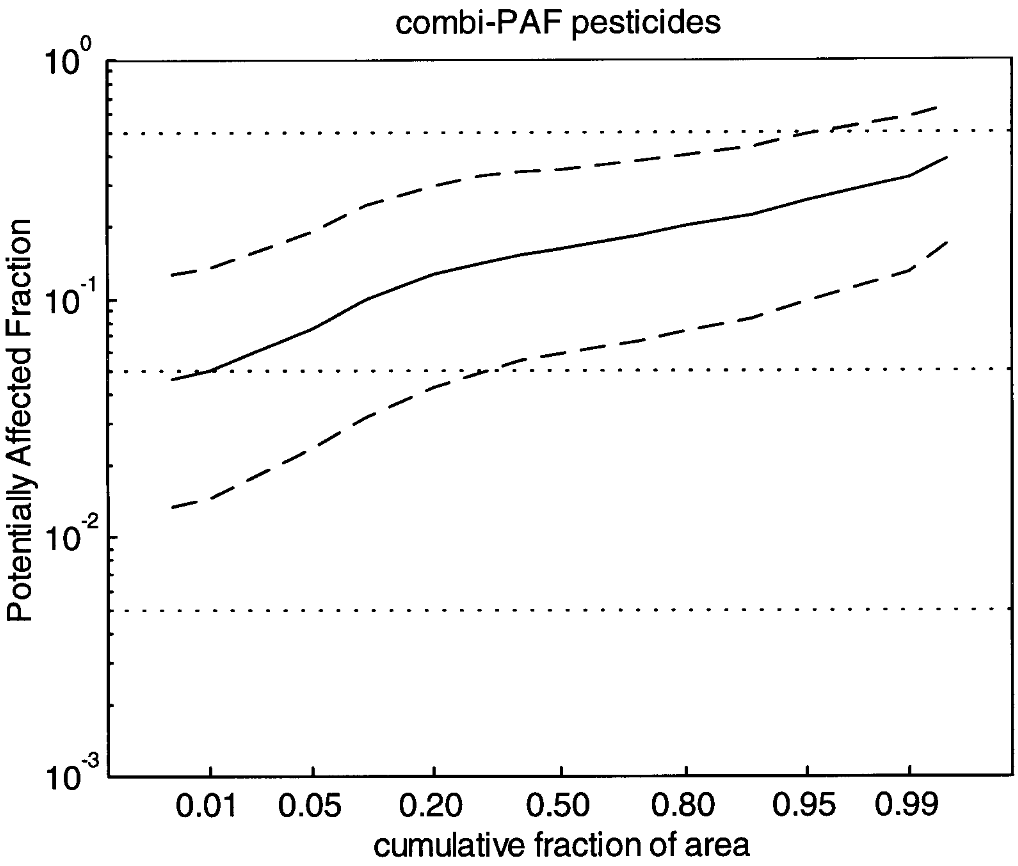


Figure 14 Cumulative spatial distribution of combination-PAF by pesticides with 5, 50 (median) and 95 percentiles resulting from parameter uncertainty (note nonlinearities of axes).

Table 3 Approximate analysis of the relative contributions (as fractions of total) by various pesticides (for codes: see Appendix III) to total deposition, to soil concentration and to PAF

code	median contribution to total deposition	median contribution to soil concentrations	median contribution to PAF
twvd	0.016	0.002	0.002
atra	0.035	0.015	0.007
azin	0.000	0.000	0.000
bent	0.445	0.127	0.089
card	0.009	0.005	0.071
dchv	0.203	0.002	0.020
diqu	0.004	0.104	0.000
diur	0.018	0.011	0.017
dnoc	0.031	0.005	0.025
ftin	0.024	0.007	0.039
lind	0.038	0.677	0.564
mane	0.034	0.011	0.032
meco	0.096	0.013	0.000
memi	0.008	0.003	0.000
mbtz	0.013	0.011	0.002
metr	0.001	0.000	0.001
mevi	0.004	0.000	0.090
moli	0.011	0.005	0.002
para	0.001	0.000	0.000
sima	0.000	0.000	0.002
thir	0.008	0.002	0.035
trif	0.000	0.000	0.000

A map of pesticide combi-PAF shows the importance of soil sensitivity (rather than inputs) to calculated PAF: because a considerable contribution to deposition (at least of the most toxic and persistent) pesticides is from long distances, a major contribution to spatial variability is caused by differences in organic matter content (and hence porewater concentration): the Wadden Islands (which receive the lowest deposition, but which generally have sandy soils poor in organic matter) have the highest calculated PAFs.

An important observation in table 3 is the change from median depositions (first column) to median concentrations and median PAFs. It appears that a number of substances have a high deposition which lead to small concentrations because of their low persistence in the upper soil; a further modification is again a result of the toxicity of the substance. Clearly, these compound-specific properties are very important in determining toxic pressure.

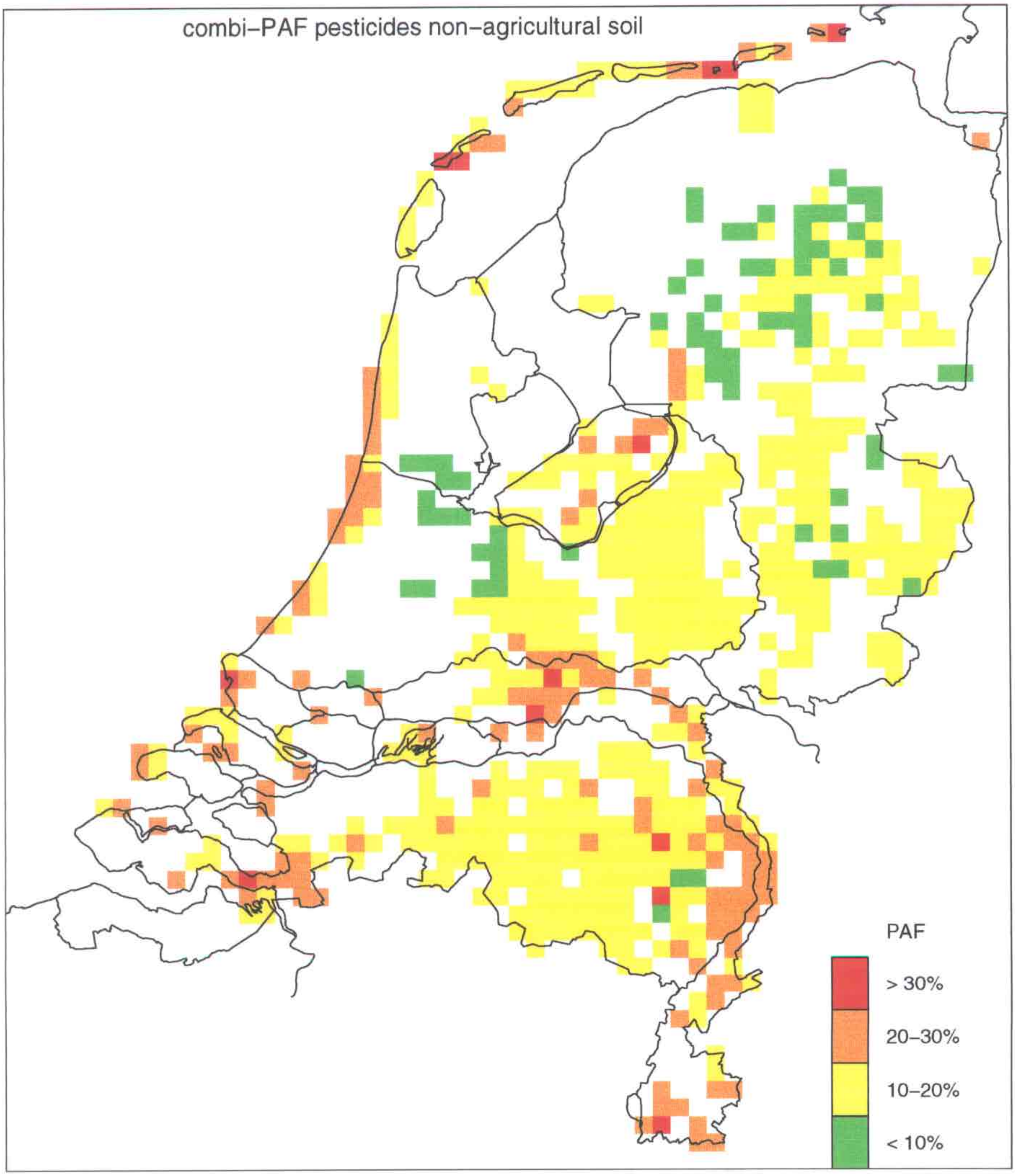
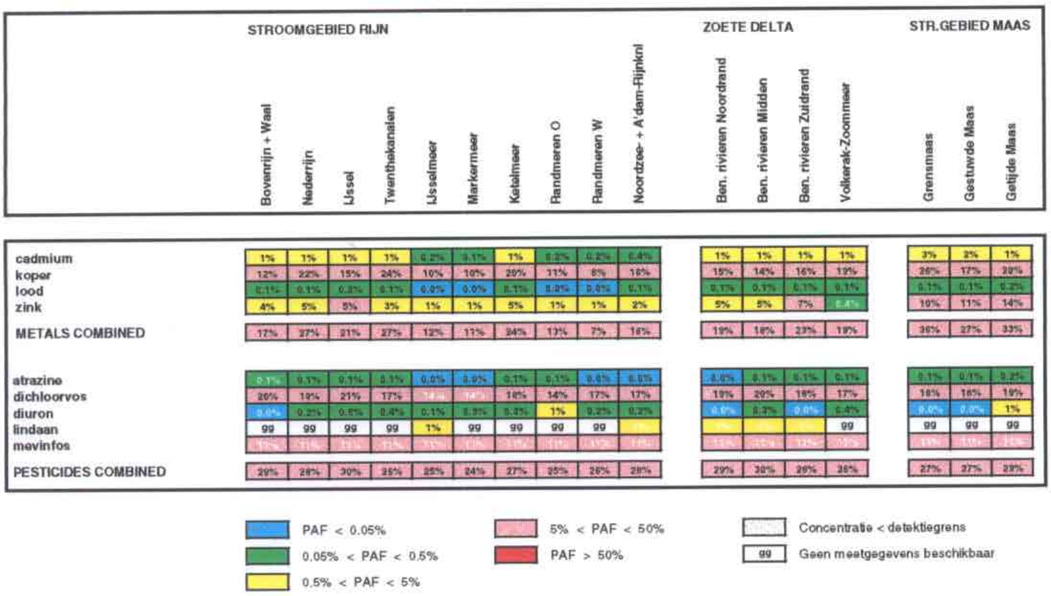


Figure 15 Map with median estimates of combi-PAF pesticides

Heavy metals and pesticides in water

Potentially Affected Fractions in water were calculated from measured concentrations as provided by RIZA and CIW. In all cases, median values of the measured concentrations were used. For a number of pesticides in regional waters, medians had to be estimated, since more than 50% of the measurements were below the detection limit (Appendix V).

For the major surface waters (figure 16), dissolved concentrations were calculated using the means of the reported suspended matter concentrations at teh monitoring sites (RIZA, personal communication), and the water-particle partition coefficients given by Bakker and Van de Meent (1997, Appendix II).

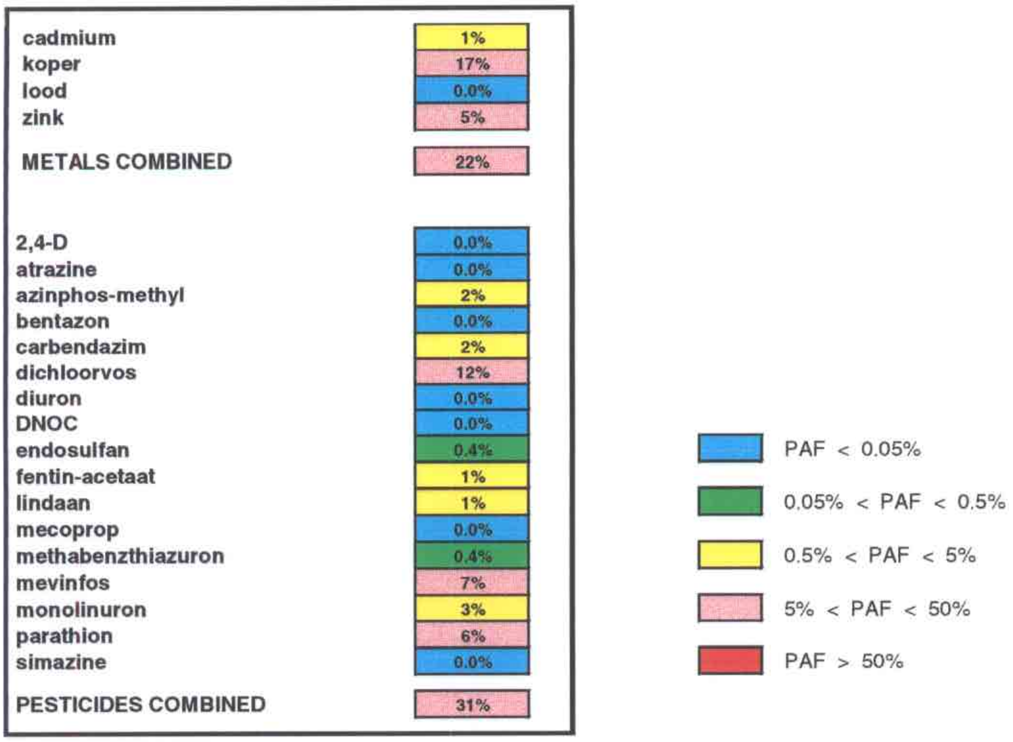


	STROOMGEBIED RIJN										ZOETE DELTA				STR.GEBIED MAAS		
	Bovenrijn + Waal	Nederrijn	IJssel	Twenthekanalen	IJsselmeer	Markermeer	Ketelmeer	Randmeren O	Randmeren W	Noordzee- + A'dam-Rijnknl	Ben. rivieren Noordrand	Ben. rivieren Midden	Ben. rivieren Zuidrand	Volkerak-Zoommeer	Grensmaas	Gestuwde Maas	Getijde Maas
cadmium	1%	1%	1%	1%	0.2%	0.1%	1%	0.2%	0.2%	0.4%	1%	1%	1%	1%	3%	2%	1%
koper	12%	22%	15%	24%	10%	10%	20%	11%	8%	18%	15%	14%	16%	19%	26%	17%	20%
lood	0.1%	0.1%	0.3%	0.1%	0.0%	0.0%	0.1%	0.0%	0.0%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.2%
zink	4%	5%	5%	3%	1%	1%	5%	1%	1%	2%	5%	5%	7%	0.4%	10%	11%	14%
METALS COMBINED	17%	27%	21%	27%	12%	11%	24%	13%	7%	18%	19%	18%	23%	19%	36%	27%	33%
atrazine	0.1%	0.1%	0.1%	0.1%	0.0%	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%	0.1%	0.1%	0.2%
dichloorvos	20%	19%	21%	17%	14%	14%	18%	14%	17%	17%	19%	20%	18%	17%	18%	16%	19%
diuron	0.0%	0.2%	0.5%	0.4%	0.1%	0.3%	0.3%	1%	0.2%	0.2%	0.0%	0.3%	0.0%	0.4%	0.0%	0.0%	1%
lindaan	gg	gg	gg	gg	1%	gg	gg	gg	gg	[illegible]	[illegible]	[illegible]	[illegible]	gg	gg	gg	gg
mevinfos	11%	11%	11%	11%	11%	[illegible]	11%	11%	11%	11%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PESTICIDES COMBINED	29%	28%	30%	25%	25%	24%	27%	25%	26%	28%	29%	30%	28%	26%	27%	27%	29%

🟦 PAF < 0.05%
🟩 0.05% < PAF < 0.5%
🟨 0.5% < PAF < 5%
▨ 5% < PAF < 50%
🟥 PAF > 50%
☐ Concentratie < detektiegrens
gg Geen meetgegevens beschikbaar

Figure 16 (in Dutch) Calculated Predicted Affected Fractions of heavy metals and pesticides in major surface waters in The Netherlands. PAF-calculations based on median values of dissolved concentration at specific monitoring sites in 1994 (RIZA-data). No adjustments were made for natural background concentrations.

For the regional waters (figure 17), no suspended matter concentrations were available. Dissolved metal concentration were calculated with the same water-suspended matter partition coefficients as for the major waters, assuming a mean suspended matter concentration of 15 mg/L. For pesticides the total concentrations were taken, since for most of the pesticides dissolved fractions are thought to be large anyway.



cadmium	1%
koper	17%
lood	0.0%
zink	5%
METALS COMBINED	22%
2,4-D	0.0%
atrazine	0.0%
azinphos-methyl	2%
bentazon	0.0%
carbendazim	2%
dichloorvos	12%
diuron	0.0%
DNOC	0.0%
endosulfan	0.4%
fentin-acetaat	1%
lindaan	1%
mecoprop	0.0%
methabenzthiazuron	0.4%
mevinfos	7%
monolinuron	3%
parathion	6%
simazine	0.0%
PESTICIDES COMBINED	31%

🟦 PAF < 0.05%
🟩 0.05% < PAF < 0.5%
🟨 0.5% < PAF < 5%
▨ 5% < PAF < 50%
🟥 PAF > 50%

Figure 17 Calculated Potentially Affected Fractions of heavy metals and pesticides in regional surface waters in The Netherlands. PAF-calculations based on median values of total concentrations, measured at different locations in 1992/1992 (CIW-data). No adjustments were made for natural background concentrations.

No attempts were made to take the natural background concentrations in water into account. The anthropogenic contribution to total load of metals in the river Rhine (Van der Weijden and Middelburg, 1989) and in recent sediments (Salomons and De Groot, 1978) is thought to be dominant, estimates by these authours range from 83 to 99% for the metals discussed here. Because anthropogenic metal loads are more easily exchangeable than natural amounts, the anthropogenic contribution to the ecotoxicologically most relevant *dissolved* concentration may be even higher. Although this analysis referes to the Rhine river only, it may be tentatively concluded that subtraction of natural background levels would not make a large difference in calculated PAF values for surface waters.

Uncertainties in the PAF-calculations were not quantified. They are probably lower than those of the soil calculations[12].

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[12] The conversion of total levels to (pore)water concentrations involves a considerably lower uncertainty: in the soil, porewater concentrations are inversely proportional to K_d because nearly 100% of the metals is adsrobed to the soil; in water (with the much lower particulate matter concentration) this is about 50%. For this reason , an uncertainty in K_d directly translates into the same relative uncertainty in soil-porewater concentration, but is halved in the case of surface water concentration. In addition, more is known about surface water K_d (it is much easier to measure directly) and laboratory pH is almost identical to field pH, not requiring any (uncertain) extrapolation for this factor.

4. Discussion

Heavy metals in soils

The calculated metal-PAFs are high, despite the fact that we took into account a non-exchangeable amount, subtracted a natural PAF and included a possibly lower availability in the field. How can this be reconciled with the fact that Dutch Target Values are rarely exceeded (in about 5-15% of total area)? Three remarks can be made:

- It should be noted that the present analysis is based on the interpolated data by Tiktak et al (1997). Because a grid of 500 x 500 m was used, smoothing occurs relative to measurements: all other things being equal[13], the fraction of *measurements* above target values is higher than the fraction of *inerpolated area.*
- The Dutch Target Values do *not* represent ambient levels, and certainly not the natural background. They represent the 90% percentile of observations in relatively undisturbed areas (Lexmond and Edelman, 1993). That most observations in rural areas (the present analysis did not include urban areas and 'hot spots' caused by local pollution) fall below the 90%-line is in some sense trivial. The derivation of the target values is completely independent from any ecotoxicological considerations: exceeding them does not imply any ecotoxicological effects, nor can ecotoxicological effects be excluded at concentrations below target values..
- The major systematic differences between laboratory and field more than compensate each other, leading to an overall *increased* availability in the field. In the laboratory the added amount is generally much larger than any non-exchangeable amount, whereas this makes up about 50-70% of natural concentrations. On top of this, there may be a lowered availability in the field of some 50% (Appendix II). Together, these would make field availability 40% of 50% = 20% of laboratory availability. However, the pH in the laboratory is near neutral (Appendix I): about 6.8[14], in contrast median field pH is 4.9 (Fig. 18). The pH-coefficient in equation 7 has a value of around 0.5, causing a mean difference in porewater concentration by this factor alone of 1 unit on log scale, i.e. a factor 10 *higher* availability (Figs. 17-20): the net effect is an approximate factor 2 (10 x 0.2) *higher* availability in the field.

The latter considerations are site- and metal specific, the different factors (anthropogenic contribution, pH factor) are mapped in figures 19-22.

---

[13] Several problems arise in a comparison between the distribution of measurements and interpolated values: the sample of measurements may not be representative of the entire area considered; measurement errors are smoothed as well (this may be considered an advantage of smoothing, but it does reduce areal exceedence percentage), and in a multivariate context, the distinction between inter- and extrapolation is not well defined. A discussion of these and similar problems is outside the scope of this report.

[14] For Cd, Cu, Pb and Zn the average laboratory pH's are 6.51, 6.82, 6.82 and 6.90, respectively. The method of determining pH in the soil toxicity tests is not entirely clear: according to OECD guidelines, measurements as pH_{KCl} are required, as is standard in soil analysis. The relatively high values (at least for Dutch conditions) are deliberately set to provide a favourable environment for soil organisms (springtails, worms). Some of the older references may have reported pH_{H2O}. In this case the difference in pH with Dutch field conditions would be less.

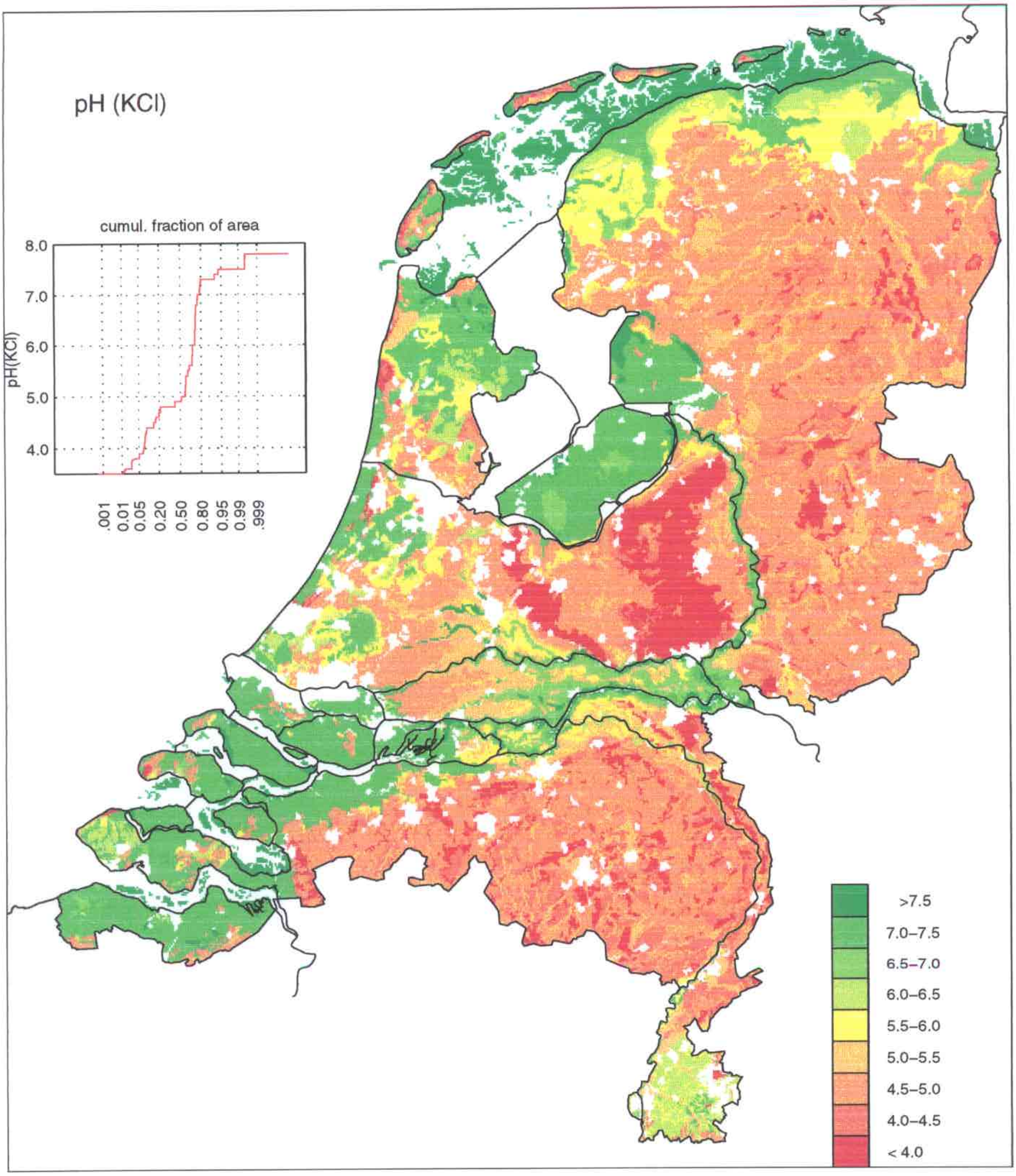

Figure 18 average pH (KCl) of soil units based on 1:250,000 soil map of the Netherlands (source: Staring Center)

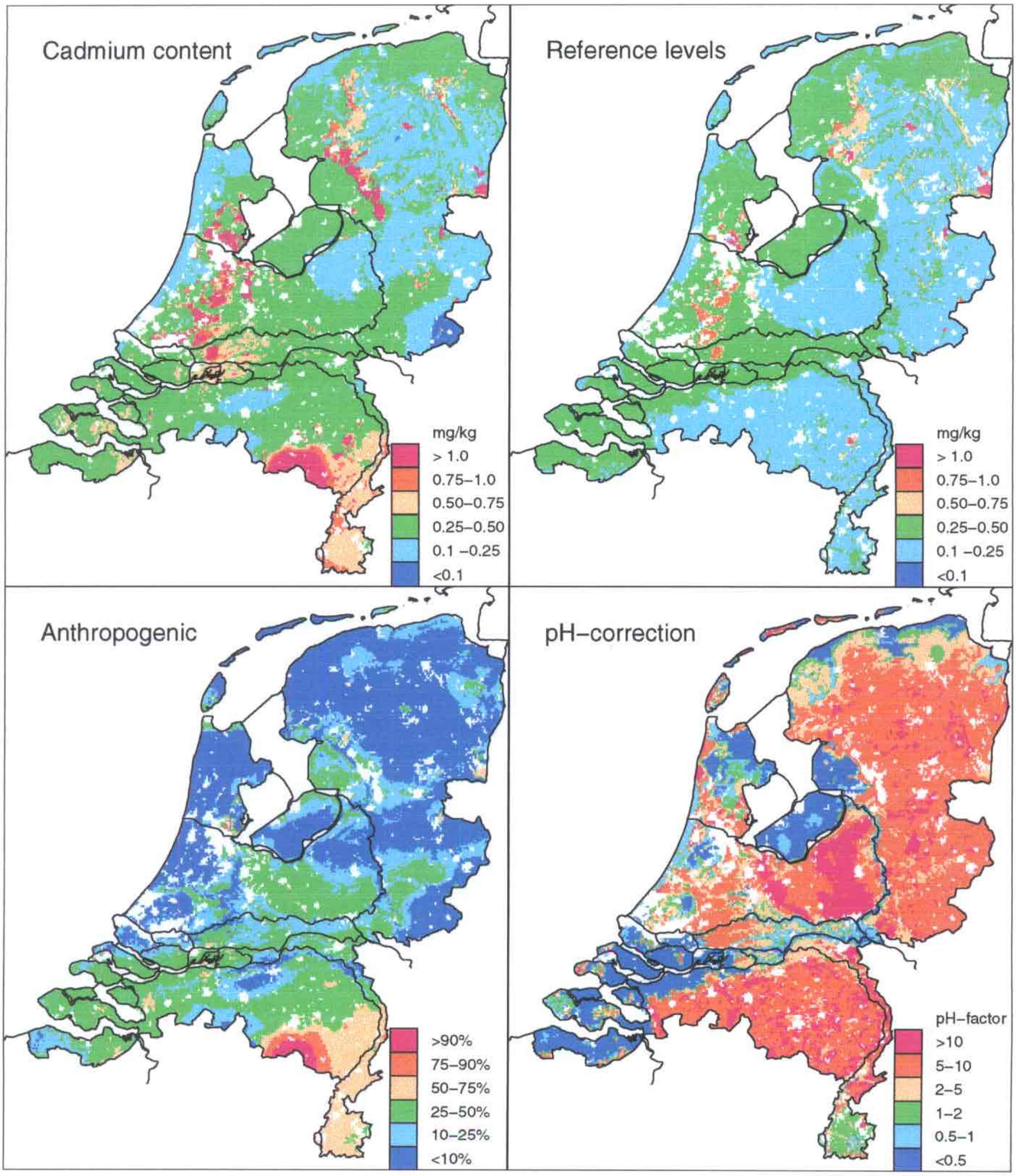

Figure 19 Cadmium concentrations, estimated "unpolluted" levels (reference values), anthropogenic contribution (by comparison of eq. 3 with actual concentrations) and pH-factor (giving the increase in availability due to the lower field-pH)

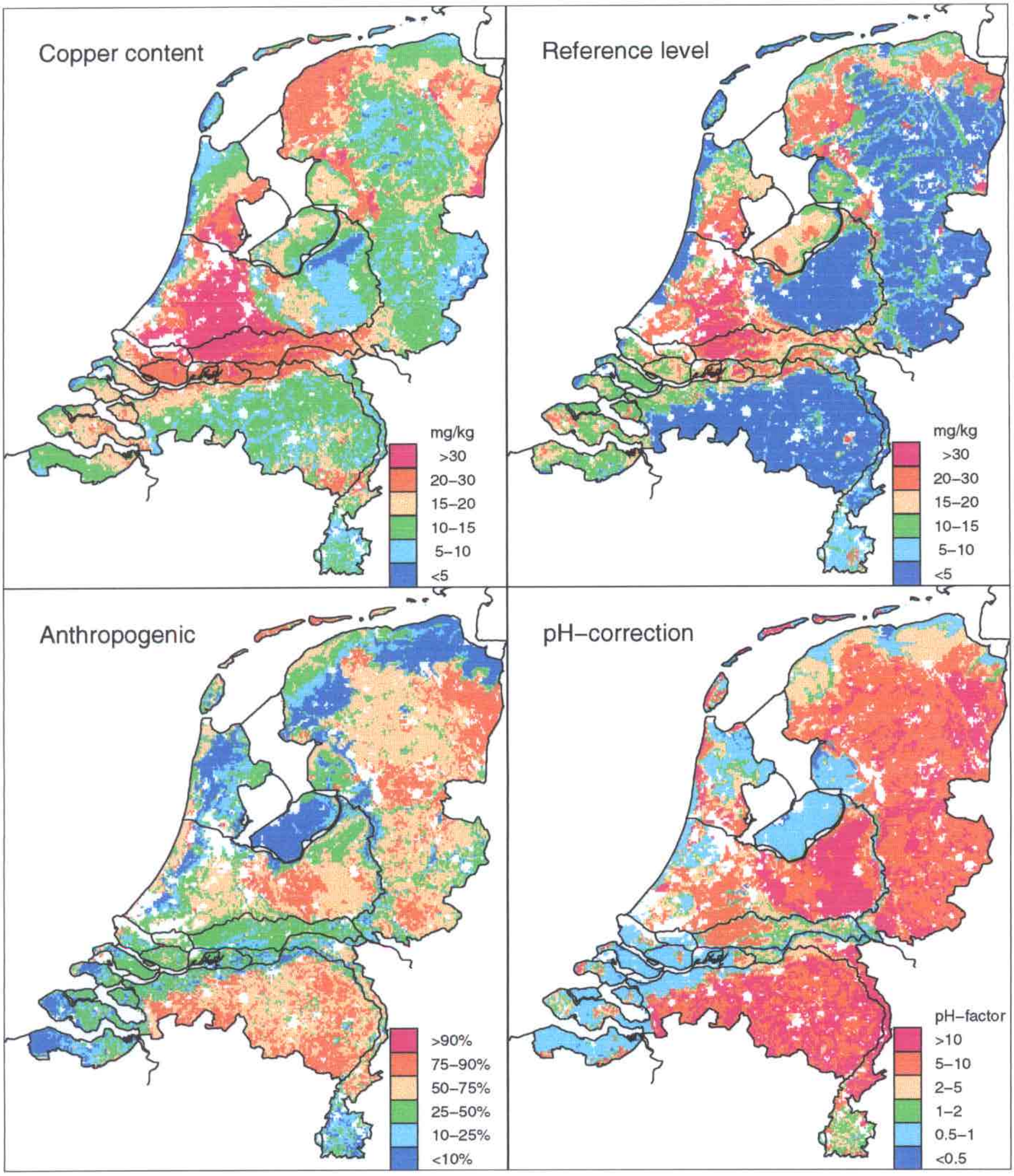

Figure 20 Copper concentrations, estimated "unpolluted" levels (reference values), anthropogenic contribution (by comparison of eq. 3 with actual concentrations) and pH-factor (giving the increase in availability due to the lower field-pH)

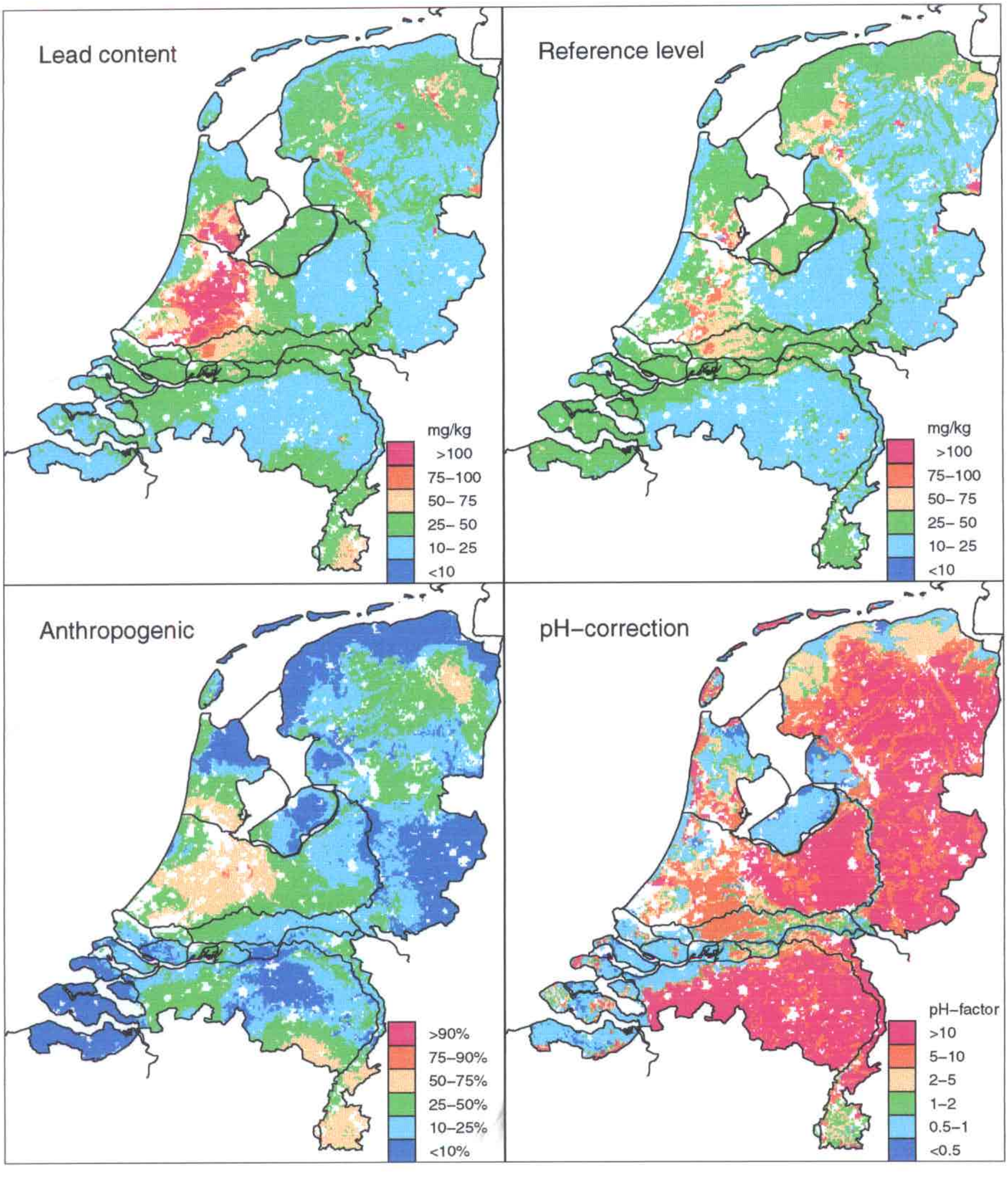

Figure 21 Lead concentrations, estimated "unpolluted" levels (reference values), anthropogenic contribution (by comparison of eq. 3 with actual concentrations) and pH-factor (giving the increase in availability due to the lower field-pH)

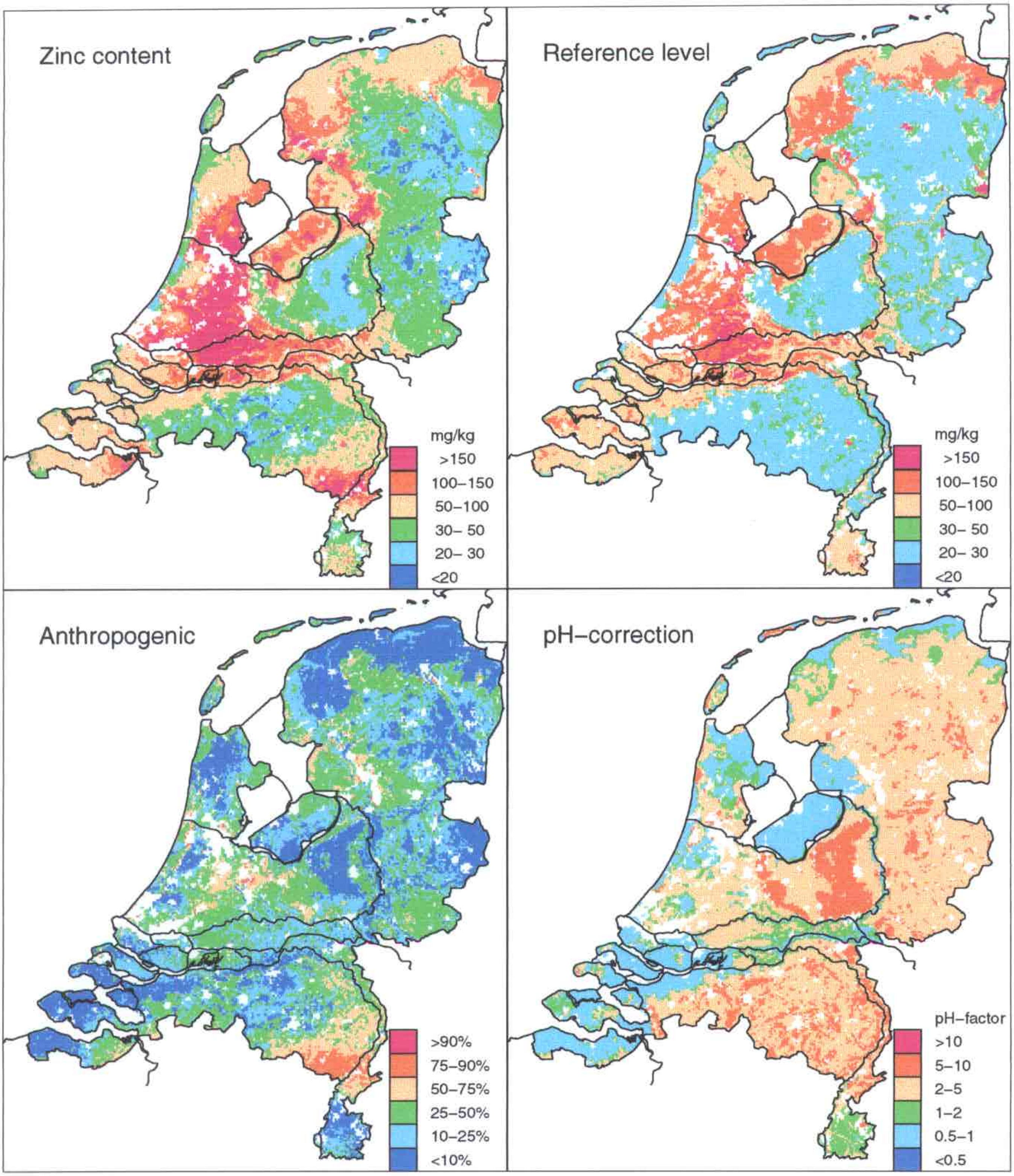

Figure 22 Zinc concentrations, estimated "unpolluted" levels (reference values), anthropogenic contribution (by comparison of eq. 3 with actual concentrations) and pH-factor (giving the increase in availability due to the lower field-pH)

Uncertainties in the results can be traced back to various model assumptions (in the form of parameter values). Which assumptions were the most critical in the total outcome? In table 4, the Monte Carlo results were fitted to a log-linear model, which generally gave a satisfactory explained variance of 80-96%. The analysis shows that a limited number of parameters cause most of the uncertainty. For total-PAF the most important uncertainties are pH-factor (phfac), uncertainty about mean toxicity for porewater-exposed organisms (avgperr), about non-exchangeable metal content (omnonx, sndnonx) and field availability (fldavbl). For anthropogenic PAF the factor interpolating between the two estimates for natural background level ("backgr") is important. A low importance can be assigned to uncertainties about the properties of the food-exposed organisms (clwgth, avgferr, stdferr).

Table 4. Contribution of uncertainty in various parameters to total uncertainty. The Monte Carlo results were fitted to a log-linear model: total variance explained ranges from 80-96%. The parameters are sorted to their average contribution to overall variance (last column). For parameter names and meaning in the model: see table 1.

	Cadmium		Copper		Lead		Zinc		cumulat.
	total	anthr.	total	anthr.	total	anthr.	total	anthr.	average
phfac	0.263	0.188	0.667	0.583	0.450	0.030	0.110	0.003	0.287
backgr	0.000	0.156	0.001	0.056	0.004	0.826	0.000	0.764	0.513
avgperr	0.072	0.080	0.097	0.117	0.194	0.033	0.217	0.073	0.623
fldavbl	0.047	0.064	0.137	0.159	0.102	0.038	0.209	0.070	0.726
omnonx	0.335	0.249	0.001	0.000	0.000	0.000	0.036	0.007	0.804
sndnonx	0.011	0.006	0.004	0.000	0.125	0.036	0.198	0.020	0.855
stdperr	0.142	0.149	0.017	0.006	0.027	0.002	0.034	0.002	0.902
clnonx	0.067	0.056	0.000	0.003	0.040	0.001	0.104	0.019	0.938
fpore	0.007	0.011	0.016	0.023	0.029	0.019	0.040	0.017	0.958
clayfac	0.030	0.019	0.017	0.018	0.014	0.011	0.019	0.001	0.974
omfac	0.013	0.006	0.040	0.031	0.002	0.000	0.010	0.002	0.987
fexcmin	0.010	0.015	0.001	0.002	0.001	0.002	0.022	0.020	0.996
concfac	0.002	0.002	0.001	0.002	0.007	0.000	0.002	0.000	0.998
clwgth	0.001	0.000	0.000	0.000	0.004	0.000	0.000	0.002	0.999
avgferr	0.000	0.000	0.000	0.001	0.000	0.002	0.001	0.002	1.000
stdferr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
expl.	0.958	0.897	0.931	0.906	0.913	0.800	0.939	0.840	

Pesticides in non-agricultural soils

The results for combi-PAF of pesticides have an uncertainty comparable to the one of the heavy metals. However, this result strongly depends on the method of independent sampling in the Monte Carlo analysis. For the heavy metals, sources of information for various parts of the model (toxicity, background levels, partitioning) were in fact independent, for the pesticides this is much less so, in particular because we are combining 24 pesticides in a single number. For example, choices had to be made in selecting a basis for the toxicity estimate (Appendix I) and in selecting a model for emission factors. These were treated as independent, but this may not be correct: if the model relating emission factors to vapor-pressure (Appendix III) is incorrect, *all* emissions will be substantially lower; if the method to derive soil toxicity from acute aquatic toxicity's is incorrect[15], pesticide toxicity in soil may be considerable lower *for all pesticides.* In addition, not all uncertainty was incorporated in the model, and uncertainty concerning atmospheric behavior (in particular, decay) and soil fate (decay, partitioning) could be important. The result of these two points (assumed independence and additional uncertain factors) is that overall uncertainty could be larger than calculated. For this reason, the results for pesticides should be treated with great caution.

Nevertheless, several important conclusion can be drawn from the calculations:

- toxic pressure by pesticides may be large, possibly affecting a substantial fraction of species
- a considerable fraction of pesticide deposition originates from abroad
- because deposition fields are rather uniform (as a result of the often remote sources), the most highly affected areas need not be close to agricultural areas, but are mainly those with sensitive soils
- major factors affecting toxic stress are substance-specific (volatility, persistence in atmosphere and soil) which make it worthwile to pursue a policy aimed at these properties, i.e. reducing the use of the most volatile and persistent pesticides may substantially reduce total toxic pressure on ecosystems

The present results are probably mainly useful for signaling a potential problem and in pointing out main areas of further research.

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[15] As discussed in appendix I the available data on chronic soil NOEC's were inconsistent with the estimates based on extrapolation of acute aquatic toxicity.

Implications of PAF

If we calculate PAF values indicating that a considerable faction of species is exposed above its NOEC, the question naturally arises what this means in terms of field effects.

In general, the PAF is a conservative figure, and one should not expect that a PAF of 50% implies that 50% of species is unhealthy or even extinct. In the first place, the NOEC is generally an underestimate of the concentrations where effects start to occur. Ignoring statistical considerations (Kooijman and Bedaux, 1996), the NOEC will generally be *below* the first effect-concentration[16], generally by a factor 2. In addition, laboratory test organisms are often selected on sensitivity (one wants to be able to measure something), although this bias may partly be compensated by the requirement of a certain robustness of the species (it has to survive in a test-tube). An important factor is that the NOEC is based on *some* effect (however small) on *some* function, in some cases even the most sensitive one (generally only a single function is tested, if more than one endpoint is determined, the most sensitive one is used in the NOEC database) . Although the functions selected as endpoints are characterized as "essential" (growth, metabolism, reproduction, mortality) the translation to population level is not straightforward. In practice, a decrease in reproduction need not be meaningful if a species population level is determined by food availability (Ferson et al., 1996): the population may only be affected at reproduction rates close to zero. In addition, field populations may be (genetically) adapted: in the laboratory a species shows negative effects, but in the field the organism has time for physiological adaptation, or a resistant population develops by selection.

Against these arguments pointing to a conservative nature of the PAF, there are some reasons to expect field effects at *lower* concentrations than laboratory NOECs. As pointed out by Kooijman and Bedaux (1996), the NOEC gives the highest concentration which does not differ in a *statistically significant* way from blank. Because many lab tests have high variance (low number of observations, low reproducibility), statistical significance may mask *ecologically significant* effects. In fact, some NOEC's may be higher than LC50. In addition many "chronic" tests have in fact a short duration and effects could occur after longer exposure, perhaps even after several generations. Of particular concern in this respect are effects on reproduction which may occur at toxic stress levels well below the NOEC for commonly determined endpoints (Kime, 1997). In conclusion: toxic effects probably arise at concentrations above the NOEC, but this is not always the case, and occasional field effects may occur below this level.

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[16] A typical series of test concentrations is 1, 3, 10, 30, etc. If the first effects are observed at 10 units, the NOEC is 3. Because of the gap between 3 and 10, the actual threshold concentration must be somewhere in-between, around 5 units. In this example that would imply that NOEC is approximately factor 2 lower than threshold; in general this underestimate equals the square root of the step in the concentration-series.

In a comparison with field observations problems arise with variability and the determination of the proper reference-situation. In the laboratory a 5%-effect may be significant, in the field much larger effects are required to be observed at a statistically significant level. In addition, neutralizing effects occur in the field: if at a certain location a number of species disappears other, less sensitive, species will take their place. The reverse is possible (due to the disappearance of some species, the food-chain collapses) but a certain redundancy seems more likely than such a domino effect. Because of this redundancy, ecosystem functions (such as primary production, decomposition of organic matter) and biodiversity will generally decrease less than one would expect on the basis of primary effects. If we knew the reference situation well enough, such an adaptation ("Pollution Induced Tolerance") or change in species composition could be a sensitive indicator of toxic effects. In practice, observations in gradient studies are generally on a macroscopic scale (total number of species, decomposition rate), and effects are masked by this kind of adaptation.

We therefore have a double problem: we do not know whether we have field effects at a certain PAF-value, and if there are any field effects, these are hard to observe[17]. This does not imply that there are *no* field effects: as discussed in Appendix I there is generally a factor 10 in concentration between chronic NOEC and acute mortality (LC50): for some of the PAF levels we calculate, acute mortality may be expected for some species. Clearly, there is a reason for concern.

In conclusion, the validity of the use of a NOEC distribution to derive safe environmental concentrations (at concentrations below NOEC effects are probably rare though cannot be ruled out) cannot be readily reversed: concentrations above the NOEC need not immediately lead to toxic effects. However, at the highest PAF's significant toxic stress seems probable.

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[17] A viable approach may be to study gradients in the vicinity of "hot spots" (point sources). A description of the situation near Budel (near the Belgian border) is given by Reve (1982): "Thereafter, the foreman invited me to ride along with him, as he wanted to show me something ‘I had never seen before’. Indeed, who doesn’t want such a thing? Therefore I abode with him, though for a brief moment I thought that the man wanted something about which one sometimes reads in the newspapers and is not allowed at all. We rode through a vast sand plain where only jeeps and caterpillars could plough through, after which we arrived at a huge, dead pine forest, stretching from horizon to horizon, as torched by a biblical judgement, but not scorched by fire: killed slowly, at that time, by the fumes from the zinc factory of mister Dor, that doesn’t emit dirt anymore." (Letter to Simon Carmiggelt, 25 April 1972, translated by T.P. Traas)

5. Conclusion

The main advantage of the method presented in this report is the possibility to compare this measure for toxic stress between species and compounds: PAF's can be compared and even combined to obtain a comprehensive view. At the same time, the method is simple enough to be practically useable for purposes of mapping, risk assessment schemes and model studies. Both metals and pesticides show considerable areas in The Netherlands where toxic stress is a reason for concern. For pesticides in non-agricultural soils uncertainty is too large to draw any firm conclusion; the main result is to signal a possibly serious problem and to point at major gaps in knowledge on environmental fate and toxicity of these compounds.

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Appendix I Toxicity data

AI.1 Heavy metals in soils

Heavy metal toxicity data have been collected and screened by Janus and Crommentuijn (pers. comm., 1996). In summary, a literature search was performed for chronic no-observed effect concentrations (NOEC) for soil organisms with some additional soil properties (pH, organic matter and clay content), taking the following points into account:

- only "essential" processes are regarded: respiration or metabolism, reproduction and growth
- if several endpoints were determined for a single species, the lowest NOEC value was used
- if the same endpoint was determined in separate tests, a mean value was calculated: the normal mean for the soil properties and the geometric mean for the NOEC's
- microbial processes and enzyme activities determined in different soils were regarded as different species (in fact, communities) and entered separately in the tables
- in a number of cases no NOEC's have been reported but a certain percentage of the maximum effect. In this case the following rules are used to estimate a NOEC:

percentage of max. effect	NOEC
< 10	=EC
11-19	EC/2
20-49	EC/3
50-90	EC/10

- in some cases only added amounts of metal were reported, in other cases total amount. The added amounts have been converted to totals using equations for background levels (for Cd, Cu, Pb - see appendix IV). For zinc sufficient data for both added and total amounts were present to calculate a background regression directly from the data.
- in contrast to the standard procedure, NOEC's were *not* converted to a standard soil

In figure I.1-I.4 the NOEC's and fitted log-logistic distribution functions are presented. Note that the data were *not* used in this raw form to calculate PAFs: this requires a calculation of biological availability and laboratory/field differences (see section 2 of main report for calculation procedure)

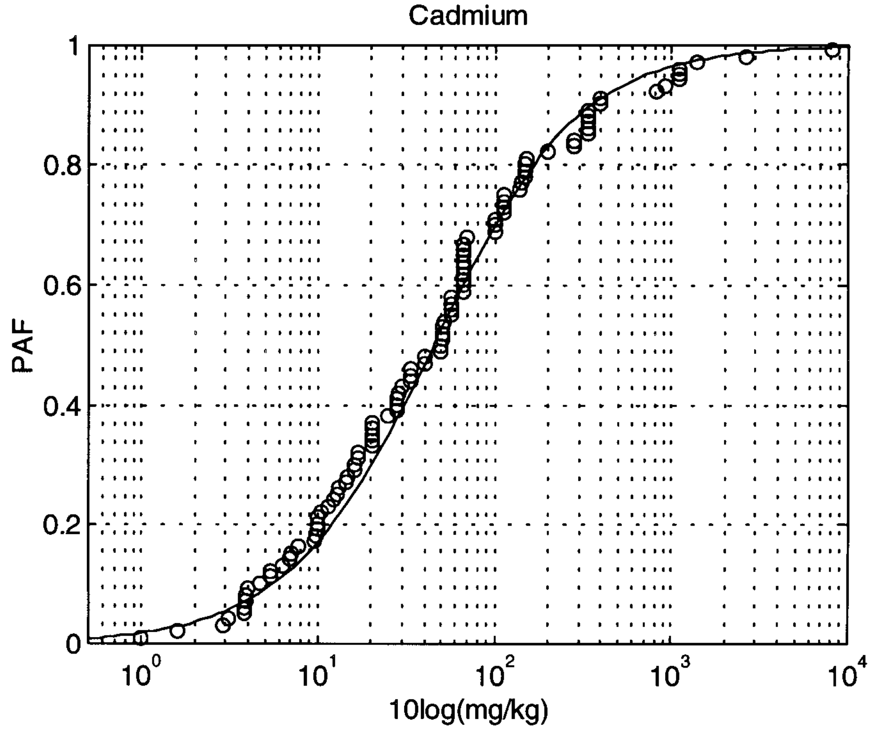

Figure I.1 Soil toxicity data Cadmium.

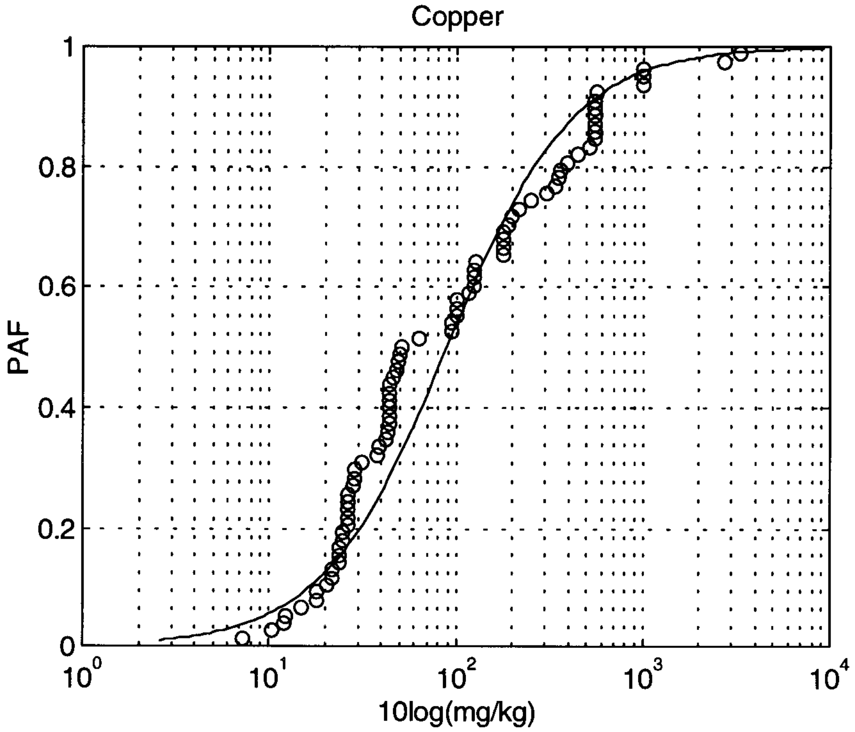

Figure I.2 Soil toxicity data Copper.

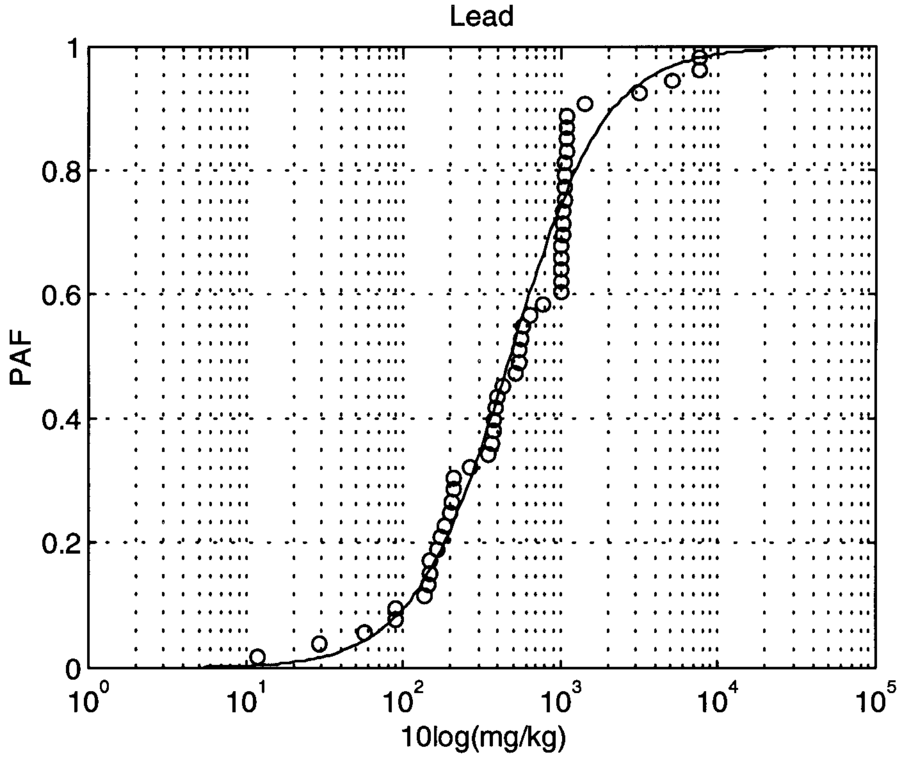

Figure I.3 Soil toxicity data Lead.

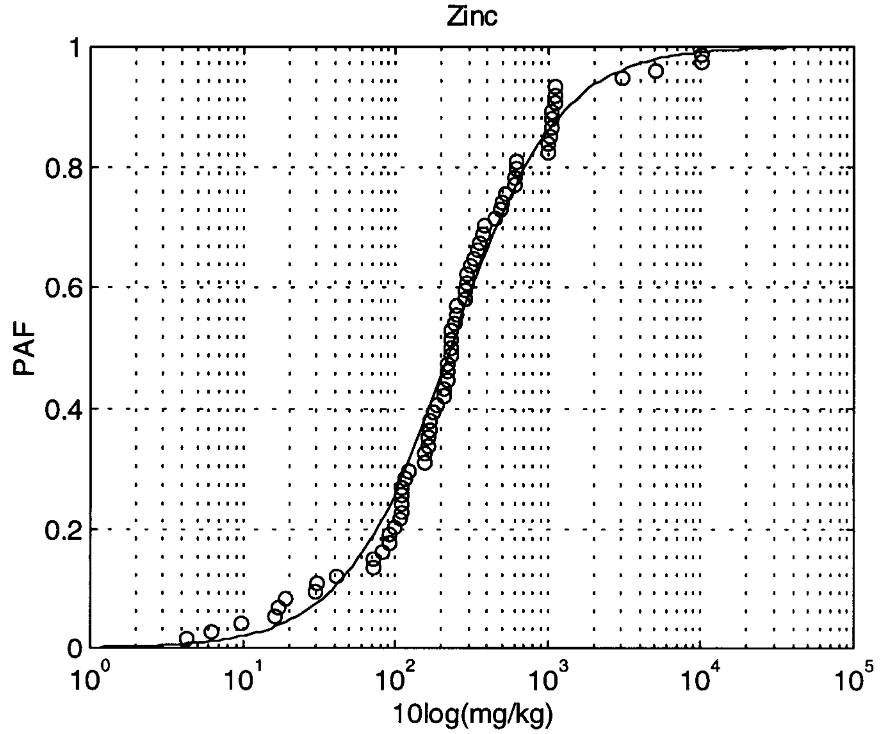

Figure I.4 Soil toxicity data Zinc.

Table I.1 Chronic toxicity of cadmium to soil organisms. From Crommentuijn et al. (1997). For some organisms several tests were available; from these the geometric mean has been calculated. In this case, numbers between brackets give the number of tests; otherwise a single test is reported. "Route" column gives the exposure route: 0 = porewater; 1 = organic matter. "Source" column gives source of cadmium: 0 = via soil; 1 = directly via food. Background column indicates wether total metal content was given directly (0) or obtained from adding backround levels (1) as estimated by the Lexmond and Edelman (1992) equations (see appendix IV)

Organism/process	route	source	pH	OM%	clay%	NOEC (mg/kg)	backgr
Bacteria	0	0	7.5	1.4	55.2	5.4	1
Actinomycetes	0	0	7.5	1.4	55.2	50.4	1
Fungi	0	0	7.5	1.4	55.2	10.4	1
Fungi	0	0	8	1.3	52.5	400.4	1
Grain species	0	0	5.6	1.6	7.8	13.0	0
Grain species	0	0	5.4	2.4	26.0	7.1	0
Grain species	0	0	5.2	3.2	37.7	51.0	0
Grain species	0	0	5	3.4	2.6	6.4	0
Grain species	0	0	5.4	6.8	3.3	50.0	0
Grain species	0	0	4.6	19.4	2.6	7.0	0
Raphanus sativa (3)	0	0	5.4	3.0	18.0	70.2	0
Spinacea oleracea (6)	0	0	6.2	2.8	24.3	1.6	0
Triticum aestivum (3)	0	0	6.5	2.2	10.5	11.6	1
Helix aspera	1	1	6.5	86.0	0.0	10.0	0
Dendrobaena rubida	0	0	6.5	9.7	5.0	101.0	0
Eisenia andrei	0	0	6.5	8.0	10.0	10.0	0
Eisenia fetida (5)	0	0	6.4	18.0	17.0	9.8	0
Lumbricus rubellus	0	0	7.3	3.4	17.0	10.0	0
Lumbricus terrestris	0	0	6.5	8.0	10.0	200.0	0
Porcellio scaber (2)	1	1	6.6	95.0	0.0	12.2	0
Folsomia candida (2)	1	0	5.6	9.0	15.0	49.7	0
Orchesella cincta	1	1	6.5	95.0	0.0	4.7	0
Platynothrus peltifer	1	1	6.5	95.0	0.0	2.9	0
Arginine-ammonification	0	0	5.5	3.6	5.0	20.2	1
Arginine-ammonification	0	0	5.7	2.2	4.0	66.9	1
ATP-content	0	0	6.6	1.2	9.0	50.2	1
Cellulose respiration	0	0	5.8	0.8	2.2	112.2	1
Fe(III)reduction	0	0	5.1	3.8	4.0	40.2	1
Glucose respiration	0	0	5.8	0.8	2.2	112.2	1
Nitrification	0	0	7.5	1.4	55.2	5.4	1
Nitrification	0	0	8	1.3	52.2	17.1	1
Nitrification	0	0	6.6	1.2	9.0	25.2	1
N-mineralization	0	0	8.5	0.1	0.2	337.2	1
N-mineralization	0	0	5.8	0.2	2.2	1124.2	1
N-mineralization	0	0	6.2	0.9	19.0	337.3	1

N-mineralization	0	0	6.4	5.4	27.6	337.3	1
N-mineralization	0	0	5.7	12.2	28.7	337.3	1
Respiration	0	0	5.1	5.7	9.0	30.2	1
Respiration	0	0	7.7	1.6	2.0	13.2	1
Respiration	0	0	7.4	2.6	19.0	28.3	1
Respiration	0	0	4.3	12.8	5.0	52.2	1
Respiration	0	0	7.7	1.6	2.0	150.2	1
Respiration	0	0	5.1	5.7	9.0	150.2	1
Respiration	0	0	7.4	2.6	19.0	150.3	1
Respiration	0	0	6.8	3.2	60.0	150.5	1
Respiration	0	0	4.3	12.8	5.0	400.2	1
Respiration (2)	0	0	4.9	3.6	5.2	16.0	0
Respiration	0	0	8.5	0.1	0.2	33.9	1
Respiration	0	0	5.8	0.2	2.2	33.9	1
Respiration	0	0	6.2	0.9	19.0	112.3	1
Respiration	0	0	6.4	5.4	27.6	112.3	1
Respiration	0	0	5.7	12.2	28.7	337.3	1
Respiration	0	0	6.9	2.2	21.3	3.9	1
Respiration	0	0	7	2.6	3.2	3.8	0
Respiration	0	0	5.6	1.7	7.0	14.5	0
Arylsulphatase	0	0	7	1.6	2.0	3.8	0
Arylsulphatase	0	0	6	5.7	9.0	3.9	0
Arylsulphatase	0	0	7.7	2.4	19.0	7.7	0
Arylsulphatase	0	0	7.5	3.2	60.0	28.6	0
Arylsulphatase	0	0	4.4	12.8	5.0	2664.0	0
Dehydrogenase	0	0	6	1.5	7.0	33.5	1
Dehydrogenase	0	0	6.6	1.2	9.0	16.9	1
Dehydrogenase	0	0	5.4	1.8	5.0	100.2	1
Dehydrogenase	0	0	5.5	3.6	5.0	20.2	1
Dehydrogenase	0	0	5.8	1.0	8.0	66.9	1
Dehydrogenase	0	0	5.9	4.3	12.0	66.9	1
Dehydrogenase	0	0	7.9	2.0	13.0	66.9	1
Dehydrogenase	0	0	7	7.6	29.0	67.0	1
Dehydrogenase	0	0	5.7	2.2	4.0	20.2	1
Dehydrogenase	0	0	8.5	2.1	30.0	20.3	1
Dehydrogenase	0	0	7.5	1.4	16.0	20.3	1
Dehydrogenase	0	0	7	4.0	23.0	100.3	1
Dehydrogenase	0	0	8	2.4	28.0	67.0	1
Dehydrogenase	0	0	8	5.7	38.0	67.1	1
Dehydrogenase	0	0	8.2	1.2	17.0	67.0	1
Dehydrogenase	0	0	8.2	6.2	16.0	67.0	1
Phosphatase (acid)	0	0	4.3	93.0	0.5	1125.5	1
Phosphatase (acid)	0	0	6.3	13.0	29.0	1124.3	1
Phosphatase (acid)	0	0	6.5	4.4	23.0	140.3	1
Phosphatase (alkaline)	0	0	6.5	6.4	30.0	280.3	1
Phosphatase	0	0	6.5	9.3	34.0	933.6	1
Phosphatase	0	0	11	6.4	30.0	280.3	1

Phosphatase	0	0	7	1.6	2.0	9.6	1
Phosphatase	0	0	7	1.6	2.0	16.3	1
Phosphatase	0	0	6	5.7	9.0	8071.2	1
Phosphatase	0	0	6.5	7.7	2.4	1406.2	1
Phosphatase	0	0	6.5	7.7	2.4	14.7	1
Phosphatase	0	0	6.5	7.5	3.2	141.2	1
Phosphatase	0	0	6.5	7.5	3.2	830.2	1
Phosphatase	0	0	7	1.6	2.0	40.6	1
Phosphatase	0	0	6	5.7	9.0	1.0	1
Phosphatase	0	0	7.7	2.4	19.0	3.1	1
Phosphatase	0	0	7.5	3.2	60.0	4.0	1
Urease	0	0	5.1	2.6	17.0	56.3	1
Urease	0	0	6.1	5.6	30.0	56.3	1
Urease	0	0	5.8	4.4	23.0	56.3	1
Urease	0	0	7.8	6.4	30.0	28.3	1
Urease	0	0	6.8	7.4	42.0	56.4	1
Urease	0	0	7.4	9.3	34.0	28.3	1

Table I.2 Chronic toxicity of copper to soil organisms. From BKH (1995) and (for directly exposed organisms) Janus et al. (1987). For some organisms several tests were available; from these the geometric mean has been calculated. In this case, numbers between brackets give the number of tests; otherwise a single test is reported. "Route" column gives the exposure route: 0 = porewater; 1 = organic matter. "Source" column gives source of cadmium: 0 = via soil; 1 = directly via food. Background column indicates wether total metal content was given directly (0) or obtained from adding backround levels (1) as estimated by the Lexmond and Edelman (1992) equations (see appendix IV)

organism/process	source	route	pH	OM%	clay%	NOEC (mg/kg)	backrg
nitrification	0	0	4.4	72.0	15.0	519.6	1
respiration	0	0	4.9	3.6	5.2	12.1	0
ethylene production	0	0	6.1	5.4	59.0	45.6	1
ethylene production	0	0	6.3	4.4	48.0	39.2	1
ethylene production	0	0	3.9	3.9	26.0	26.5	1
ethylene production	0	0	6.8	3.6	21.0	23.6	1
ethylene production	0	0	6.6	2.8	26.0	26.5	1
ethylene production	0	0	7.4	2.8	54.0	42.7	1
ethylene production	0	0	7.4	2.6	23.0	24.7	1
ethylene production	0	0	7.5	2.0	46.0	38.1	1
ethylene production	0	0	5.9	1.9	21.0	23.6	1
ethylene production	0	0	7.6	1.9	26.0	26.5	1
ethylene production	0	0	8.6	1.5	26.0	26.5	1
ethylene production	0	0	6.3	1.3	26.0	26.5	1
ethylene production	0	0	7.7	1.2	23.0	24.7	1
ethylene production	0	0	7.2	0.8	18.0	21.8	1
ethylene production	0	0	7.0	0.8	16.0	20.7	1
ethylene production	0	0	8.6	0.7	29.0	28.2	1

ethylene production	0	0	8.6	0.6	64.0	48.5	1
ethylene production	0	0	8.2	0.6	34.0	31.1	1
ethylene production	0	0	7.2	0.5	18.0	21.8	1
phosphatase (acid)	0	0	6.5	4.4	23.0	94.2	1
phosphatase (acid)	0	0	6.5	6.4	30.0	548.8	1
phosphatase (acid)	0	0	6.5	9.3	34.0	551.1	1
phosphatase (alkaline)	0	0	11.0	9.3	34.0	180.1	1
phosphatase (alkaline)	0	0	11.0	6.4	30.0	548.8	1
phosphatase (acid)	0	0	6.5	4.4	23.0	94.2	1
phosphatase (acid)	0	0	6.5	6.4	30.0	548.8	1
phosphatase (acid)	0	0	6.5	9.3	34.0	551.1	1
phosphatase (alkaline)	0	0	11.0	9.3	34.0	180.1	1
phosphatase (alkaline)	0	0	11.0	6.4	30.0	548.8	1
phosphatase	0	0	7.0	1.6	2.0	7.2	0
phosphatase	0	0	7.0	1.6	2.0	12.3	0
phosphatase	0	0	6.0	5.7	9.0	445.0	0
phosphatase	0	0	7.7	2.4	19.0	192.0	0
phosphatase	0	0	7.5	3.2	60.0	342.0	0
phosphatase	0	0	4.4	12.8	5.0	63.3	0
arylsulphatase	0	0	7.0	1.6	2.0	10.4	0
arylsulphatase	0	0	6.0	5.7	9.0	353.2	0
arylsulphatase	0	0	7.7	2.4	19.0	308.4	0
arylsulphatase	0	0	7.5	3.2	60.0	2719.0	0
arylsulphatase	0	0	4.4	12.8	5.0	3342.0	0
urease	0	0	7.0	1.6	2.0	24.0	0
urease	0	0	6.0	5.7	9.0	126.5	0
urease	0	0	7.7	2.4	19.0	362.0	0
urease	0	0	7.5	3.2	60.0	572.0	0
urease	0	0	4.4	12.8	5.0	215.5	0
urease	0	0	6.5	3.7	31.0	44.4	1
urease	0	0	7.3	2.0	31.0	44.4	1
urease	0	0	6.5	3.7	31.0	44.4	1
urease	0	0	7.3	2.0	31.0	44.4	1
urease	0	0	6.5	3.7	31.0	44.4	1
urease	0	0	7.3	2.0	31.0	44.4	1
urease	0	0	5.1	2.6	17.0	43.3	1
urease	0	0	6.1	5.6	30.0	50.8	1
urease	0	0	5.8	4.4	23.0	17.9	1
urease	0	0	7.8	6.4	30.0	125.5	1
urease	0	0	6.8	7.4	42.0	29.0	1
urease	0	0	7.4	9.3	34.0	181.1	1
urease	0	0	5.1	2.6	17.0	117.9	1
urease	0	0	6.1	5.6	30.0	125.5	1
urease	0	0	5.8	4.4	23.0	17.9	1
urease	0	0	7.8	6.4	30.0	125.5	1
urease	0	0	6.8	7.4	42.0	29.0	1
urease	0	0	7.4	9.3	34.0	181.1	1

Avena sativa	0	0	5.5	2.2	12.4	1000.0	0
Cucumis sativa	0	0	5.5	2.2	12.4	1000.0	0
Glycina max	0	0	5.5	2.2	12.4	1000.0	0
Banksia ericifolia	0	0	5.5	2.2	12.4	100.0	0
Casuarina distyla	0	0	5.5	2.2	12.4	100.0	0
Eucalyptus exima	0	0	5.5	2.2	12.4	100.0	0
Caenorhabditi elegans (5)	0	0	6.2	2.5	26.0	390.7	1
Eisenia fetida (3)	0	0	6.6	10.0	20.0	48.7	0
Sheep	1	1	7.0	100.0	0.0	15.0	0
Cattle	1	1	7.0	100.0	0.0	50.0	0
Pig	1	1	7.0	100.0	0.0	250.0	0
Chicken	1	1	7.0	100.0	0.0	200.0	0

Table I.3 Chronic toxicity of lead to soil organisms. From Janus (pers. comm., 1996). For some organisms several tests were available; from these the geometric mean has been calculated. In this case, numbers between brackets give the number of tests; otherwise a single test is reported. "Route" column gives the exposure route: 0 = porewater; 1 = organic matter. "Source" column gives source of cadmium: 0 = via soil; 1 = directly via food. Background column indicates wether total metal content was given directly (0) or obtained from adding backround levels (1) as estimated by the Lexmond and Edelman (1992) equations (see appendix IV). Tests using PbO were excluded because of the low solubility of this salt.

organism/process	source	route	pH	OM%	clay%	NOEC (mg/kg)	backrg
respiration	0	0	7.7	1.6	2.0	182.0	0
respiration	0	0	5.1	5.7	9.0	163.0	0
respiration	0	0	7.4	2.6	19.0	1042.0	0
respiration	0	0	6.8	3.2	60.0	3130.0	0
respiration	0	0	4.3	12.8	5.0	176.0	0
respiration	0	0	4.9	4.0	5.0	12.0	0
respiration	0	0	6.9	2.0	44.0	29.0	0
respiration	0	0	6.7	2.0	80.0	5077.0	1
respiration	0	0	6.8	1.5	5.0	1020.8	1
respiration	0	0	6.0	95.0	5.0	1013.0	0
N-mineralization	0	0	6.9	2.0	44.0	202.0	0
N-mineralization	0	0	5.8	4.0	23.0	551.3	1
N-mineralization	0	0	6.6	5.0	45.0	567.8	1
N-mineralization	0	0	7.8	6.0	30.0	384.5	1
N-mineralization	0	0	7.4	9.0	34.0	1077.5	1
nitrification	0	0	5.8	4.0	23.0	379.3	1
nitrification	0	0	7.8	6.0	20.0	1067.0	1
nitrification	0	0	7.4	9.0	34.0	1077.5	1
glucose mineralization	0	0	5.0	1.0	9.0	1023.8	1
cellulose mineralization	0	0	6.0	3.0	18.0	137.0	0
cellulose mineralization	0	0	6.0	3.0	18.0	150.0	0
amylase activity	0	0	6.0	95.0	5.0	1013.0	0
cellulase activity	0	0	6.0	95.0	5.0	1013.0	0

dehydrogenase activity	0	0	4.1	2.8	12.0	401.0	1
dehydrogenase activity	0	0	7.0	3.2	96.0	7589.0	1
dehydrogenase activity	0	0	5.6	46.0	3.0	7522.0	1
phosphatase (acid) (2)	0	0	6.5	4.0	23.0	551.3	1
phosphatase (alkaline) (2)	0	0	10.0	9.0	34.0	559.5	1
urease activity (2)	0	0	6.5	4.0	31.0	90.3	1
urease activity (2)	0	0	7.3	5.0	31.0	90.3	1
urease activity (2)	0	0	9.0	3.0	17.0	761.8	1
urease activity (2)	0	0	9.0	6.0	30.0	637.5	1
urease activity (2)	0	0	9.0	4.0	23.0	265.3	1
urease activity (2)	0	0	9.0	6.0	30.0	366.5	1
urease activity (2)	0	0	9.0	7.0	42.0	1083.5	1
urease activity (2)	0	0	9.0	9.0	34.0	145.5	1
xylanase activity	0	0	6.0	95.0	5.0	1000.0	0
Avena sativa (7)	0	0	5.2	4.0	12.2	518.0	0
Lolium perenne	0	0	7.2	4.4	5.0	1062.0	0
Medicago sativa	0	0	7.2	2.0	15.0	212.0	0
Plantago lanceolata	0	0	7.2	4.4	5.0	1062.0	0
Raphanus sativa	0	0	5.4	3.0	18.0	150.0	0
Trifolium repens	0	0	7.2	4.4	5.0	1062.0	0
Triticum aestivum	0	0	6.0	3.0	18.0	377.0	0
Zea mays	0	0	7.2	3.0	12.0	212.0	0
Dendrobaena rubida	0	0	5.5	9.7	5.0	345.0	0
Eisenia foetida (2)	0	0	7.0	40.0	5.0	1439.3	1
Lumbricus rubellus	0	0	7.3	3.4	17.0	200.0	0
Arion ater	1	1	7.0	100.0	0.0	1017.1	1
Porcellio scaber	1	1	7.0	100.0	0.0	57.1	1
Onychiuris armatus	1	1	7.0	100.0	0.0	1096.0	0
Platynothrus peltifer	1	1	7.0	100.0	0.0	430.0	0

Table I.4 Chronic toxicity of zinc to soil organisms. From Janus (1993). For some organisms several tests were available; from these the geometric mean has been calculated. In this case, numbers between brackets give the number of tests; otherwise a single test is reported. "Route" column gives the exposure route: 0 = porewater; 1 = organic matter. "Source" column gives source of cadmium: 0 = via soil; 1 = directly via food. Background column indicates wether total metal content was given directly (0) or obtained from adding backround levels (1) as estimated by the equation Zn (mg/kg) = 14.0 + 0.75 OM% + 1.41 clay%.

organism/process	source	route	pH	OM%	clay%	NOEC (mg/kg)	backrg
respiration	0	0	4.8	7.0	3.0	71.5	1
respiration	0	0	7.0	95.0	5.0	111.0	0
respiration	0	0	4.9	4.0	5.0	4.3	0
respiration	0	0	6.9	2.0	44.0	19.0	0
respiration	0	0	6.0	4.0	5.0	537.0	0
respiration	0	0	7.7	2.0	2.0	164.0	0
respiration	0	0	5.1	6.0	9.0	167.0	0

respiration	0	0	7.4	3.0	19.0	3103.0	0
respiration	0	0	6.8	3.0	60.0	626.0	0
respiration	0	0	4.3	13.0	5.0	188.0	0
N-mineralization	0	0	5.8	4.0	23.0	211.9	1
N-mineralization	0	0	6.6	5.0	45.0	243.6	1
N-mineralization	0	0	7.8	6.0	30.0	223.2	1
N-mineralization	0	0	7.4	9.0	34.0	231.1	1
N-mineralization	0	0	6.9	2.0	44.0	107.0	0
ammonification	0	0	6.0	2.0	1.0	1016.9	1
ammonification	0	0	7.0	2.0	1.0	350.2	1
ammonification	0	0	7.7	2.0	1.0	116.9	1
ammonification	0	0	6.2	3.0	17.0	1057.0	0
ammonification	0	0	7.4	3.0	17.0	1057.0	0
ammonification	0	0	8.5	3.0	17.0	10057.0	0
nitrification	0	0	5.8	4.0	23.0	81.9	1
nitrification	0	0	7.8	6.0	30.0	169.1	1
nitrification	0	0	7.4	9.0	34.0	176.9	1
nitrification	0	0	7.0	3.0	17.0	157.0	0
nitrification	0	0	7.4	3.0	17.0	1057.0	0
nitrification	0	0	8.5	3.0	17.0	10057.0	0
nitrification	0	0	5.6	2.0	28.0	236.0	0
nitrification	0	0	5.3	2.0	8.0	124.0	0
nitrification	0	0	6.0	1.0	2.0	17.0	0
glucose mineralization	0	0	5.0	6.0	9.0	5031.2	1
glutamic acid mineralization	0	0	7.7	2.0	2.0	41.4	0
glutamic acid mineralization	0	0	5.1	6.0	9.0	1017.0	0
glutamic acid mineralization	0	0	7.4	3.0	19.0	503.0	0
glutamic acid mineralization	0	0	6.8	3.0	60.0	626.0	0
glutamic acid mineralization	0	0	4.3	13.0	5.0	1038.0	0
amylase activity	0	0	7.0	95.0	5.0	1111.0	0
arylsulphatase activity	0	0	7.7	2.0	2.0	91.4	0
arylsulphatase activity	0	0	5.1	6.0	9.0	219.7	0
arylsulphatase activity	0	0	7.4	3.0	19.0	449.3	0
arylsulphatase activity	0	0	6.8	3.0	60.0	308.6	0
cellulase activity	0	0	7.0	95.0	5.0	1111.0	0
phosphatase activity	0	0	7.7	2.0	2.0	16.4	0
phosphatase activity	0	0	5.1	6.0	9.0	298.7	0
phosphatase activity	0	0	7.4	3.0	19.0	286.3	0
phosphatase activity	0	0	6.8	3.0	60.0	293.6	0
phosphatase (acid)	0	0	7.0	6.0	30.0	602.4	1
phosphatase (acid)	0	0	7.0	9.0	34.0	610.3	1
phosphatase (acid)	0	0	6.5	4.0	23.0	211.4	1

phosphatase (alkaline)	0	0	10.0	6.0	30.0	223.2	1
phosphatase (alkaline)	0	0	10.0	9.0	34.0	230.6	1
protease activity	0	0	7.4	3.0	19.0	330.3	0
urease activity	0	0	9.0	3.0	17.0	72.7	1
urease activity	0	0	9.0	6.0	30.0	169.1	1
urease activity	0	0	9.0	4.0	23.0	157.7	1
urease activity	0	0	9.0	6.0	30.0	92.7	1
urease activity	0	0	9.0	7.0	42.0	110.9	1
urease activity	0	0	9.0	9.0	34.0	100.6	1
urease activity	0	0	6.5	4.0	31.0	110.6	1
urease activity	0	0	7.3	5.0	31.0	111.4	1
urease activity	0	0	7.7	2.0	2.0	30.4	0
urease activity	0	0	5.1	6.0	9.0	6.2	0
urease activity	0	0	7.4	3.0	19.0	353.3	0
urease activity	0	0	6.8	3.0	60.0	31.1	0
urease activity	0	0	4.3	13.0	5.0	9.8	0
xylanase activity	0	0	7.0	95.0	5.0	1111.1	0
Eisenia fetida (7)	0	0	6.0	8.0	8.0	231.3	1
Arion ater	1	1	7.0	95.0	0.0	385.6	1
Porcellio scaber	1	1	7.0	95.0	0.0	485.6	1
Medicago sativa (10)	0	0	7.1	4.3	16.0	289.0	0
Zea maus (12)	0	0	6.9	4.1	16.0	255.0	0
Lactuca sativa (11)	0	0	6.9	4.2	16.0	252.0	0
Avena sativa (6)	0	0	5.2	4.1	11.4	373.0	0

A1.2 Pesticides: estimating NOECs for soil organisms

For the calculation of the Potentially Affected Fraction by pesticides a literature search of toxicity data was performed by Brandes, Kalf and Luttik (personal communications, 1996). Four sets of data were collected:

1. for all pesticides in use in the Netherlands the acute toxicity (as LC50 = concentration which is lethal to 50% of the test organisms within the prescribed time or EC50 = the concentration for which 50% of the organisms experience a particular effect) is recorded *for the most sensitive* species in three groups: algae, crustaceans and fish.
2. for a number of pesticides a larger number of acute toxicity studies for aquatic organisms was available, allowing to calculate an *average* effect concentration
3. for some aquatic organisms a chronic NOEC is known
4. for some soil organisms a chronic NOEC is known

For the problem at hand the fourth set of data seems the most useful; because this set is not complete we also need to consider the other three to arrive at a chronic soil-NOEC. This requires a short discussion of the four sets of data (table I.5).

Table 1.5 Toxicity data for pesticides. Aquatic data are given as 10log($g.l^{-1}$), soil data as 10log($g.kg^{-1}$).

dataset	Low EC50 (1)		Mean EC50 (2)		Aquatic NOEC (3)			Soil NOEC (4)	
	mean	n	mean	n	mean	std.dev.	n	mean	n
2,4-D	-2.35	3	-1.47	8	-2.59	1.17	7	-1.48	6
atrazine	-2.59	3			-4.03	0.75	18	-1.49	5
azinphos-methyl	-4.79	3			-5.82	1.16	11	-1.45	2
bentazon	-0.90	3	-0.87	2					
carbendazim	-4.17	3	-3.07	6	-4.15	1.20	2	-2.06	3
dichloorvos	-4.20	3	-4.19	17	-2.04	0.41	2		
diquat-dibromide	-2.87	3							
diuron	-3.80	3	-2.97	17	-5.07	0.70	6		
DNOC	-3.36	3	-3.38	6	-3.00	1.00	16		
endosulfan	-4.20	3			-4.55	1.46	5	-0.43	3
fentin-acetaat	-5.22	3	-4.34	6	-6.17	0.92	1		
lindaan	-4.47	3	-4.78	7	-4.77	1.52	6	-1.89	7
malathion	-4.18	3			-4.93	1.49	13	-1.34	15
maneb	-3.94	3	-2.37	13	-4.50	0.35	2		
mecoprop	-0.62	3	-0.37	3	-1.87	0.87	2		
metamitron	-1.73	3	-0.61	3					
methabenz	-2.66	3	-1.73	4					
metribuzin	-3.07	3							
mevinfos	-4.54	3	-5.17	7					
monolinuron	-2.91	3							
parathion	-3.97	3			-6.05	1.64	9	-1.86	6
simazine	-3.68	3	-2.73	8	-4.78	0.51	3	-1.53	2
thiram	-5.11	3						-1.38	5
trifluralin	-4.20	3	-3.58	14	-5.67	0.07	2		

Between the four sets we have some systematic differences. Group 2 has an higher average value than group 1: on average the LC50 is a factor 4.5 higher. The most probable explanation is the difference between a *mean* and a *lowest* value. Group 3 has a lower average value than group 1, the average ratio between groups 1 and 3 is 4.6. The most probable explanation is the fact that a chronic exposure leads to effects at lower concentrations than an acute exposure in combination with the fact that dataset 1 concerns *50%* effects and dataset 3 gives an upper bound for *no* effects. Generally, acute:chronic ratio's of around 10 are found (De Zwart, pers. comm. 1996), the higher factor may be partly attributed to the fact that data set 1 contains *lowest* values.

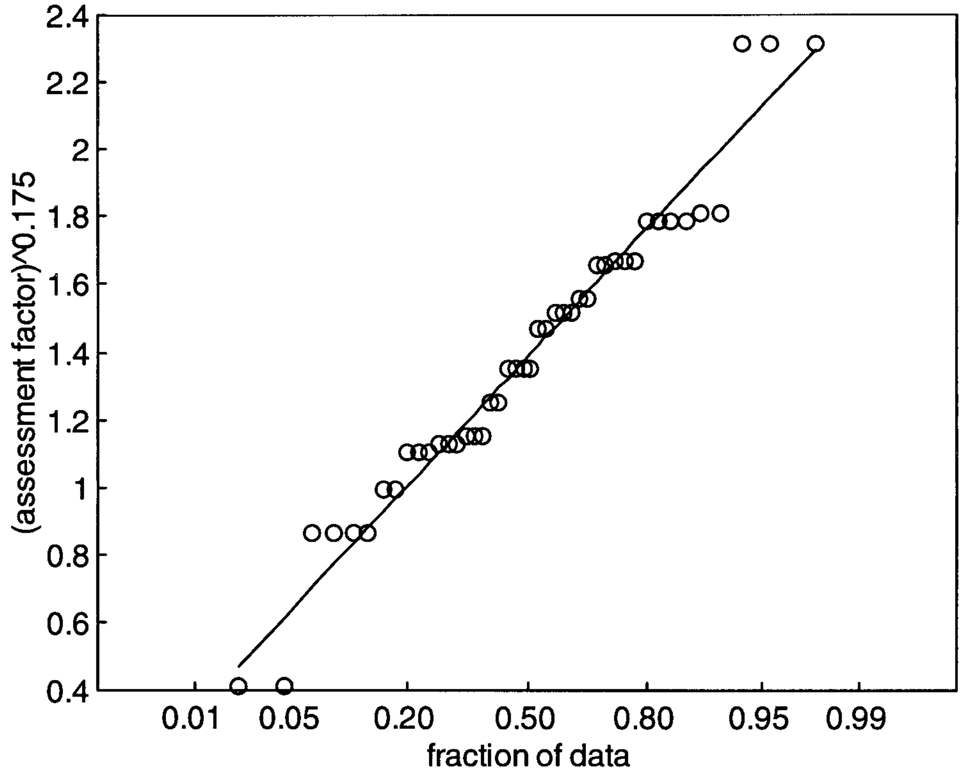

Figure I.5 The ratio acute:chronic (datasets 1 and 3) has a skewed distribution If we transform the ratios from table I.5 (AF) as $AF^{0.175}$ we have approximately a normal distribution. This transformed variable is normally distributed with mean = 1.385 and standard deviation = 0.453.

Data set 4 has a different dimension as compared to the first three: $g.kg^{-1}$ in stead of $g.l^{-1}$. To convert the two we may use the partion coefficient Kp (see appendix II):

$$NOEC_{total\text{-}soil} = NOEC_{porewater}\ Kp$$

In this way we can recalculate measured soil-NOEC to the equivalent aquatic NOEC. Doing this, it appears that these NOEC's are systematically *higher* than the LC50's from group 1: this is not only true for the 6 substances in table I.5 for which we have a soil NOEC, but also for a larger set of 10 other pesticide soil-NOEC's. The average acute:chronic ratio was 0.11. The most probable explanation for this apparent discrepancy[1] is that other species (or endpoints) were tested. Does this signify that soil organisms are *generally* less sensitive for pesticides?

At this point we have three ways to estimate the required NOEC's:

1. use the measured soil-NOEC's where available
    a) estimate missing NOEC's using dataset (1) using Kp and an assessment factor of 0.11
    b) estimate missing NOEC's from (1) with an assessment factor of 4.6
2. estimate *all* soil NOEC's from (1) with an assessment factor of 4.6

Method 1a is the most consistent with the data collected in table I.5, but is contrary to general ecotoxicological experience. It seems improbable that soil organisms are considerably less sensitive than aquatic organisms. More likely, a number of species-groups does not occur in data set 4. An important example are herbicides, which are generally highly toxic for algae. Terrestrial plants have generally not been tested for these substances (at least, not under the heading ecotoxicology). Route 1b gives a more plausible extrapolation to obtain estimated NOEC's, but now the data set is no longer consistent: if by chance we have a measured soil NOEC, the substance will be evaluated as considerably less toxic. Had we estimated the NOEC for this substance on the basis of the LC50, we would arrive at a 40 times (4.6/0.11) lower NOEC! Method 2 ignores part of the data, but generates a consistent picture which is compatible with ecotoxicological expertise. This is the method we followed.

A1.3 Spread in NOEC data for pesticides

For the calculation of PAF the spread (standard deviation) of NOEC's is of importance: because the concentration is generally below the average NOEC, a higher standard deviation leads to a higher PAF. For an estimate of standarddeviations we used dataset 3: aquatic NOEC's. The spread in acute LC50's (data set 1) does not provide a reliable basis as we have only three values per substance. For the same reason, the estimate for an individual substance is not reliable: we have pooled all standard deviations in the following analysis.

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[1] For the same species and endpoint, an acute effect occurs by definition at a higher concentration than a chronic effect, particularly if we compare no-effect concentration and 50%-effect concentration.

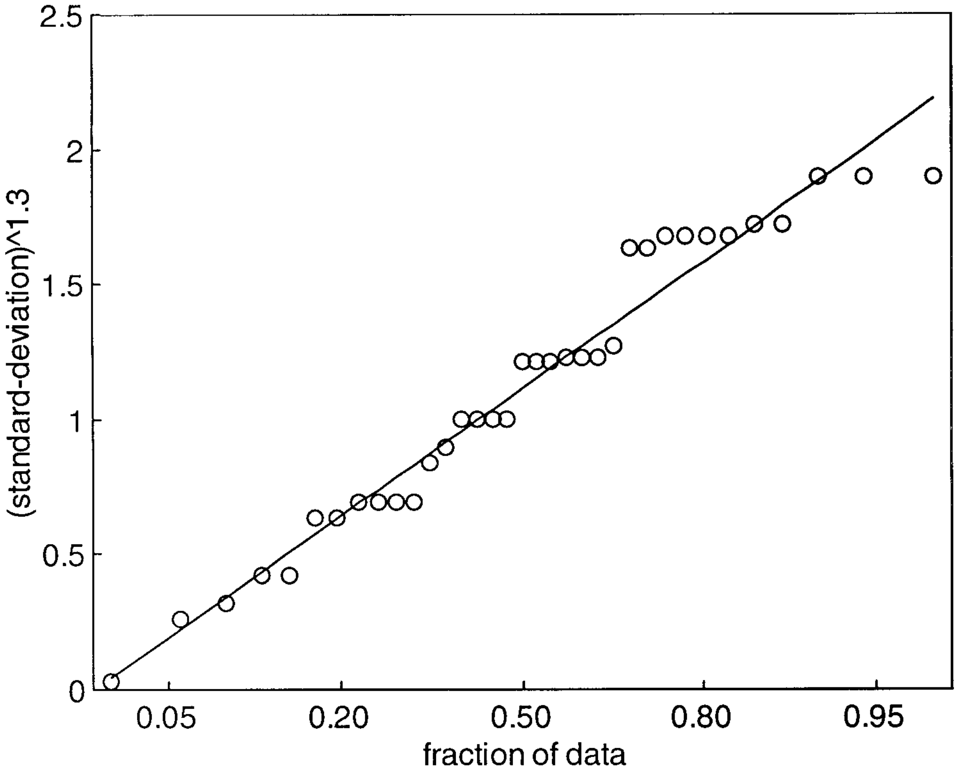

Figure I.6 The standard deviations of the NOEC's have a skewed distribution: many values around 1 (10-log units) with some lower values. If we transform the data as std$^{1.3}$ we obtain a normal distribution with mean 1.11 and standard debiation 0.559.

The standard deviation is on average 1.16. The observations show a considerable spread: some low values (0.07, 0.35), with a majority around 1. After transformation we obtain an approximately normal distribution (figure I.2).

I.4 Aquatic toxicity data

Table I.6 Aquatic toxicity data (L. Brandes, personal communication). Numbers in bold were obtained from NOEC data that were sufficient for deriving environmental quality standards; in these cases fitted values were obtained from ETX (Aldenberg and Slob -1993)[2].

	avg (log NOEC) (g/L)	std (log NOEC) (g/L)
cadmium	**-4.80**	**0.31**
copper	**-4.89**	**0.25**
lead	**-3.84**	**0.21**
zinc	**-4.06**	**0.21**
2,4-d	**-2.59**	**0.36**
atrazin	**-4.03**	**0.23**
azinphos-methyl	**-5.82**	**0.35**
bentazone	-1.60	0.52
carbendazim	-4.07	1.25
dichloorvos	-4.90	3.16
diquat-dibromide	-3.57	1.81
diuron	-5.06	0.64
dnoc	-3.00	1.00
endosulfan	-4.55	1.46
fentin-acetaat	-6.17	0.92
lindane	-4.77	1.52
malathion	-5.16	1.66
maneb	-3.37	0.66
mecoprop	-1.32	0.23
metamitron	-2.42	1.73
methabenz	-3.35	1.52
metribuzin	-3.77	2.32
mevinfos	-5.24	2.37
monolinuron	-3.61	2.68
parathion	-6.05	1.64
pentachloorphenol	-	-
simazin	-4.38	0.62
thiram	-5.81	1.89
trifluralin	-5.42	0.36

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[2] The ETX program reports parameters alpha and beta; these were recalculated for the present report: alpha is the mean of the logistic distribution, beta a measure of the spread, related to standard deviation (sigma) as sigma = 0.5513 beta.

Appendix II. Partitioning of toxicants

AII.1 Partitioning in water

Dissolved concentrations in water are calculated according to

$$C_{dissolved} = C_{total} / (1 + Kp.\ SM) \qquad \text{(II.1)}$$

where SM is the concentration of suspended particulate matter in water (in $kg.l^{-1}$), and Kp is the suspended particle-water partition coefficient (in $l.kg^{-1}$). The same partition coefficients as in Bakker (1997) were used.

Table II.1. Water-particle partition coefficients used for calculation of dissolved concentrations in water. Typical values for the fraction dissolved are given for a suspended matter concentration of 15 $mg.l^{-1}$.

	log Kp ($l.kg^{-1}$)	Fraction dissolved (15 $mg.l^{-1}$)
cadmium	5.11	34%
copper	4.70	57%
lead	5.81	9%
zinc	5.04	38%
atrazin	1.60	100%
dichlorovos	0.90	100%
diuron	1.82	100%
lindane	2.85	99%
mevinfos	-0.45	100%

AII.2 Partitioning of metals in soil

Biological uptake of toxicants by soil organisms may take place either via direct exposure or via food intake. For a particular uptake route we should consider toxicity relative to the phase which determines the particular uptake route. For direct exposure in the soil this phase is the porewater; for uptake via food, the metal content in the food is relevant. For heavy metals, the porewater route is dominant (appendix I) generally concerning more than 90% of the tested organisms. For pesticides it is even the only route considered, as soil toxicity data were estimated by converting aquatic toxicity data to porewater concentrations.

porewater-referencing of metals

Both laboratory toxicity data and field concentrations are generally reported as amount (added or total) per kg soil. We therefore have to standardize both types of data to porewater. Since we are correcting both laboratory and field data sets, it is not necessary to know absolute values of porewater concentrations or activities; only relative effects of certain factors are relevant. To illustrate this by way of a fictitious example: it would be sufficient to know that porewater concentrations are inversely proportional to organic matter (OM) content of the soil to compare a certain field concentration and OM content with laboratory NOEC and OM content.

Relations between soil properties (pH, OM and clay content) and metal concentration in solution have been determined for field soils by Janssen et al. (1996) and for laboratory conditions by Elzinga et al (1996) (for Cd, Cu and Zn) and Reinds et al. (1995) (for lead).

Elzinga et al. and Reinds et al. use a Freundlich isotherm which they fit to observations from a literature survey:

$$^{10}\log\,(M_{adsorbed}) = a + b\ ^{10}\log\,(M_{water}) + c\ ^{10}\log\,(OM) + d\ ^{10}\log\,(clay) + e\ pH \quad (II.2)$$

Results are summarized in table II.2. In this table upper- and lower limits are broadly interpreted. For example, Elzinga et al. give for a specific regression equation a value of coefficient b for cadmium of 0.66 ± 0.01, with b-values for different regressions (data sets) ranging from 0.56 to 0.86. Reinds et al use a value of 0.82. The range reported here is [0.5,0.9]. In some equations, both organic matter, clay content *and* cation exchange capacity (CEC) are used. Because CEC is closely related to these first two factors (Breeuwsma et al., 1986), the equations involving CEC have not been used to derive OM or clay coefficients.

Table II.2 Coefficients in the equation (II.2) to predict adsorption from soil properties based on Reinds et al (1995) and Elzinga et al. (1996).

metal	factor	minimum	median	maximum
Cadmium	porewater (b)	0.5	0.7	0.9
	organic matter (c)	0.0	0.1	0.4
	clay (d)	0.1	0.3	0.7
	pH (e)	0.3	0.5	0.6
Copper	porewater (b)	0.5	0.65	0.8
	organic matter (c)	-0.2	0.4	0.7
	clay (d)	-0.4	-0.2	0
	pH (e)	0.2	0.4	0.7
Lead	porewater (b)	0.3	0.55	0.8
	organic matter (c)	0.4	0.8	1.2
	clay (d)	0.0	0.15	0.3
	pH (e)	0.4	0.6	0.8
Zinc	porewater (b)	0.5	0.65	0.8
	organic matter (c)	0.0	0.4	0.8
	clay (d)	0.1	0.5	0.9
	pH (e)	0.2	0.3	0.4

The coefficient **a** in (II.2) is not relevant because we need to know only the *relative* effect of soil properties on porewater concentration. This also implies that a number of definitions of soil properties are less relevant as long as there is a linear transformation between them[1].

A major difference between the field and laboratory approaches is that in the first case actual soil water concentrations are related to *total* metal content of the soil, whereas in the laboratory only *adsorbed* metal is determined. In addition, laboratory tests take hours to days, in the field an equilibrium may be established over years or more, allowing part of the adsorbed metal to be incorporated into the soil matrix. These

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[1] For example, we have $pH_{CaCl2} = -0.658 + 1.003\ pH_{H2O}$ and $pH_{CaCl2} = 0.56 + 0.943\ pH_{KCl}$. If we have a pH_{H2O} coefficient of 0.4 in equation (II.2), this transforms to 0.401 relative to pH_{CaCl2} and 0.42 relative to pH_{KCl}. These differences are negligible compared to the uncertainty in the coefficient, even though the pH as measured by the various techniques may differ by a whole pH-unit. Similar arguments hold for the difference organic matter / organic carbon and concentrations vs. activities.

differences may explain why Janssen et al. (1996) found that for a certain porewater concentration, estimated adsorbed amounts were considerably lower (factor 3-10) than field totals. In the following we will discuss the possible consequences of both factors (adsorbed vs. total and time effects) on lab → field extrapolation.

It may be assumed that a certain amount of metal in the soil is *non-exchangeable*: it is for practical purposes an inert part of the soil matrix and may only be released by very slow processes (weathering). If we try to estimate this amount by different methods (appendix IV) a reasonably consistent picture emerges: for current background levels of metals, around 80% of the metal content may be considered as non-exchangeable; for higher concentrations this fraction decreases[2]. If we subtract non-exchangeable metal from the "Janssen totals", the field and laboratory results are better comparable, see figs. II.1-3

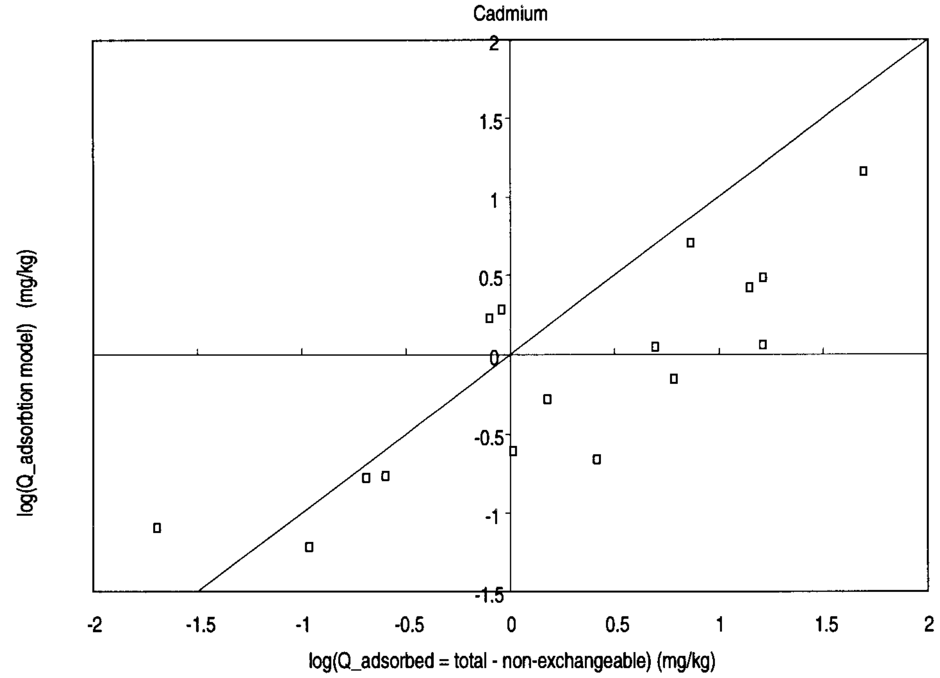

Figure II.1 (Adapted from Janssen et al., 1996). Field adsorption (x) vs. laboratory-based model (y) for Cadmium. Points *below* the 1:1 line indicate lower adsorbed concentrations calculated by the lab-based model *given* observed field porewater concentrations, i.e. a relatively low porewater concentration in the field.

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[2] In fact, it is more informative to describe a non-exchangeable *amount* than a non-exchangeable *fraction.*

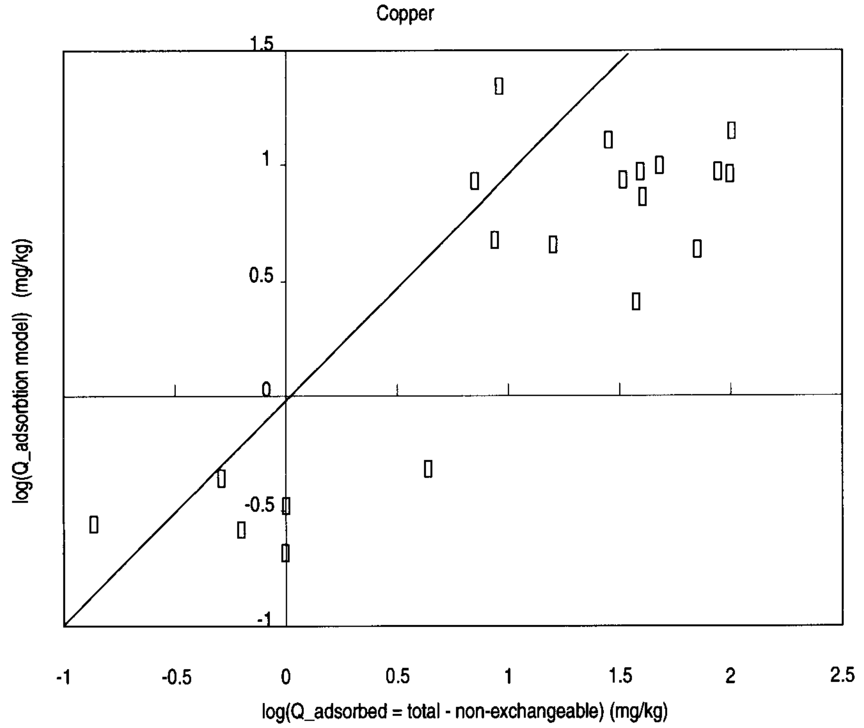

Figure II.2 (Adapted from Janssen et al., 1996). Field adsorption (x) vs. laboratory-based model (y) for Copper. Points *below* the 1:1 line indicate lower adsorbed concentrations calculated by the lab-based model *given* observed field porewater concentrations, i.e. a relatively low porewater concentration in the field.

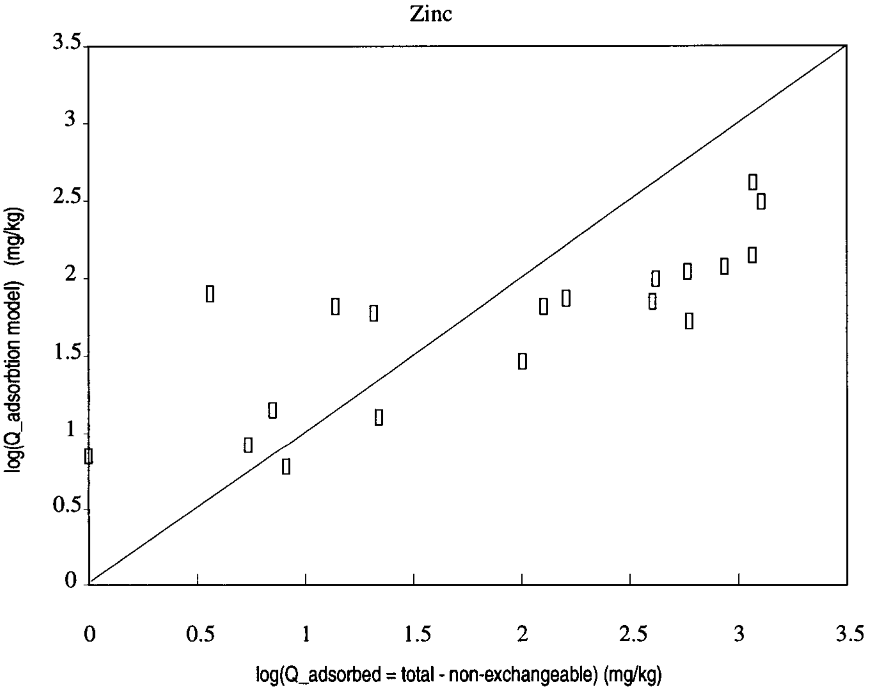

Figure II.3 (Adapted from Janssen et al., 1996). Field adsorption (x) vs. laboratory-based model (y) for Zinc. Points *below* the 1:1 line indicate lower adsorbed concentrations calculated by the lab-based model *given* observed field porewater concentrations, i.e. a relatively low porewater concentration in the field.

From figures II.1-3 it emerges that systematic differences between laboratory and field are not entirely explained by the non-exchangeable amount in the field. The systematic differences noted by Janssen et al., (1996) are now reduced to a factor 3 (cadmium, copper), and appear to be absent altogether for zinc. Janssen et al. name some factors relating to experimental procedure that might further reduce the difference between the two data sets. *As a first hypothesis, we may assume that (as long as added amounts of metals are considerd), no systematic differences in porewater partitioning between field and laboratory exist.* Such an hypothesis would be consistent with long-term experiments on cadmium sorption by Christensen (1984) which did not show significant differences between initial sorption at a typical laboratory time-scale of hours and long term sorption (35-67 weeks) which would be typical for field conditions

On the other hand, there is evidence in the literature that initial adsorption (after hours-days) gives an underestimate of total adsorption after prolonged periods. Barrow (1986) found an increase in adsorption of Zn of a factor 4-7 after 1000 days. A similar effect is termed hysteresis: after a prolonged period of adsorption, not all metal is released again on desorbtion. This implies that part of the metal does not participate in short-term partitioning, which would make field-porewater concentrations lower than calculated from short-term lab experiments. Amacher et al (1988) found that soils released 5-65% of adsorbed Cd and 2-50% of adsorbed Cr after 14 days of adsorption. Ainsworth et al. (1994) found hysteresis for adsorption to amorphous iron oxide (which is an important part of the soil adsorption complex for some soils) at low pH after 16 weeks of "aging", ranging from 20% for Cd and 53% for Co. These data are consistent with the lower field porewater concentrations in figures II.1-2, and lead to the second possibility: *there is evidence that field porewater concentrations are a factor 2-5 lower than would be calculated from short-term partitioning data.*

Although there are hypotheses about the nature of this "aging" effect (Ainsworth et al., 1994), the available data do not permit a detailed analysis. For cadmium and copper, there appears to be a constant factor between field and lab, for zinc there seems a concentration-dependent effect, but it must be emphasized that the graphs III.1-3 are the results of a rather delicate edifice of assumptions and models, making any inference highly uncertain. In the calculations we will simply use an "aging factor" of 0.2-1.0 to multiply field porewater concentrations relative to calculated lab values.

Combining the non-exchangeable fraction (Appendix IV) with the coefficients in table II.2 and the "aging coefficient" we are able to standardize both field and laboratory data to porewater concentrations in order to calculate a PAF.

Organic matter referencing of metals

A relatively small subset of the organisms in appendix I (± 10%) is exposed to metals via food uptake. For this group it is necessary to calculate the metal content of their food, i.e. the soil organic matter. For this purpose we would need data on the partitioning of total metal content of the soil over mineral and organic phases. Unfortunately, these appear to be absent and some assumptions are required to arrive at an estimate. Two approaches will be followed: an analysis of metal adsorption isotherms and of the cation exchange capacity (CEC).

Equation (II.2) is nonlinear and the clay and organic matter contributions occur in a multiplicative fashion: metal adsorption is proportional to

$$\mathrm{OM}^c\ \mathrm{clay}^d \qquad \text{(II.3)}$$

which makes the relative contributions of OM and clay dependent on their relative contents[3]. If we linearize the equation (defining the contribution of OM as $\partial M_{adsorbed}/\partial OM$) for a standard soil with 25% OM and 10% clay we can calculate the ratio of relative contributions by clay and OM as[4]:

$$r = 2.5\ d/c \tag{II.4}$$

In addition to the nonlinear adsorption model we used the linear sorption models by Van de Meent et al. (1990); these do not require the assumption of a standard soil.

Numerous equations exist to describe CEC as a function of soil properties. CEC is closely related to metal adsorption (metals are cations, CEC also plays an important role in empirical regressions for metal adsorption, see Reinds et al., 1995 and Elzinga et al., 1996). Although the two are not identical, we will use the relative contribution of OM to total-CEC as an approximation to the contribution of OM to metal adsorption. Empirical models for the CEC are generally of the form[5]:

$$CEC = p\ clay + q\ OM \tag{II.5}$$

For our purpose we do not need to know CEC, but only relative contributions. Hence we can again define:

$$r = p/q \tag{II.6}$$

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[3] As can be seen from equation (II.2), it gives the curious prediction that there is **no** metal adsorption in the absence of either OM or clay, even though the other fraction may be abundantly present....

[4] The relative contirbution of clay is proportional to OM:clay ratio, hence the factor 2.5 for the standard soil.

[5] Helling et al. (1964) use a (small) non-zero intercept; this was set to zero. Konsten and Sarwani (1990) describe heavy clay soils and give a relation with OM only; their intercept has been assigned to the clay fraction. Some references use organic carbon rather than organic matter. This was converted as OC = 0.6 OM.

Table II.3 Relative contributions of clay relative to organic matter in metal adsorption (eqs. II.3-6).

r	reference
1.5	Cd, median values from table II.2
< 0	Cu, median values from table II.2
0.62	Pb, median values from table II.2
3.12	Zn, median values from table II.2
0.33	Cd, Van de Meent et al. (1990)
0.5	Cu, Van de Meent et al. (1990)
0.5	Pb, Van de Meent et al. (1990)
2.0	Zn, Van de Meent et al. (1990)
0.0	Cd, Lee et al. (1996)
1.02	CEC, Helling et al. (1964), pH=2.5
0.61	CEC, Helling et al. (1964), pH=3.5
0.41	CEC, Helling et al. (1964), pH=5.0
0.42	CEC, Helling et al. (1964), pH=6.0
0.36	CEC, Helling et al. (1964), pH=7.0
0.29	CEC, Helling et al. (1964), pH=8.0
0.20	CEC, Breeuwsma et al. (1986) B-horizons of Haplaquods
0.33	CEC, Breeuwsma et al. (1986) other soil horizons and/or units
0.25	CEC, Konsten and Sarwani (1990)

The various methods broadly agree in their results, although adsorption-based values are more variable. It appears that the ratio **r** may be metal-specific: for example it seems relatively low for copper and high for zinc. The data in table II.3 are not sufficient to draw any firm conclusions on this aspect. A general ratio for all metals of 0.4 (median) with a range of [0,2] (i.e., excluding the two extreme values <0 and 3.62) may be used.

Appendix III. Calculation of soil concentrations of pesticides in non-agricultural areas

Introduction

The toxicological impact of the use of pesticides is obviously most pronounced in the intended target areas. However, the observation that, for example, an insecticide does in fact kill most of the insects in a sprayed field is rather trivial. Moreover, from an ecological viewpoint, such *planned* effects would be of little concern *as long as the effects are confined to the intended area and period of time*. In the present project we have therefore focused on pesticide effects in non-agricultural areas. For water, the analysis could be based on measurements (described elsewhere), for soil the analysis had to be based on model calculations due to a lack of direct measurements.

The main transport route from an agricultural field to a non-agricultural area is by volatilization. A more direct route from the drift of droplets during spraying is of importance for field margins and ditches (and due to downstream transport to other water bodies), but has negligible impact on soils at a distance of more than 10-100 metres. The transport route we will consider in this appendix is therefore:

volatilization → atmospheric transport → deposition

Combining deposition flux with a leaching and decay in the soil we are able to derive a concentration in the upper soil layer, which in turn may be used to calculate a toxic pressure in terms of PAF. In this appendix we will discuss the selection of substances and calculations of emissions, transport and soil concentrations.

Selection of pesticides

The basis for the analysis is an overview of 180 agricultural pesticides. This number is too large to perform detailed calculations, so that a selection has to be made. As a first screening, total use per compound (Van der Linden, pers. comm.) was divided by LC_{50} (see appendix I for toxicity data), resulting in three values for the "toxic equivalents" per compound (for fish, crustaceans and algae). These toxic equivalents showed a strongly skewed distribution: in all cases, the first 10 compounds usually comprised > 99% of the total. Combining the three groupings a first selection of 47 substances was made (table III.1).

For the next selection step, the SimpleBox model (Brandes et al., 1996) was used which describes partitioning over soil, water and air in two nested boxes: one for the Netherlands and one for the rest of Europe. In this screening round, the assumption was made that pesticides were applied at the same rate per hectare agricultural land in the rest of Europe as in the Netherlands. Chemical properties were collected (table III.1) that allow a calculation of volatilization, atmospheric tarnsport, decay and deposition and the resulting porewater concentration in Dutch non agricultural soil.

Table III.1 Chemical, physical and microbiological properties of 47 compunds as used in the second screening level and SimpleBox results for porewater concentrations in non-agricultural soils in the Netherlands. The last column gives foreign contribution to total concentration.

Compound name	Mol. weight	log Kow	Vapor pressure	Solubility	Melting point	Henry	DT50 soil	DT50air	DT50 water	DT50 sediment	Porew. Conc.	Foreign
	g/mol	[-]	Pa	mg/l	oC	[-]	days	days	days	days	g/l	(-)
2,4-D	221.0	2.81	1.10E-02	7.60E+02	140.5	1.4E-09	8.0	1.7	4.0	4.0	2.16E-14	0.001
aldicarb	190.3	1.13	1.30E-02	6.16E+03	99.5	2.2E-07	2.4	0.6	6.0	6.0	1.34E-10	0.105
amitraz	293.4	6.50	3.40E-04	9.40E-02	87.0	4.3E-04	0.2	0.1	0.2	0.2	6.36E-26	0.119
atrazine	215.7	2.60	4.00E-05	3.00E+01	175.8	1.2E-07	50.0	0.1	18.0	85.0	1.74E-10	0.056
azinphos-methyl	317.3	2.75	1.00E-06	2.75E+01	73.5	2.2E-04	52.0	0.1	1.8	1.8	6.64E-13	0.129
benomyl	290.3	2.42	5.00E-09	3.90E+00	140.0	2.0E-10	67.0	0.0	18.3	56.0	1.96E-14	0.065
bifenthrin	422.9	6.00	2.40E-05	1.00E-01	69.3	4.1E-02	219.0	0.3	8.0	251.0	1.65E-16	0.302
captan	300.2	2.35	1.00E-03	3.70E+00	178.0	2.4E-04	1.0	0.1	1.0	1.0	1.04E-14	0.096
carbendazim	191.2	1.52	1.00E-06	7.50E+00	304.5	2.5E-06	197.5	0.1	410.5	171.5	6.25E-09	0.360
chlorfenvinphos	359.6	3.80	5.30E-04	9.50E+01	-21.0	3.5E-08	36.0	0.2	7.0	33.5	1.58E-14	0.029
chlorothalonil	265.9	2.88	7.60E-05	6.00E-01	250.5	1.4E-05	10.0	1726.4	5.8	5.8	2.15E-12	0.739
chlorpyriphos	350.6	5.04	2.50E-03	1.18E+00	42.8	5.0E-04	94.0	0.1	18.8	80.0	1.12E-16	0.275
deltamethrin	505.2	5.80	4.00E-08	2.00E-03	101.0	5.1E-03	25.0	0.3	3.0	4.0	6.96E-18	0.272
diazinon	304.4	3.95	1.45E-02	4.00E+01	5.0	4.5E-02	21.0	0.1	11.0	11.0	1.11E-14	0.163
dichlorvos	221.0	1.90	1.60E+00	1.00E+04	5.0	1.8E-05	2.0	1.2	0.4	0.4	1.08E-12	0.543
dienochlor	474.6	3.30	1.00E-03	2.50E-02	122.5	2.2E-04	22.6	9.6	16.9	16.9	4.79E-14	0.783
dinoterb	240.2	3.74	1.50E-04	4.50E-01	125.8	3.3E-05	9.8	17.4	17.3	86.5	2.46E-14	0.741
diquat-dibromide	344.1	-4.60	1.00E-05	7.18E+05	300.0	2.0E-05	1000.0	0.3	34.1	880.0	2.36E-08	0.495
diuron	233.1	2.82	2.30E-07	3.85E+01	157.0	9.2E-07	94.0	0.3	29.0	27.5	8.45E-11	0.313
DNOC	198.1	2.39	8.70E-03	1.30E+02	84.0	5.5E-06	8.5	51.7	17.3	31.5	2.51E-11	0.650
esfenvalerate	419.9	6.20	3.50E-05	2.00E-03	59.6	3.0E-03	108.0	0.3	19.0	83.5	1.29E-17	0.293
ethofumesate	286.3	2.70	8.60E-05	8.00E+01	70.0	3.6E-07	37.0	0.2	13.0	2.0	1.86E-11	0.148
fenbutatinoxide	1052.7	5.20	8.50E-08	5.00E-03	138.5	2.0E-04	365.0	0.3	23.3	319.5	5.66E-15	0.360

Table III.1 Chemical, physical and microbiological properties of 47 compunds as used in the second screening level and SimpleBox results for porewater concentrations in non-agricultural soils in the Netherlands. The last column gives foreign contribution to total concentration.

Compound name	Mol. weight	log Kow	Vapor pressure	Solubility	Melting point	Henry	DT50 soil	DT50air	DT50 water	DT50 sediment	Porew. Conc.	Foreign
	g/mol	[-]	Pa	mg/l	oC	[-]	days	days	days	days	g/l	(-)
fenitrothion	277.2	3.60	8.00E-04	3.00E+01	3.4	3.0E-06	28.0	0.2	12.0	12.0	2.99E-15	0.220
fentin-acetate	409.0	3.43	1.80E-04	1.57E+01	122.0	5.0E-06	46.0	0.3	7.0	37.6	2.84E-12	0.318
fluazinam	465.1	5.70	5.10E-06	3.96E-01	100.0	9.7E-06	107.0	0.2	19.0	91.5	1.41E-16	0.218
lambda-cyhalothrin	449.9	7.00	2.00E-07	5.00E-03	49.2	7.4E-06	41.0	0.2	5.0	33.2	1.85E-22	0.232
lindane	290.9	3.85	2.20E-02	7.30E+00	112.5	6.1E-05	1406.0	7.9	36.0	1239.4	6.84E-11	0.751
malathion	330.3	2.89	5.30E-04	1.45E+02	2.9	4.8E-05	1.0	0.2	1.0	1.0	7.43E-17	0.205
maneb	265.3	0.01	9.70E-08	1.00E-04	198.0	1.0E-04	56.0	0.3	18.1	46.4	1.31E-06	0.501
MCPA	200.6	2.68	2.00E-04	1.50E+03	159.8	1.1E-08	15.0	0.9	17.4	10.2	3.81E-12	0.013
mecoprop	214.6	2.26	3.10E-04	6.20E+02	94.5	1.4E-09	11.0	0.6	17.4	6.6	1.67E-12	0.006
metam-sodium	129.2	-5.00	1.00E-05	7.22E+05	300.0	7.2E-12	0.0	0.3	17.2	0.0	2.23E-16	0.005
metamitron	202.2	0.83	2.00E-06	1.82E+03	166.6	4.5E-07	30.0	0.3	19.0	23.4	2.37E-08	0.254
methabenzthiazuron	221.3	1.98	1.50E-05	6.00E+01	120.0	2.0E-06	135.0	0.3	90.0	135.0	2.79E-09	0.380
metolachlor	283.8	3.13	1.70E-03	5.30E+02	5.0	3.7E-07	101.0	0.2	34.0	34.0	2.22E-11	0.132
metribuzin	214.3	1.65	5.80E-05	1.20E+03	126.0	4.3E-09	34.0	0.3	27.0	27.0	5.01E-11	0.013
mevinfos	224.1	0.55	2.22E-01	6.00E+05	14.0	6.0E-08	1.2	0.1	5.0	18.5	5.1E-12	0.031
monolinuron	214.6	2.20	6.00E-03	5.70E+02	81.5	9.3E-07	50.0	0.3	18.0	41.1	2.55E-10	0.217
parathion	291.3	3.81	5.00E-03	2.40E+01	6.1	2.5E-04	49.0	0.1	3.5	4.3	2.27E-14	0.221
permethrin	391.3	6.50	4.50E-05	2.00E-01	40.5	3.6E-05	13.0	0.3	23.0	23.0	4.2E-21	0.287
pirimicarb	238.3	1.48	4.00E-03	2.70E+03	90.5	1.4E-07	108.0	0.0	19.0	92.4	4.86E-09	0.049
propachlor	211.7	1.80	3.10E-02	6.13E+02	77.0	4.3E-06	5.2	0.5	4.5	4.5	4.52E-11	0.355
simazin	201.7	2.18	8.00E-07	4.25E+00	226.0	1.6E-08	58.0	0.1	45.5	48.2	9.42E-11	0.044
terbutryn	241.4	3.50	2.00E-04	2.35E+01	104.5	8.6E-07	74.0	0.1	27.0	27.0	2.41E-13	0.130
thiram	240.4	1.82	3.20E-03	3.00E+01	155.5	3.3E-07	18.0	0.0	12.8	12.8	1.71E-10	0.050
tolylfluanid	347.2	4.48	8.80E-05	1.08E+00	96.0	1.9E-05	1.0	0.1	14.0	1.0	6.13E-19	0.207

Again, calculated porewater concentrations were scaled to toxicity and the results ranked. A new selection was made that combined the most toxic compunds in each group of organisms. In addition some compounds that were included in the water compartment were added to the list.

Table III.2 Selected agricultural pesticides and codes

name	code	name	code
2,4-D	twvd	maneb	mane
atrazine	atra	mecoprop	meco
azinphos-methyl	azin	metamitron	memi
bentazon	bent	methabenzthiazuron	mbtz
carbendazim	carb	metribuzin	metr
dichlorvos	dchv	mevinfos	mevi
diquat-dibromide	diqu	monolinuron	moli
diuron	diur	parathion	para
DNOC	dnoc	simazin	sima
fentin-acetate	ftin	thiram	thir
lindane	lind	trifluralin	trif

Chemical and physical properties

For the selected compounds, a more intensive survey of properties was conducted (J. Bakker, pers. comm.), in some case leading to a revision of earlier estimates. In addition some properties were required for the calculation of emissions (distribution over landuse categories) and deposition (scavenging ratio, effective deposition velocity and particulate fraction).

The atmospheric behaviour of the compounds may be complex, consisting of a balance between deposition (wet an dry) and re-emission (volatilization). The OPS-model (Van Jaarsveld 1989, 1995) that was used to calculate spatially explicit depositions is able to deal with one-way fluxes only (either emission or deposition), so that the balance of the two has to be expressed as a net flux or (if we divide this flux by gaseous concentration) an *effective deposition velocity*[1]. For wet deposition the situation is simpler; here the main factor is the ratio of concentration in rain to that in air (scavenging ratio). Effective deposition velocities and scavenging ratios were calculated by Van Jaarsveld and Van Pul (pers. comm) with the DEPASS model (table III.4). The method as used in this report is similar to that followed by Baart et al. (1995).

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[1] Note that this effective deposition velocity concerns gaseous substances only, or in case of compounds with mixed behaviour, the gaseous fraction. If there is wet deposition, there may be a net upward flux in gaseous form: this leads to a *negative effective deposition velocity*. In practice, the OPS deals with this by setting Vd_{eff} to zero.

Table III.3 Description of chemical and physical properties for calculations of soil concentrations of the pesticides in table III.2

molwt	molecular weight
vap.prs	vapour pressure (at room temperature)
Henri	dimensionless Henri-coefficient
log(Kow)	10log of octanol-water partitioncoefficient
log(Koc)	10log of soil organic carbon - water partition coefficient
t1/2_l	Half-life in air. This property was only used for gaseous dispersal. Particulate bound compounds are assumed to be refractory.
t1/2_s	Half-life in soil.
vdeff	Effective deposition: results of DEPASS model.
Scav.rat.	Scavenging ratio, being the ratio of concentration in rain to that in air.
fpart.	Fraction of the compound bound to particles
fgrs, fara, fpcr	Fraction of the compound being applied to grassland, arable land or permanent crops (fruit and others), respectively. These fractions are required to distribute country totals for European countries (with the exception of the Netherlands) within a country on the basis of landuse.
Mpoint	melting point
Hvapor	Heat of vaporization
Hsolub	Heat of solution
Pdept	Effective depth over which a compound is mixed after application. This column usually reads -1, in which case this depth is calculated by SimpleBox as a function of decay, leaching and evaporation fluxes.
period	Application period. To obtain a soil content the total deposition has to converted to a flux. If the substance is applied during May-July, the application period is set to 90 days and daily deposition is 1/90 of total (yearly) deposition

Table III.4 Properties of pesticides as collected by J.Bakker from various sources (Linders et al., 1994; RIZA, 1996; ARS Pesticides Properties Database) and results of DEPASS calculations by Van Pul and Van Jaarsveld (Pers. Comm.) based on these values. For a description of pesticide codes see table III.2, for properties see III.3.

code	molwt	vap.prs	solub.	Henri	log(K_{ow})	log(K_{oc})	$t_{1/2}$_l	$t_{1/2}$_s	vd_{eff}	Scav	fpart.	fgrs	fara	fpcr	M_{point}	H_{vapor}	H_{solub}	P_{dept}	period
	g/mol	Pa	g/m3	[-]	[-]	[-]	hours	hours	cm/s	rat.	[-]	[-]	[-]	[-]	oC	Kj/mol	Kj/mol	m	(days)
twvd	221	1.10E-03	7.60E+02	4.80E-08	2.81	1.60	55.2	192	1.000	7.20E+05	0.010	0.22	0.20	0.58	140.5	50	10	-1	90
atra	215.7	4.00E-05	3.00E+01	1.20E-07	2.60	2.08	0.88	1200	0.700	7.30E+05	0.200	0.00	1.00	0.00	175.8	50	10	-1	60
azin	317.3	1.00E-06	2.75E+01	3.06E-08	2.75	3.16	0.89	1248	0.180	7.20E+05	0.890	0.00	0.80	0.20	73.5	50	10	-1	180
bent	240.3	1.70E-04	5.00E+02	1.00E-8	0.62	0.22	9999	1152	0.100	6.90E+05	1.000	0.04	0.96	0.00	138.0	50	10	-1	60
card	191.2	1.00E-06	7.50E+00	1.03E-08	1.52	1.90	0.6	4740	0.150	7.30E+05	0.890	0.00	0.70	0.30	304.5	50	10	-1	240
dchv	221	1.60E+00	1.00E+04	1.81E-05	1.90	2.15	37.1	48	0.040	1.40E+05	0.000	0.00	0.00	1.00	5.0	50	10	-1	240
diqu	344.1	1.00E-05	7.18E+05	1.93E-12	5.07	5.07	48	24000	0.130	7.20E+05	0.470	0.00	1.00	0.00	300.0	50	10	-1	30
diur	233.1	2.00E-04	3.85E+01	4.08E-07	2.82	2.60	3.77	2256	0.100	6.90E+05	0.050	0.00	0.30	0.70	157.0	50	10	-1	30
dnoc	198.1	8.70E-03	1.30E+02	5.50E-06	2.39	1.60	619.9	204	-0.050	3.90E+05	0.001	0.00	1.00	0.00	84.0	50	10	-1	60
ftin	409	1.80E-04	1.57E+01	5.00E-06	3.43	3.35	137	1104	-0.040	4.30E+06	0.060	0.00	1.00	0.00	122.0	50	10	-1	150
lind	290.9	2.20E-02	7.30E+00	6.10E-05	3.85	3.03	252.6	33744	-0.040	4.10E+04	0.000	0.00	0.56	0.44	112.5	50	10	-1	60
mane	265.3	9.70E-08	1.00E-04	1.04E-04	2.61	2.38	4	1344	-0.500	1.00E+06	0.990	0.00	0.93	0.07	198.0	50	10	-1	150
meco	214.6	3.10E-04	6.20E+02	1.40E-04	2.26	3.10	19.7	264	1.100	7.20E+05	0.030	0.00	1.00	0.00	94.5	50	10	-1	90
memi	202.2	2.00E-06	1.82E+03	4.50E-07	0.83	2.26	3.52	720	-0.420	6.10E+05	0.800	0.00	1.00	0.00	166.6	50	10	-1	60
mbtz	221.3	1.50E-05	6.00E+01	2.23E-08	1.98	2.83	3.95	3240	0.620	7.00E+05	0.380	0.00	1.00	0.00	120.0	50	10	-1	60
metr	214.3	5.80E-05	1.20E+03	4.30E-09	1.65	1.78	3.6	816	0.930	7.20E+05	0.150	0.00	1.00	0.00	126.0	50	10	0.2	60
mevi	224.1	2.22E-01	6.00E+05	6.00E-08	0.55	0.20	4	28.8	1.010	7.20E+05	0.000	0.00	0.87	0.13	14.0	50	10	-1	90
moli	214.6	6.00E-03	5.70E+02	9.30E-07	2.20	2.51	3.43	1200	-0.050	6.30E+05	0.010	0.00	1.00	0.00	81.5	50	10	-1	60
para	291.3	5.00E-03	2.40E+01	2.50E-04	3.81	3.47	1.43	1176	-0.020	2.30E+04	0.020	0.41	0.57	0.02	6.1	50	10	-1	120
sima	201.7	8.00E-07	4.25E+00	1.60E-08	2.18	2.00	2.5	1392	0.080	7.00E+05	0.990	0.00	0.39	0.61	226.0	50	10	-1	60
thir	240.4	3.20E-03	3.00E+01	3.30E-07	1.82	2.81	0.4	432	0.350	7.10E+05	0.020	0.00	0.07	0.93	155.5	50	10	-1	30
trif	335.3	9.50E-03	3.20E-01	2.19E-03	4.83	3.81	103	2208	-0.005	7.90E+03	0.010	0.00	1.00	0.00	49.0	50	10	-1	150

Pesticide Use

Pesticide use for the Netherlands was based on municipal data. The method to assign national consumption data to municipalities on the basis of landuse (ISBEST data base) has been described by Merkelbach and Lentjes (1993); estimated use per municipality for 1993 was kindly provided by Merkelbach (pers. comm.)[2]. The data were assigned to the centre of each municipality (fig. III.1), which gives a resolution comparable to the 5 x 5 km receptor grid (discussed below).

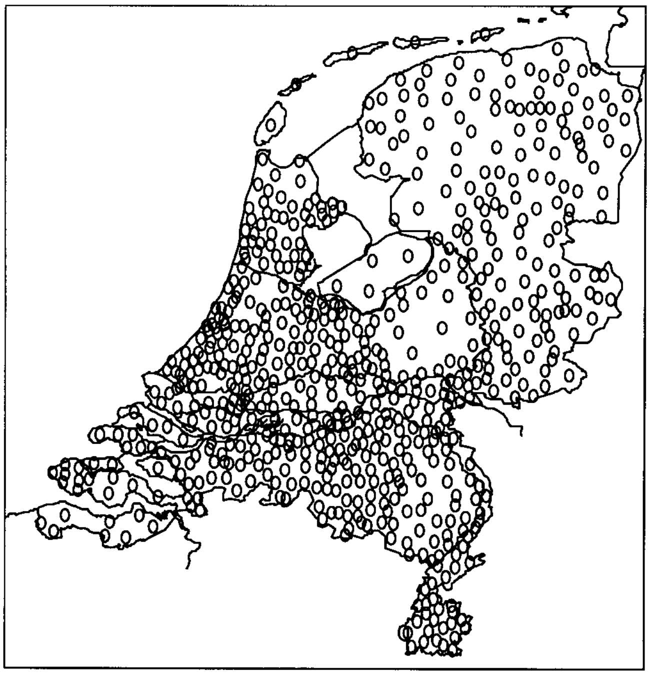

Figure III.1 The midpoints of the municipalities used as emission points in the Neteherlands

Recent foreign use data are available on an aggregated level only (totals for insecticides, herbicides, etc.). To obtain an estimate per compound, the following steps were followed:

(1) For most compounds we know the use per hectare in the Netherlands (Merkelbach and Lentjes, 1993). We have assumed that foreign specific use is the same. Obviously, this assumption becomes less tenable as we move further from the Netherlands (other agro-economic factors, other climate), but then the impact on calculated Dutch depositions will become less pronounced as well. Using FAO statistics (FAO, 1996) on crop area (or, in some cases total production) a total could be calculated for most countries and substances. By means of a check this was done also for the Netherlands: the estimated totals were in reasonable agreement with ISBEST totals[3]. Only in two cases pronounced differences (defined as < 1/5 or > 5 times the ISBEST total) occured: dichlorvos and atrazine. In the latter case the reason appears to be that the FAO category "maize" (corn) refers only to corn for human consumption: the actual

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[2] Trifluralin does not occur in the ISBEST database. A Dutch total use is mentioned by Teunissen-Ordelman and Schrap (1996); this was distributed over municipalities by scaling to average herbicide use.

[3] Clearly, this "check" is largely a circular argument: we are only able to check wether the ISBEST crop-categories agree with the (generally coarser) FAO classification.

maize area in the Netherlands (which is largely used as fodder) is much larger than the area reported by FAO.

(2) For compounds for which the first method did not work (large deviations mentioned above; compounds not described by Merkelbach and Lentjes, 1993) the use per category (herbicides, insecticides) was scaled to totals as reported by OECD (1995). For example: if substance X forms 13% of total herbicide use in the Netherlands, it is assumed to make up 13% of herbicide use in France, Germany, etc.

(3) OECD does not give totals for all European countries: in these cases the use is scaled to landuse in three classes: grassland, arable land and permanent crops. For example: if substance Y is used at a rate of 0.07 kg/hectare total arable land in the Netherlands, then also 0.07 kg/ha in Romania.

The method used for each substance and country is given in table III.5.

Table III.5. Method of estimating pesticide use of European countries. Meaning of codes: 1: use of ISBEST approximation. (use per hectare for specific crop types; FAO categories); 2: scaled to country-totals of Herbicides/Pesticides according to OECD. 3: Similar approach, but based on generalized land-use categories (arable land, permanent crops, grassland).

country	code	twd	atra	bent	card	dchv	diqu	diur	dnoc	flin	lind	mane	meco	memi	mbtz	metr	mevi	moli	para	sima	thir	trif
Albania	101	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Armenia	102	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Austria	104	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Azerbaijan	105	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Belgium-Lux	199	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Belarus	108	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Bosnia Herze.	124	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Bulgaria	107	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Croatia	109	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Czech Rep	110	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Denmark	111	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Estonia	112	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Finland	114	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
France	115	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Germany	116	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Georgia	117	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Greece	118	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Hungary	119	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Iceland	120	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Ireland	113	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Italy	121	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Latvia	126	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Lithuania	123	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3

Macedonia	152	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Malta	150	1		1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Moldova Rep	127	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Netherlands	128	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Norway	129	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Poland	130	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Portugal	131	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Romania	133	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Russian Fed.	132	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Slovekia	144	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Slovenia	146	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Spain	135	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Sweden	137	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Switzerland	138	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Turkey	139	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
UK	141	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Ukraine	140	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3
Yugoslavia Fed Rep	143	1	3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3

Country totals were distributed over landuse classes as indicated in table III.4, using the European Landuse Map on a $^1/_6$ x $^1/_6$ degree grid (Van de Velde et al., 1994). The map has been converted to a stereographic projection around Amersfoort in the centre of the Netherlands, and resolution was decreased as a function of distance to the reception area.

Emission grids were generated separately for the Netherlands, EU-Europe and Non-EU Europe. This allows calculation of the three contributions to total depositon in the Netherlands.

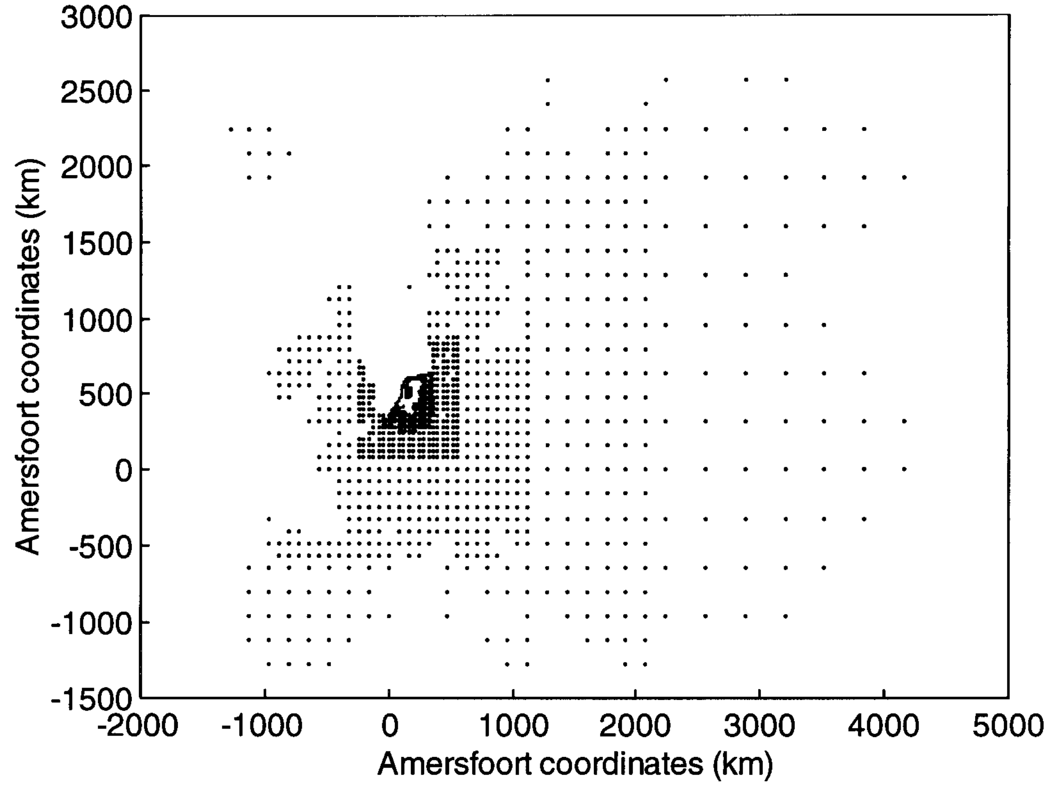

Figure III.2 Map of Europe in stereographic projection around the centre of the Netherlands showing aggregation of emission points.

Deposition was calculated on a 5 x 5 km grid. Because only non-agricultural and non-urban areas were of interest, only grid cells with ≥ 10% natural area were taken into consideration.

Emission factors and calculation of soil concentrations

The uncertainty in atmospheric emission from volatilization is one of the main factors that determine total uncertainty in estimated pesticide concentrations. For this reason, a range of emission factors (expressed as a fraction of total applied dose) was used based on two estimates.

The first estimate is based on the emission factors used in the "Emission Assessment" report (Woittiez et al., 1996), based on vapour pressure only[4]. A second estimate is based on the SimpleBox model (Brandes et al., 1996), which combines vapour pressure with other chemical and physical properties of the compund (soil

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[4] In the Emission Assessment report, emission factor is given as a function of vapour pressure in separate classes. For the present report, a smooth curve was fitted through the middle of each class.

partitioning, vertical transport, decay). In nearly all cases, the first estimate is higher than the second estimate; in some cases, the first estimates was deemed unrealistic and an upper limit based on expert judgement (Van de Linde, pers. comm.) was set.

Table III.6 Minimum and maximum emission factors (fraction). The columns "Simplebox" were calculated using the chemical properties in table III.4 in the SimpleBox 2.0 model (Brandes et al., 1996); the VP columns refer to the estimate based on vapour pressure classes described by Woittiez et al. (1996). In the cases labeled with an asterix an alternative upper limit was applied.

name	SimpleBox	VP	name	SimpleBox	VP
twvd *	1.29E-03	5.00E-02	mane	8.10E-03	5.08E-04
atra	5.31E-03	5.33E-02	meco *	8.42E-05	5.00E-02
azin	1.55E-03	3.14E-03	memi	1.50E-02	5.39E-03
bent	2.28E-08	1.49E-01	mbtz	2.17E-03	2.55E-02
card	1.22E-03	3.14E-02	metr *	7.20E-05	1.00E-02
dchv	7.13E-03	9.96E-01	mevi	3.67E-03	9.79E-01
diqu	4.71E-08	1.87E-02	moli	1.35E-02	7.39E-01
diur	1.05E-02	1.65E-01	para *	6.24E-04	5.00E-02
dnoc *	7.24E-03	5.00E-02	sima	1.42E-03	2.64E-03
ftin *	2.58E-03	5.00E-02	thir	1.01E-02	6.34E-01
lind	2.68E-03	8.87E-01	trif	1.82E-04	8.02E-01

Emissions could now be calculated from use per grid cell and emission factor. For deposition two runs with the OPS were performed and total deposition calculated as:

deposition = fpart * [total deposition of the compound as particles] +
(1-fpart) * [total deposition of the compound as gas]

In order to arrive at a soil concentration in the upper 20 cm, the deposition (in g.m^{-2}) has to converted to a flux (in g.m^{-2}.day^{-1}). At this point it is assumed that application rate is constant through the application period (table III.4), and that the application is synchronous in the different source areas. As a result of input, decay and leaching the concentration will rise during the application period (possibly attaining steady state), and decay afterwards. For persistent compounds, the concentration at the start of the application period may be non-zero. Chronic toxicity tests are most commonly performed during 28 days; for this reason, the soil concentration was averaged over the last 28 days before the end of application (i.e. when soil concentrations reach a maximum).

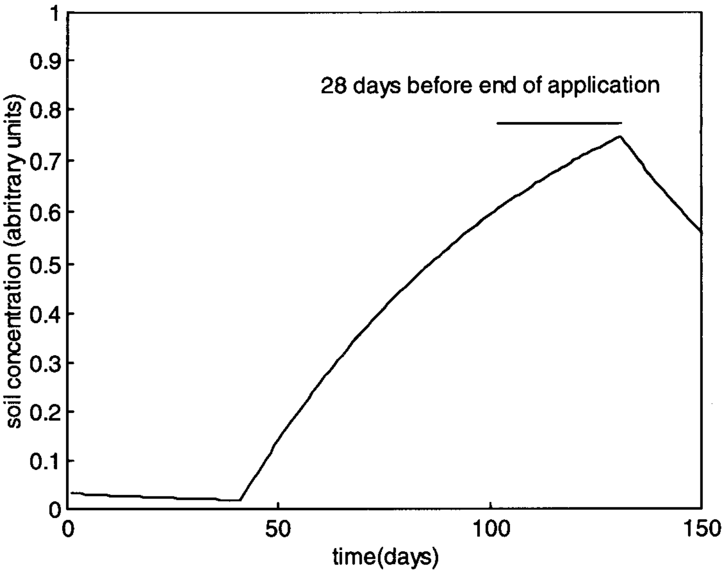

Figure III.3 The soil concentration is a function of time. The model calculates the average concentration during the last 28 days of the emission period.

Results

Calculated depositions and soil concentrations (28-day maxima as defined above) are listed in table III.7. The totals are summed from three sources: the Netherlands, the European Union (without the Neverlands) and the rest of Europe. These sources have been expressed as fractions for each pesticide. It can be observed that for most compounds the dominant source is the Netherlands itself, but for a number of substances sizable fractions or even most of the total originates from abroad. The contribution from non-EU countries is generally small. Uncertainty in the results, and a translation to toxic pressure is given in the main report.

Table III.7 Analysis of sources, median depositions (yearly totals) and median soil concentrations (28-day maxima)

code	Relative contributions from:			deposition	soil conc
	Netherlands	EU	rest Europe	(g/m2/yr)	(mg/kg)
twvd	0.468	0.520	0.011	1.40E-05	5.79E-06
atra	0.908	0.088	0.004	3.03E-05	5.66E-05
azin	0.313	0.555	0.132	3.55E-08	4.41E-08
bent	0.434	0.545	0.021	3.87E-04	4.83E-04
card	0.070	0.845	0.085	8.20E-06	2.07E-05
dchv	0.406	0.583	0.011	1.77E-04	7.05E-06
diqu	0.558	0.411	0.032	3.12E-06	3.96E-04
diur	0.669	0.326	0.005	1.54E-05	4.04E-05
dnoc	0.195	0.670	0.135	2.73E-05	1.76E-05
ftin	0.547	0.362	0.090	2.07E-05	2.67E-05
lind	0.349	0.590	0.061	3.29E-05	2.58E-03
mane	0.718	0.229	0.054	3.00E-05	4.32E-05
meco	0.738	0.259	0.003	8.34E-05	4.85E-05
memi	0.562	0.417	0.021	6.93E-06	1.07E-05
mbtz	0.169	0.787	0.044	1.11E-05	4.32E-05
metr	0.894	0.099	0.008	6.75E-07	1.07E-06
mevi	0.976	0.024	0.000	3.90E-06	2.45E-07
moli	0.717	0.279	0.003	9.65E-06	1.82E-05
para	0.586	0.388	0.026	7.13E-07	1.09E-06
sima	0.453	0.506	0.041	4.06E-07	7.90E-07
thir	0.916	0.082	0.002	6.63E-06	8.28E-06
trif	0.262	0.627	0.111	4.13E-07	8.64E-07

Appendix IV. Natural background levels of metals

Introduction

For the calculation of an anthropogenic Potentially Affected Fraction it is important to know the natural background level of metals. This must be distinguished from "current background" levels, which may include diffuse sources of anthropogenic inputs. For highly polluted local "hot spots", background levels refer to the situation in a comparable (relatively) undisturbed site. In the present context we define "natural background" levels as the original, pristine situation, undisturbed by human activities.

The metal content of the soil can be thought of to com from two sources:

1. Natural levels in certain minerals. These are of geological origin and form a stable part of the soil matrix. If there is any exchange with the soil solution it is a slow process, comparable to the natural weathering of minerals.
2. Levels associated with a certain natural atmospheric input. Part of the atmospheric input is of natural origin (volcanic and continental dust; sea spray); in contrast to the previous fraction this may be considered a mobile fraction and subject to leaching; for a certain input and leaching rate a steady-state concentration will result.

In this appendix we will compare several methods to obtain an estimate of the natural background level for the four metals considered in this study.

Statistical analysis of soil samples from reference sites in the Netherlands

A collection of current background concentrations in the Netherlands was analyzed by Lexmond and Edelman (1992). The same locations were sampled by De Wilde et al. (1992) and Van de Hoop (1995a) who found similar levels; we will follow the original analysis of Lexmond and Edelman, because their sample size was the largest. As already pointed out, current background levels may be influenced by anthropogenic inputs; we may consider them as an upper limit to the natural background levels.

Table IV.1 Coefficients in regression equations for metal contents in the upper soil layer of natural areas (Lexmond en Edelman, 1992). These values are known as "Dutch Reference Values"[1]. The equations read:

$M = a + b\ \mathrm{clay}$ for $\mathrm{OM} < 25\%$
$M = a + b\ \mathrm{clay} + c + d\ \mathrm{OM}$ for $\mathrm{OM} \geq 25\%$

with M -total metal content in mg/kg
clay - weight percentage < 2μm
OM - organic matter in per cent

metal	intercept1 (a)	slope clay (b)	intercept2 (c)	slope OM (d)
cadmium	0.18	0.0047	-0.14	0.016
copper	1.4	0.58	9.3	0.003
lead	17	0.75	0.05	0.90
zinc	17	2.66	-35	1.19

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[1] Note that Dutch Target Values are derived from the same dataset, but represent 90% percentiles of all data and are considerably higher.

In a discussion of their results, Lexmond and Edelman argue that only the clay-related fraction (represented by the term **b clay**) can be considered natural. Natural metal contents of sands (the content of pure sand (zero OM and clay) is represented by the intercept **a**) are negligible, and the organic-matter related fraction can in fact be seen as a dilution effect (also described by Ruppert et al., 1991): if there is a certain input of metal in the upper soil layer (i.e. in g/m^3) this will result in an increase in content with increasing OM, because of the decreasing bulk density of the soil (kg/m^3).

As a first estimate of natural levels we would therefore have M = b clay, with the full equations in table IV.1 as an upper limit.

Non-exchangeable metal contents

Metals are bound to the soil with a variable level of affinity: part of the metal can be removed by shaking the soil with water, with mild salt solutions, a chelating agent (EDTA); a larger amount can be removed using a moderately strong acid (0.1 M HNO_3). Almost complete extraction results from treatment with concentrated acid (HNO_3 or H_2SO_4), a further destruction of the sand fraction by HF finally results in an additional minor increase of the extracted metal. It is hard to identify any of these fractions with immobile metal (i.e. the amount that would not be leached from the soil in a hypothetical situation with zero atmospheric input): this probably depends on soil properties and the history of the sample (age, origin of the metal). However, the difference between the amount extracted by strong acid (i.e. close to the total) and with 0.1 M HNO_3 (which is considerably more acid than any natural soil solution) as a reasonable approximation to this immobile fraction (Peijnenburg, pers. comm.), which we will term "non-exchangeable fraction".

Non-exchangeable metal contents were determined for the soils analyzed by Van den Hoop (1995b) and kindly provided by Peijnenburg. For most metals, close correlations exist between non-exchangeable metal and soil properties, in particular clay content. For lead no relation was found, and only an average can be reported.

Table IV.2 Regression coefficients for non-exchangeable metal content (mg/kg) as M = a + b clay + c OM (with clay, OM in %). Non-significant coefficients set to zero.

metal	a	b	c	r^2
Cadmium	-	0.00303	0.00288	0.734
Copper	-	0.444	-	0.869
Lead	35.03	-	-	-
Zinc	-	2.193	-	0.791

General geochemical data

In the foregoing, we have considered only Dutch soil data. A different perspective is to look at general properties of the parent materials of the soils. Thornton (1996) reviews metal contents of different minerals. The most relevant of these are clays and shales (which we will identify with the clay fraction) and sandstones (which we will identify with the sand fraction). Generally, a wide range in contents is found (a range of 3-10 times the average) and for the present we will use mean values.

The parent material of organic matter is decayed plant material. Some metals have no specific biochemical role, and bioconcentration in plant tissue may be viewed as a passive process. If the soil would contain none of these metals, the plant would neither. Metals in this group include cadmium and lead. Other metals (copper, zinc) do play a significant biochemical role: without any of these in the soil (or an alternative source such as atmospheric deposition), there would be no plants growing at the (hypothetical) site. For these metals, the plant content is not a passive process, but a matter of active uptake. Although it is possible that the soil organic matter does not have a constant content of these metals[2]; as a first approximation the metal contents in living plants (reviewed by Jørgensen 1979) may be taken as an estimate for soil organic matter.

Table IV.3 Metal contents (mg/kg)[3] for different parent materials of soil components (Thornton, 1996). Values are given as ranges (min max) and means. Organic matter values from Jørgensen (1979).

metal	clay	sand	organic matter
cadmium	(0-11) 1.4	0.05	(0.04-10) 3.6
copper	(18-120) 50	2	(1-15) 4.5
lead	(16-50) 20	(1-31) 12	(0.5-8) 2.0
zinc	(18-180) 90	(2-41) 16	(15-190) 40

Natural background atmospheric deposition and resulting soil levels

Metals in the atmosphere are present as microscopic particles which have long residence times and may be transported at an intercontinental scale. This makes it hard to estimate background deposition levels during present-day conditions: even remote sites may experience anthropogenic inputs. Also there is a considerable problem with contamination (Ross, 1987), often leading to overestimates at remote sites[4]. We have estimated background depositions using three data sets.

The first set of data (Injuk et al., 1990) gives deposition to the North Sea. There is a close correlation between both wet and dry deposition and wind direction: the depositions during northern and northwestern winds (i.e., air originating from the Atlantic) are considerably lower (a factor 10 or more) than for air masses form continental or British origin; we will consider de north + northwest depositions to be representative of natural background values.

A second set of data was collected by Arimoto et al. (1985) at Enewetak Atoll in the tropical Pacific. The problem with this site is that it may underestimate natural depositions in the Netherlands: being so remote from continental influences, the contribution of (natural) continental dust may be lower than in the Netherlands.

A third set of data was collected by Ross (1987) in Sweden. Although we used only the two northernmost stations (close to the arctic circle), there may be a substantial anthropogenic contribution at these sites. Ross collected wet deposition data only.

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[2] For example, the nitrogen content of organic matter generally decreases during decay, so that living tissue has a higher N:C ratio than soil organic matter. Contents of essential metals -if in short supply- may behave similarly.

[3] To compare the figures in table IV.3 with previous tables we should consider that the regression coeficients are to be multiplied with percentages. For example, for 100% clay we would have 100x0.44=44 mg/kg non-exchangeable copper according to IV.2, and 50 mg/kg in table IV.3

[4] As an example of probable contamination, Injuk et al (1990) report zinc deposition on a (metal!) gas platform that were a 100 times higher than at North Sea coastal sites.

Table IV.4 Atmospheric depositions (wet + dry) of four metals in remote sites. All data in mg.m^{-2}.y^{-1}. North Sea (Atlantic sector) from Injuk et al. (1990); Enewetak Atoll from Arimoto et al. (1985) and Northern Swedish data (wet deposition only) from Ross (1987)

metal	North Sea	Enewetak	Sweden
cadmium	0.02 + 0.02	0.0035 + nd	0.026
copper	0.09 + 0.11	0.04 + 0.09	0.47
lead	0.60 + 0.76	0.07 + 0.11	1.41
zinc	0.13 + 0.12	0.17 + 0.60	3.55

A comparison between the three data sets (Table IV.4) shows that the depositions from Injuk et al. are generally intermediate between the other sources. We will use these for further calculations.

A simple model can be made to relate atmospheric deposition to steady state soil contents. Under steady state we have a leaching equal to deposition (I). Leaching is equal to precipitation surplus (P_n = rainfall minus evapotranspiration) times porewater concentration (C_p). Porewater concentration can be related to total metal contents (C_t) by the partition coefficient (K_d)

$$C_t = I\, K_d / P_n \qquad \text{(IV.1)}$$

For the present purpose of a -as it will turn out- minor adjustment of the estimated background levels, a simple linear model for K_d by Van de Meent et al. (1990) can be used[5].

Table IV.5 Coefficients to relate K_d (l/kg) to organic matter and clay (in %) as K_d = a + b clay + c OM. From Van de Meent et al. (1990).

metal	a	b	c
cadmium	95	1.7	5.1
copper	225	9	9
lead	1400	28	28
zinc	90	5.4	2.7

For the Netherlands we have a precipitation surplus of approximately 300 mm/yr. Combining this with the inputs in table IV.4 (first column) and the K_d in table IV.5, we obtain steady-state metal concentrations from atmospheric input as a function of organic matter and clay.

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[5] This model may be less accurate than the one by Elzinga et al. presented in Appendix II, but for the present purpose it is probably sufficient, and it has the advantage that combination of factors in eq. IV.1 results in a linear equation which is directly comparable to those in the other tables.

Table IV.6 Coefficients to relate estimated steady state metal contents (mg/kg) from natural atmospheric deposition to organic matter and clay (in %) as M = a + b clay + c OM.

metal	a	b	c
cadmium	0.013	2.3e-4	6.8e-4
copper	0.15	6.0e-3	6.0e-3
lead	6.35	0.13	0.13
zinc	0.075	0.024	0.012

The atmospheric contributions should be added to the non-exchangeable amounts (either from empirical extractions or mineralogical evidence) to obtain a total natural concentration. Comparing table IV.6 with tables IV.2 and IV.3 shows that this correction is minor for all metals except lead.

Synthesis

A summary of the models is given in figure IV.1. For copper the various methods give very similar results, and the models to estimate natural background levels agree to within 10-20%. For the other metals the exchangeable metal based on Peijnenburg's data is generally close to the Lexmond and Edelman model, the Thornton data usually lead to a lower estimate. For lead the Peijnenburg data did not give a significant correlation to any soil properties, and only an average can be given. It can be seen that for low clay contents this average lies above the empirical upper limit, and must be discarded. Using the various estimates (including Lexmond and Edelman's upper limit) we can estimate natural background levels for cadmium, lead and zinc to an accuracy of a factor 2-5.

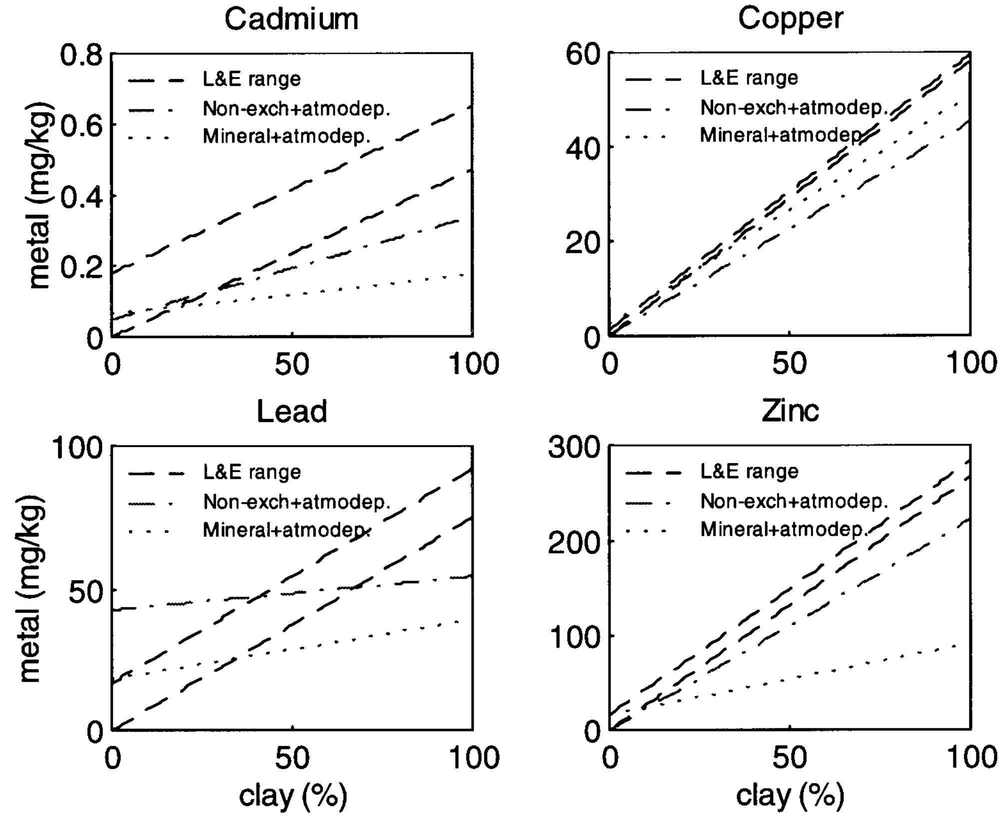

Figure IV.1 An analysis of natural background levels, lines are related to percentage clay, assuming 10% organic matter. The Lexmond and Edelman lines (--) represent an empirical upper limit to the natural background (upper line) and their model of natural (clay-related) background. The other lines combine estimated non-exchangeable metals (-.- from soil analysis and .... from the composition of parent material) with atmospheric contribution.

In view of the uncertainty about non-exchangeable metal and size of the (relatively uncertain) atmospheric input, it seems not worthwile to estimate the latter separately. We will simply use the non-exchangeable amount as a lower bound, and the Dutch Reference Values as an upper bound. The three estimates discussed have been combined in the ranges for this non-exchangeable fraction listed in table IV.7

Table IV.7 Ranges in coefficients to calculate non-exchangeable amount of metal (also used as minimum estimate for natural background level) from soil constituents clay, organic matter and silt + sand. Ranges are set to include uncertainty expressed in previous tables. All units as [(mg.kg^{-1}).(%)$^{-1}$]

		Cadmium	Copper	Lead	Zinc
clay	min	0	0.40	0	0.46
	max	0.017	0.62	0.95	3.10
OM	min	0	0	0	0
	max	0.045	0.056	0.025	0.50
silt+sand	min	0	0	0	0
	max	0.0006	0.025	0.15	0.20

Appendix V: Concentrations in regional waters

Concentrations of heavy metals were provided by RIZA (A.Wilting, personal communication). The same data as used for the Watersysteemverkenningen were taken, and the same procedure for deriving the resulting concentrations in "regional waters" were followed (RWS, 1996), but now the median values were taken in stead of the 90-percentiles (Table V.1).

Table V.1 Median concentrations of heavy metals in "regional waters" as provided by RIZA.

	unit	small streams	ditches	lakes	canals	used
cadmium	ug/L	0.1135	< 0.2076	< 0.1934	< 0.1771	0.11
copper	ug/L	5.8333	2.3979	3.6	4.1979	4.0
lead	ug/L	2.5285	0.9082	0	2.5	1.5
zinc	ug/L	35.8333	13.0497	11.438	14.821	19
suspended matter	mg/L	10		10.025	14.975	15

Table V.2 Concentrations of heavy metals and pesticides in regional waters. Median metal concentrations provided by RIZA. Pesticide data obtained from CIW. Median concentrations of pesticides estimated from CIW data by back-extrapolation.

		n	% ">"	90-p	50-p	est 50-p	Fr disslvd	Used
cadmium	ug/L					0.11	34%	0.04
copper	ug/L					4.0	57%	2.3
lead	ug/L					1.5	9%	0.1
zinc	ug/L					19	38%	7.1
24d	ng/L	759	16%	1000	<	10	great	10
atrazine	ng/L	1599	44%	200	<	11	great	11
afm	ng/L	1723	7%	100	<	6	great	6
bentzn	ng/L	725	28%	600	<	43	great	43
carbazim	ng/L	153	56%	1080	200	132	great	200
dcv	ng/L	2109	39%	360	<	4	great	4
diquat		2	0%					-
diurn	ng/L	288	49%	618	10	33	great	10
DNOC	ng/L	855	9%	300	<	4	great	4
aEndo	ng/L	2724	31%	21	<	1	great	1
tfenSn	ng/L	18	94%	9.3	4	0	great	4
cHCH	ng/L	3597	71%	21	4	3	great	4
maneb								-
mecoprop	ng/L	711	29%	500	<	40	great	40
metamitron								-
Metbtzm	ng/L	377	22%	200	<	11	great	11
metribuzin								-
mev	ng/L	2023	12%	50	<	2	great	2
Monlnrn	ng/L	100	11%	41	<	3	great	3
pare	ng/L	2138	30%	100	<	3	great	3
parm	ng/L	2024	11%	50	<	1	great	1
PCP	ng/L	1276	20%	50	<	2	great	2
simazine	ng/L	1578	41%	500	<	10	great	10
thiram								-
tfa	ng/L	9	0%		<	<		-

Concentrations of pesticides were obtained from CIW (J. Geenen, personal communication). In 1992/1993 an inventory was made of the measurements made by local water quality managers (Geenen and Van der Geest, 1995). In this inventory, results of more than 500 different locations were obtained. For the present purpose, the results were combined. Useful data sets were obtained for 19 different pesticides (table V.2). It was expected that the concentrations of these pesticide would be higher during the growing season than at other times. However, plots of the measurements (generally hundreds of measurements obtained for one chemical at different locations) against the time of sampling did not show distinct periodicity (for an example, see figure V.1).

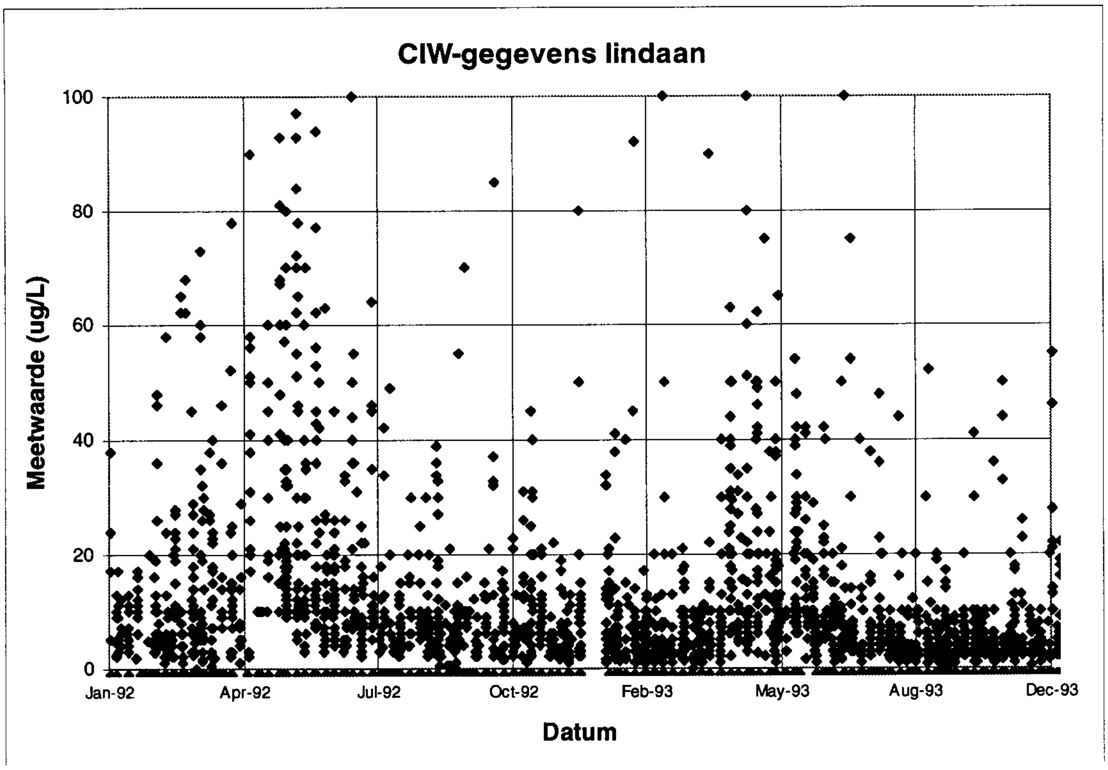

Figure V.1 Measured concentrations (ng/L) of lindane at different locations in regional surface waters in the period 1993-1993; data from CIW.

Therefore, long-term median values of the concentrations at all different locations together were taken as the exposure concentration in "regional waters". A complication was that for only 4 of the 19 pesticides, more than 50% of the measurements were above the detection limit; for the 15 other pesticides, no numeric value for the median could be obtained directly from the measurements, since the medians were "<". In these cases medians were estimated by back-extrapolation of the percentiles of measurements above the detection limit (for an example, see figure V.2).

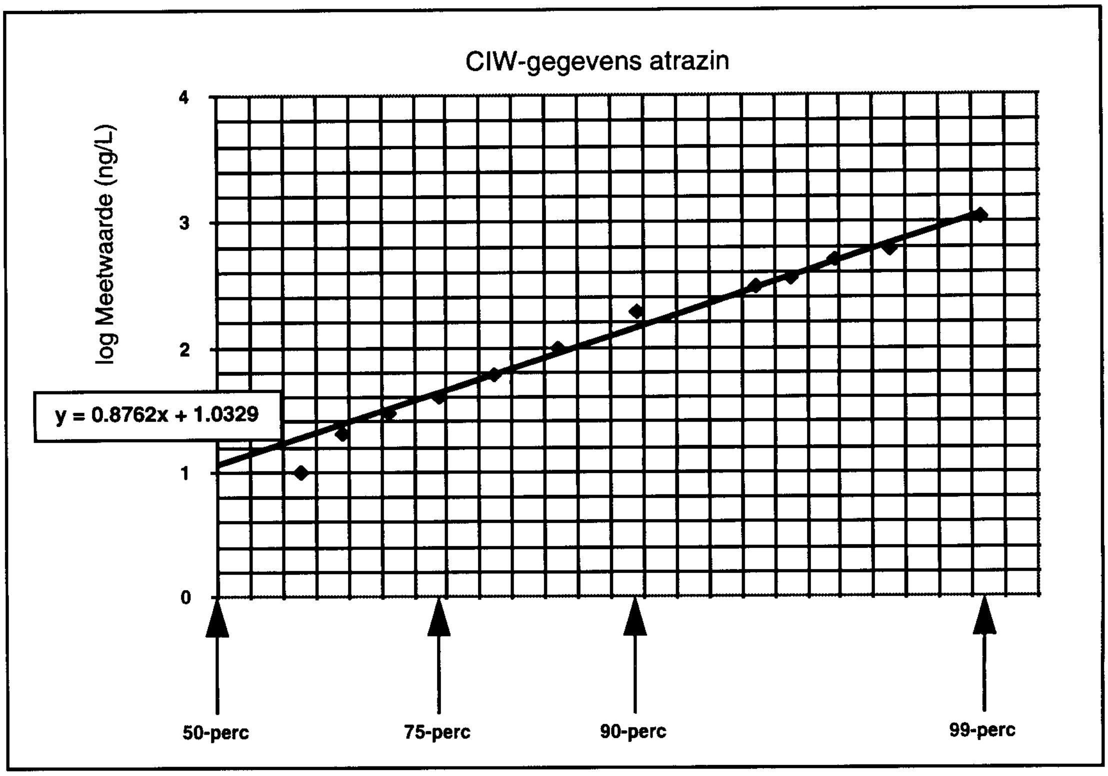

Figure V.2 Estimation of median values in case more than 50% of the measurements fall below the detection limit. Probabilistic plots were linear, indicating that the measurements have a log-normal distribution. In this case, a median value (50-percentile) of 11 ng/L was obtained as the result.