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Pesticides in ground water: occurrence and ecological impacts

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Abstract

The ecotoxicological risk concept as a fundament for setting environmental quality objectives is applied to pesticides in ground water. Therefore, several approaches for setting ecotoxicological critical concentrations for ground water are elaborated in an explorative sense. Next these are compared with the actual European Union standard for pesticides in ground water and with critically reviewed groundwater monitoring data. Moreover, for aldicarb, atrazine and MITC results of geographic modelling are ecotoxicologically evaluated. The study focuses mainly on the Netherlands but an excursion is made to Europe.
Many reported groundwater monitoring data are strongly correlated. The number of localities where pesticides have been detected preferably judges extension of groundwater contamination. Shallow Dutch groundwater monitoring data reveal that aldicarb, 1,3-dichloropropene, 1,2-dichloropropane, dinoseb, dinoterb, ethoprophos, and MITC are ecotoxicologically the most hazardous pesticides. Of the pesticides found in monitoring programs critical levels are lower than 0.1 µg/l for aldicarb and aldicarb-sulfoxide, dinoseb, dinoterb, ethoprophos, heptachlor, MITC, parathion-ethyl, and pirimicarb.
When ecotoxicological risk levels for ground water are needed one should focus on extrapolation methods with as input basic toxicity data and taking the ecological characteristics of the system into account. Development of ecotoxicity tests with specific groundwater organisms appears to be no meaningful direction to follow.

Contents

Samenvatting

In deze studie wordt het ecotoxicologisch risicoconcept gehanteerd bij het afleiden van algemene milieukwaliteitsdoelen voor bestrijdingsmiddelen in grondwater. De doelstellingen van de studie zijn: 1) Ecotoxicologische evaluatie van monitoringgegevens van bestrijdingsmiddelen in met name het ondiepe grondwater, tot 10 m beneden maaiveld. 2) Het ontwikkelen van verschillende benaderingen voor het afleiden van ecotoxicologische kritische grondwaterconcentraties. 3) Ecotoxicologische evaluatie van de huidige Europese Unie kwaliteitsnorm voor bestrijdingsmiddelen in grondwater. Grondwater wordt in deze studie beschouwd als ecosysteem, een uitgangspunt dat goed is onderbouwd in de wetenschappelijke literatuur.

Bestaande monitoringgegevens zijn kritisch geëvalueerd en geanalyseerd om vast te stellen wat de grootte van het probleem is, om welke stoffen het vooral gaat en in welke concentraties zij voorkomen. Veel gerapporteerde waarnemingen van bestrijdingsmiddelen in grondwater zijn sterk onderling gecorreleerd. De verbreiding van grondwaterverontreiniging door bestrijdingsmiddelen dient bij voorkeur te worden vastgesteld aan de hand van het aantal verschillende locaties waar middelen zijn gevonden. Het aantal verschillende onderzochte locaties is echter gering. In ondiep grondwater is ca. 75% van de gerapporteerde middelen aangetroffen in concentraties ≥ 0,1 µg/l. Voor 50% van de middelen is de mediaan van de positieve waarnemingen > 0,1 µg/l. Enkele middelen komen in concentraties > 10 µg/l (aldicarb-sulfon, aldicarb-sulfoxide, bentazon, BAM, 1,3-dichloorpropeen, 1,2-dichloorpropaan, ETU en metribuzin), dit is geassocieerd met agrarische toepassingen op kwetsbare gronden (laag organisch stofgehalte). In diep grondwater zijn de aangetoonde concentraties lager maar de verontreinigde volumes zijn waarschijnlijk groter.

Bij gebrek aan chronische toxiciteitsgegevens voor grondwaterorganismen zijn toxiciteitsgegevens voor aquatische organismen toegepast in een eerste probleemverkenning. De nadruk ligt hierbij op kreeftachtigen en micro-organismen omdat zij, respectievelijk, een belangrijk deel van de grondwaterfauna vormen en de belangrijkste functionele component van grondwaterecosystemen zijn. De Hazardous Concentration 5% voor kreeftachtigen lijkt geschikt als kritische concentratie vanwege het grote aantal beschikbare gegevens. De uitwerking van de methode wordt beter indien meer chronische toxiciteitsgegevens beschikbaar komen. Voor een goede interpretatie van kritische concentraties ontbreekt vooralsnog informatie over de specifieke gevoeligheid van grondwaterecosystemen.

Uit monitoringgegevens van ondiep Nederlands grondwater blijken aldicarb (incl. metabolieten), 1,3-dichloorpropeen, 1,2-dichloorpropaan, dinoseb, dinoterb, ethoprofos, en MITC ecotoxicologisch de meest riskante middelen. Van de aangetroffen middelen (ca. 50% van de potentieel te verwachten middelen) zijn voor aldicarb en aldicarb-sulfoxide, dinoseb, dinoterb, ethoprofos, heptachlor, metam-natrium (MITC), parathion-ethyl en pirimicarb de kritische concentraties < 0.1 µg/l. De meeste zijn insecticiden. Voor de overige middelen zijn de kritische waarden > 0.1 µg/l.

Indien ecotoxicologische risicogrenzen voor grondwater nodig zijn is het aan te bevelen deze af te leiden uit standaard aquatische toxiciteitsgegevens met beschouwing van de consequenties van ecologische aanpassingen aan de omstandigheden in het grondwater (zeer voedselarm, geringe beschikbaarheid van zuurstof). Het ontwikkelen van ecotoxiciteitstesten met grondwaterorganismen lijkt geen zinvolle route om te volgen.

Summary

The background of the present study is the application of the ecotoxicological risk concept as principle for setting generic environmental quality objectives for pesticides in ground water. There are three objectives: 1) Ecotoxicological evaluation of pesticide monitoring data, with emphasis on Dutch shallow ground water, up to 10 m below soil surface. 2) Initiation of approaches for deriving ecotoxicological risk levels for ground water. 3) Ecotoxicological evaluation of the actual European Union standard for pesticides in ground water. The ecosystem approach for ground water, well founded in scientific literature, is recognised as premises.

Existing monitoring data from shallow and deep ground water are critically evaluated and analysed in order to determine the scope of the problem, relevant compounds and the level at which they are present. Many reported observations are strongly correlated. The number of localities where pesticides have been detected preferably judges extension of groundwater contamination. The number of different localities investigated is low, however. In shallow ground water ca. 75% of the reported compounds have maximum levels ≥ 0.1 µg/l. For 50% of the compounds the median of positive findings exceeds 0.1 µg/l. A few compounds are encountered at levels greater than 10 µg/l (aldicarb-sulfone, aldicarb-sulfoxide, bentazone, BAM, 1,3-dichloropropene, 1,2-dichloropropane, ETU and metribuzin), this is associated with agricultural practices on vulnerable soils (low in organic matter). In deep ground water concentrations demonstrated are lower but contaminated volumes probably larger.

By lack of chronic toxicity data for groundwater organisms the base set of aquatic toxicity data is applied for first problem recognition. Emphasis is on crustaceans and micro-organisms because they are, respectively, the most important facies of groundwater fauna and the fundamental component of groundwater ecosystems. The Hazardous Concentration 5% for crustaceans appears to be a workable ecotoxicological critical concentration because many data are available. The method can be improved when chronic toxicity data for more different species are available. The ecological significance of critical levels can be better interpreted when basic information on the specific vulnerability of groundwater systems becomes available.

Shallow Dutch groundwater monitoring data reveal that aldicarb (incl. metabolites), 1,3-dichloropropene, 1,2-dichloropropane, dinoseb, dinoterb, ethoprophos, and MITC are ecotoxicologically the most hazardous pesticides. Of the pesticides encountered in monitoring programs (ca. 50% of potentially expected compounds) critical levels are lower than 0.1 µg/l for aldicarb and aldicarb-sulfoxide, dinoseb, dinoterb, ethoprophos, heptachlor, metam-sodium (MITC), parathion-ethyl, and pirimicarb. Most of them are insecticides. For the other pesticides critical levels are higher or much higher than 0.1 µg/l.

When ecotoxicological risk levels for ground water are needed one should focus on extrapolation methods with as input basic toxicity data and taking the ecological adaptations to groundwater conditions (scarcity of food resources and oxygen) into account. Development of ecotoxicity tests with specific groundwater organisms appears to be no meaningful direction to follow.

Résumé

Le fondement de cette étude consiste en l'application du concept de risque pour poser des objectifs généraux de qualité environnementale en ce qui concerne les pesticides dans les eaux souterraines. Il y a trois objectifs: 1) Évaluation écotoxicologique des concentrations en pesticides enregistrées, l'accent étant mis sur l'eau souterraine superficielle au Pays-Bas, soit située au maximum à 10 m sous la surface du sol. 2) Amorce d'approches pour déterminer à vérifier les niveaux de risques écotoxicologiques pour les eaux souterraines. 3) Évaluation écotoxicologique des normes actuelles de l'Union Européenne pour les pesticides dans les eaux souterraines. L'approche au niveau de l'écosystème, bien établie dans la littérature scientifique, est considérée comme base pour les eaux souterraines.

Les données existantes pour les eaux souterraines superficielle et profonde sont évaluées et analysées afin de déterminer l'ampleur du problème, les composés déterminants et les niveaux auxquels ils sont présents. Beaucoup de ces données ne sont pas statistiquement indépendantes. L'extension de la contamination des eaux souterraines est jugée préférentiellement par le nombre de points d'échantillonnage où les pesticides ont été détectés bien que celui-ci soit faible. Dans l'eau souterraine superficielle, environ 75 % des composés rapportés sont présents à des niveaux ≥ 0,1 µg/l. Pour 50% la médiane des analyses positives dépasse 0,1 µg/l. Quelques composés ont été rencontrés à des niveaux supérieurs à 10 µg/l (aldicarbesulfone, aldicarbesulfoxyde, bentazone, BAM, 1,3-dichloropropène, 1,2-dichloropropane, ETU et métribuzine). Ces niveaux sont associés à des pratiques culturales sur des sols vulnérables (pauvres en matières organiques). Dans l'eau souterraine profonde, les concentrations rencontrées sont plus faibles mais les volumes contaminés sont probablement plus grands.

Par manque de données sur la toxicité chronique pour les organismes de l'eau souterraine, la base de données de toxicité aquatique est appliquée pour une première appréhension du problème. L'accent est mis sur les crustacés et les microorganismes car ce sont respectivement les animaux les plus répandus de la faune aquatique souterraine et le composant fondamental du fonctionnement des écosystèmes aquatiques souterrains. La 'Hazardous Concentration 5%' pour les crustacés apparaît comme une concentration écotoxicologique critique utilisable pour laquelle beaucoup de données sont disponibles. La méthode pourra être améliorée lorsque plus de données sur la toxicité chronique seront connues et ce pour différentes espèces. La signification écologique des niveaux critiques pourra également être mieux interprétée lorsque des informations fondamentales sur la sensibilité spécifique des écosystèmes aquatiques souterrains seront disponibles.

Les données enregistrées dans les eaux souterraines superficielles néerlandaises révèlent que l'aldicarbe (y compris ses métabolites), le 1,3-dichloropropène, le 1,2-dichloropropane, le dinosèbe, le dinoterbe, l'éthoprophos et le MITC sont les pesticides les plus dangereux du point de vue écotoxicologique.

Parmi les pesticides rencontrés dans les différents programmes de surveillance (soit 50% des composés potentiellement suspectés), les niveaux critiques sont inférieurs à 0,1 µg/l pour l'aldicarbe et l'aldicarbesulphoxyde, le dinosèbe, le dinoterbe, l'éthoprophos, l'heptachlore, le métam-sodium (MITC), le parathion-éthyl et le pirimicarbe. La plupart d'entre eux sont

des insecticides. Pour les autres pesticides, les niveaux critiques sont aumoins égaux à 0,1 µg/l.

Si les niveaux de risques écotoxicologiques deviennent nécessaires à l'établissement de normes, des méthodes d'extrapolation utilisant les données de toxicité de base devraient être développées et les caractéristiques écologiques devraient être prises en considération. Le développement de tests d'écotoxicité avec des organismes spécifiques des eaux souterraines n'apparaît pas comme une direction pertinente à suivre.

Zusammenfassung

Der Hintergrund der vorliegenden Studie ist die Anwendung des ökotoxikologischen Risikokonzeptes, das als Grundlage zur Erstellung von allgemeinen Risikonormen für Pestiziden im Grundwasser dienen soll. Das Ziel dieser Studie ist: 1. Die ökotoxikologische Begutachtung der Meßdaten von Pestiziden im Grundwasser, mit Schwerpunkt im oberflächennahen Grundwasser bis 10 m unterhalb der Oberfläche, 2. Die Entwicklung verschiedener Methodiken, die es ermöglichen, ökotoxikologische Grundwassernormen herzuleiten, 3. ökotoxikologische Begutachtung der derzeit innerhalb der Europäischen Gemeinschaft gültigen Pestizidnorm für das Grundwasser. Das Grundwasser wird im Rahmen dieser Studie als eigenständiges Ökosystem betrachtet, eine Aufassung, die innerhalb wissenschaftlichen Literatur gut untermauert ist.

Für die vorliegende Studie wurden Meßdaten kritisch begutachtet und analysiert, um eine Aussage über die Größe des Problems machen zu können und festzustellen, um welche Stoffe es sich handelt und in welchen Konzentrationen diese vorkommen. Die Mehrheit der Wahrnehmungen sind stark korreliert. Das Ausmaß der Pestizidbelastung des Grundwassers sollte vorzugsweise durch die Anzahl der Meßpunkte bestimmt werden. Dem steht jedoch gegenüber, daß die Anzahl der untersuchten Orte, von denen Meßdaten vorliegen, sehr gering ist. Im oberflächennahen Grundwasser wurden für ca. 75% der untersuchten Substanzen Konzentrationen von ≥ 0.1 µg/l gefunden. Bei ca. 50% der untersuchten Substanzen lag der Median über 0.1 µg/l. Ein paar Substanzen wurden in Konzentration von mehr als 10 µg/l gefunden (Aldicarb-Sulphon, Aldicarb-Sulphoxid, Bentazon, BAM, 1,3-Dichlopropen, 1,2-Dichlorpropan, ETU, Metribuzin). Diese Messungen sind auf die landwirtschftliche Anwendung dieser Stoffe auf empfindlichen Böden (= geringer Anteil organischer Substanz) zurückzuführen. In tieferen Grundwasserlagen sind die Konzentrationen geringer, aber das verunreinigte Volumen ist wahrscheinlich größer.

Wegen des Mangels an chronischen Ökotoxizitätsdaten für Grundwasserorganismen wurden Daten für aquatische Organismen zu einer ersten Problemerkennung herangezogen. Dabei lag der Schwerpunkt bei Krebstieren und Mikroorganismen, da diese einen großen Anteil in der Grundwasserfauna bzw. eine wichtige funktionelle Komponente in diesem Ökosystem darstellen. Die 'Hazardous Concentration von 5% (HC_5)' für Krebstiere erscheint auf Grund der Vielzahl der Ökotoxizitätsdaten geeignet als kritische Konzentration. Die Methode wirkt sich noch besser aus, wenn vorzugsweise chronische Daten für verschiedene Spezies herangezogen werden. Bislang fehlen jedoch Erkenntnisse über die spezifische Empfindlichkeit von Grundwasserökosystemen, um eine deutliche Aussage über die kritische Konzentration machen zu können.

Meßdaten von oberflächennahem Grundwasser in den Niederlanden zeigen, daß Aldicarb (incl. Metaboliten), 1,3-Dichlorpropen, 1,2-Dichlopropan, Dinoseb, Dinoterb, Ethoprofos und MITC zu den risikoreichsten Substanzen gehören. Bei den gefundenen Substanzen (ca. 50% von den potentiell zu erwartenden Substanzen) lag die kritische Konzentration für Aldicarb und Aldicarb-Sulphoxid, Dinoseb, Dinoterb, Ethoprofos, Heptachlor, Metamnatrium (MITC), Ethyl-Parathion und Pirimicarb unterhalb von 0.1 µg/l. Von diesen gehören die meisten zu de Gruppe der Insektiziden. Bei den restlichen Substanzen lag die kritische Konzentration oberhalb von 0.1 µg/l.

Für die Herleitung ökotoxikologischer Risikonormen für Grundwasserökosysteme erscheint es sinnvoller, diese auf der Basis von aquatischen Toxizitätsdaten und unter Berücksichtigung der Verhältnisse im Grundwasserökosystem herzuleiten, an statt Toxizitätsteste für Grundwasserorganismen zu entwickeln.

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1. Introduction

For many years it was assumed that soil layers form an effective protective barrier for the ground water, preventing pollution by substances of anthropogenic origin. The last decades, however, this assumption has proved to be incorrect as many incidences of groundwater pollution from both point and diffuse sources are reported. An important group of contaminants in ground water are pesticides that are able to leach from soils into ground waters, in particularly in soils with low sorption capacities.

The environmental policy with regard to pesticides in ground water has as main objective the protection of it as a potential resource for drinking water production. The Drinking Water Directive of the European Union (European Communities, 1980) states that drinking water should not contain more than 0.1 µg/l of any individual pesticide, and that the collective concentration of all such compounds should not exceed 0.5 µg/l. The Dutch policy premise is that ground water should be suitable for the preparation of drinking water, without requiring extensive purification, and should therefore comply with the standard. In accordance with this policy and with the Uniform Principles of the European Union (European Communities, 1994), the Dutch Pesticide Act includes a number of environmental criteria. One of these criteria prohibits the registration of any pesticide whose use will cause the above-mentioned standard to be exceeded at a depth of 10 meters below ground level.

The European Union countries adhere to the principle that pesticides do not belong in drinking water. Accordingly, when drawing up the standard, they equated the threshold level to contemporary detection limits for these substances. Since then, however, the sensitivity of detection techniques has increased considerably. As a result, the question of whether the current standard is still adequate is now under debate. An alternative approach would be to draw up standards underpinned by toxicological and ecotoxicological data and risk assessment for human health and the environment.

Against this background the present study regards ground water contamination by pesticides from an ecotoxicological point of view. It will focus on the risks these substances may pose to the intrinsic ecological properties of groundwater systems. The present work will not attempt to develop a rigorous systematic approach for the ecotoxicological risk assessment of pesticides in ground water. It is meant as an outline for such an approach mainly based on available ecotoxicological information and considerations on particularities of groundwater ecosystems with regard to their vulnerability. This paper has certainly not the intention of being complete and mainly aims to open scientific discussions on the impetus of contamination with toxic substances on groundwater ecosystems and to find technical solutions to quantify possible risks for legislative purposes.

The objectives of the present work are threefold: (1) Ecotoxicological evaluation of available data on the occurrence of pesticides in ground water; which compounds do occur, what are the levels in which they are determined and may these levels give rise to ecologically relevant effects. Emphasis is on the occurrence of pesticides in shallow (up to 10 m below ground level) Dutch ground water. However, data on deeper ground water and of some other European countries are also taken into account. (2) The initiation of approaches which can be used for the ecotoxicological risk assessment of pesticides in ground water, whether this is for derivation of generally applicable ecotoxicological criteria in legislation or for the

evaluation of the seriousness of locally occurring cases of groundwater pollution. (3) Ecotoxicological evaluation of the actual European Union standard for pesticides of 0.1 µg/l. Considering groundwater aquifers as hydrological, geochemical and biological systems, and being aware of the value of groundwater systems as sources of biodiversity and the role of groundwater organisms in biogeochemical cycles, the question is addressed if the actual standard for pesticides sufficiently protects these, often neglected, features of groundwater systems.

2. Groundwater Ecosystems

A general and strict characterisation of the groundwater ecosystem has the danger that it would takes away the existing variation in physicochemical and habitat conditions in the subsurface. Given the huge extent of the subsurface environment, the diversity of geological layers and the enormous volume of water present in these layers (with exclusion of ice caps and glaciers more than 95% of the fresh water on this earth is ground water), one can imagine that differences in ecological conditions are large. Groundwater systems cannot be considered in isolation, they have various hydrological connections with above-ground environments. From the ground water perspective one can consider the peripheral areas which are strongly influenced by surface waters or the terrestrial environment, and the deeper parts which experience less direct influence. At the peripheries the distinction between ground water and the epigean aquatic or terrestrial ecosystems is not always obvious. Generally, the deeper parts of the groundwater system have more stable environmental conditions, and the peripheral areas experience more variation. The extension of these peripheral areas depends on the severity and dynamics of hydrological exchange between surface and subsurface.

Organisms occur in large parts of the subsurface environment. For longer times the presence of invertebrates in groundwater habitats of floodplains and karstic systems is known. The last 20 years the rather universal presence of micro-organisms also in the very deep subsurface was established. Due to the difficulties in accessing and exploring subsurface environments our knowledge on their biodiversity and ecology is certainly rather incomplete. Despite this, impressive documentation exists on zoological and ecological studies of different areas showing a wealth of different habitat conditions each with its own characteristic species composition (Gibert *et al.* 1994).

Microbiologists also document similar findings; their studies often reach much deeper into the subsurface. Environmental biotechnologists have illustrated the degradation potential of natural and anthropogenic organics by indigenous micro-organisms in the subsurface. Microbial activity in ground water may therefore contribute to the natural attenuation of pesticides before ground water becomes drinking water. The indigenous micro-organisms in ground water may play a role in the elimination of pathogens and trace pollutants in drinking water.

Zoologists distinguish two main groups of groundwater organisms: epigean species which have penetrated from surface environments into the peripheral areas of the ground water realm and hypogean species or troglobites which are completely encapsulated in the subterranean environment. The latter are mostly highly adapted, often lack direct phylogenetic relationships with epigean species, and may have penetrated deeper into the subsurface environment. Within epigean species one distinguishes various stages of adaptation and colonisation of the peripheral areas. Epigean and hypogean species may both occur in peripheral groundwater habitats, which appear to have the largest species richness and are also the best investigated.

Groundwater habitats have in common that there is no light, the rich energy source of the photosynthetic primary production exists only as decaying organic matter. The input of it decreases from peripheral to deeper areas of the ground water. Oligotrophy characterizes many (deeper) groundwater habitats and has a large impetus on community structure and

function: low population densities, simple food chains, few trophic levels, and unspecialised feeding behaviour. The role of invertebrates in the recycling of energy and matter will in general be modest because of their low densities. At lower scales they may have a patchy occurrence and at that level their role might be considerable. As an adaptation to energy poor environments many troglobites and adapted epigean species, show typical life-histories: delayed maturity, increased longevity, fewer egg clutches, smaller clutch size, larger eggs, low percentage of mature, ovigerous females, and sex ratio skewed towards females.

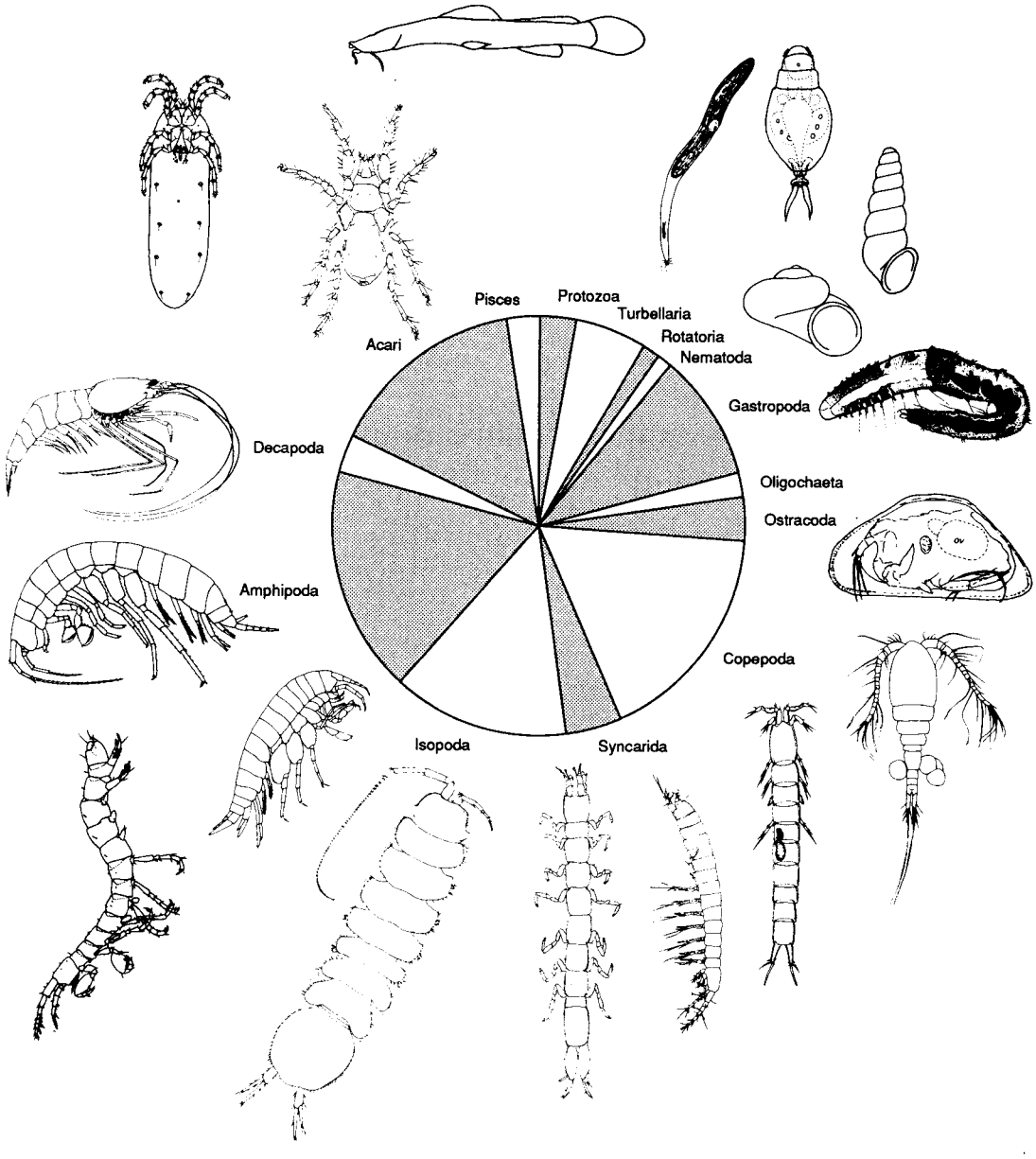

Figure 2.1. Diversity spectrum of multi-cellular stygobite organisms over all types of groundwater habitats world-wide (based on Botosaneanu, 1986).

Regarding multi-cellular biodiversity in ground water the most remarkable aspect is the highly adapted facies of stygobitic species. World-wide more than 6,000 of them are described distributed over several taxonomic Classes (Figure 2.1). Very remarkable is the high representation of many different groups of crustaceans, some of them limited in their

occurrence exclusively to ground water. They are very diversified and occur in many different groundwater habitats (Rouch and Danielopol, 1997).

The unicellular micro-organisms (bacteria, actinomycetes, fungi, algae and protists) are the most dominant life form in subsurface environments. Bacteria are the most important in abundance and they represent a wide variety of physiological types. As adaptation to the oligotrophic nature of many (deep) subsurface habitats, bacteria have a high affinity for organic substrates. So, they are able to grow even at extremely low nutrient concentrations (Madsen and Ghiorse, 1993).

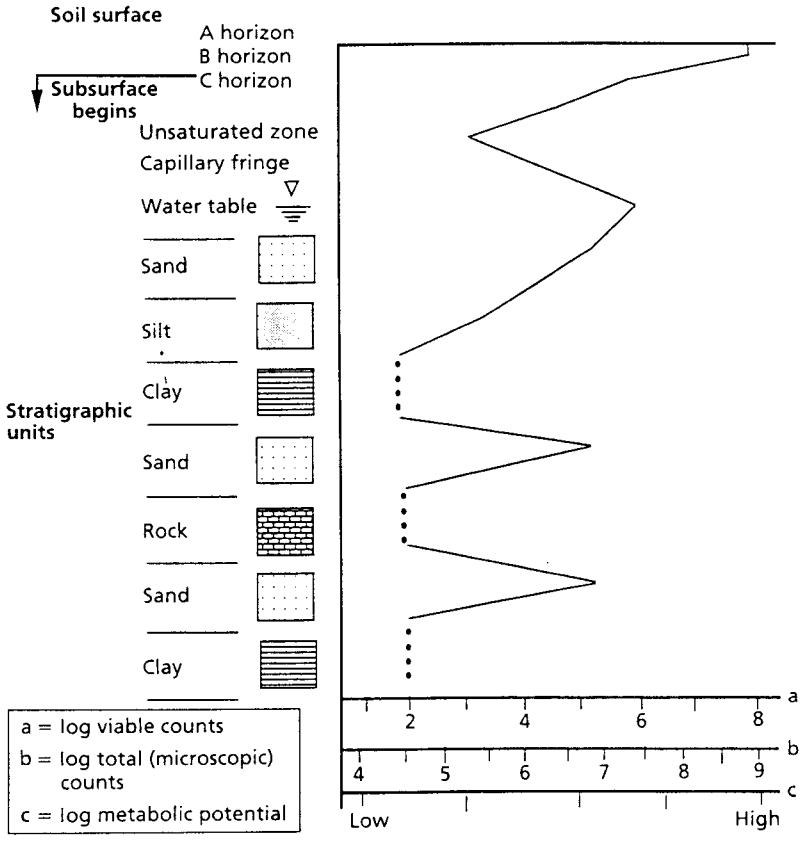

Figure 2.2 Generalized vertical profile showing relationships between microbiological parameters and geological strata in an undisturbed profile (from Madsen and Ghiorse, 1993).

A generalised model of the relationship between hydrology and subsurface sediment characteristics, and the abundance and metabolic potential of bacteria is presented in Figure 2.2. The major physicochemical key parameters influencing bacterial abundance and activity (e.g., available organic substrates, inorganic nutrients, pH, electron acceptors, predation, and dispersion) are modified in the subsurface along hydrological flow paths. Starting at the surface the abundance of bacteria declines markedly with increasing depth. However, there may be a substantial rise in density at the capillary zone and the water table (Madsen, 1995; Madsen and Ghiorse, 1993). Deeper in the water-saturated zone, bacterial abundance and activity primarily depend on the hydrological, physical and geochemical characteristics of the various sediment layers. Bacteria have been found at depths of up to 4,000 meters. The population densities of bacteria and protists in hydrocarbons polluted layers often exceed those in pristine layers.

The average bacterial cell is 1 μm in diameter, but those found in oligotrophic environments can be up to ten times smaller. As a result, they can easily penetrate the interstitial space between sediment particles. Rather than living free in the water that fills these spaces, the majority of bacteria are bound to the surface of sediment particles. The advantage of this way of life is that the water flowing over the surface brings with it a steady food supply. In addition, it promotes the establishment of consortia in which various species of bacteria supply one another with suitable substrates.

Algae, actinomycetes and fungi have not been detected in significant numbers in subsurface environments. More important appear the protists, which are larger (1-10 μm) than bacteria and their abundance increase in relation to the coarseness of the surrounding sediment structure. Ecologically their role of predator of bacteria seems to be of particular interest. This predatory capacity may accelerate the cycling of carbon and other nutrients. The population density of protists may serve as an indirect measure of *in situ* bacterial growth rate. In this regard, the presence of protists in the subsurface may be very important in documenting the expression of metabolic potential in groundwater habitats.

3. Ecological Risk Assessment

Several straightforward approaches are followed in order to obtain an indication of ecologically significant critical concentrations for pesticides in ground water. When environmental concentrations of pesticides exceed such critical concentrations, indications exist that these substances may evoke potentially harmful effects on (parts of) groundwater ecosystems (risk quotient approach). The risk is assumed to increase with the magnitude of the quotient of environmental concentration divided by ecotoxicological critical concentration. One should realise that the real consequences for community structure and ecosystem function in a given situation are hard, if at all, to determine. Such a type of answer requires extensive (long-term) field research and than still it is hard to delineate the impact of the contaminant from the natural variation in abiotic conditions and other types of anthropogenically induced stress. For the study of groundwater systems additional hindrances related to their inaccessibility and oligotrophic nature make such field studies hardly feasible. The latter argument makes also the application of specially designed field studies or mesocosms experiments in the ecotoxicological study of groundwater ecosystems not realistic.

The degradation potential of a pesticide in ground water is certainly an aspect to consider in risk assessment. However, data are lacking due to the little experience with degradation studies in subsurface sediments and technical difficulties to maintain relevant and realistic experimental conditions. As such, methods for pesticide degradation in sub-soils are not yet suitable for standardisation at their current stage of development.

The risk assessment approaches applied here are based on different sets of considerations. Possibilities to work them out all equally are limited by practical limitations and data availability. In combination they may circumstantially indicate the potential harmfulness of a particular pesticide for groundwater ecosystems. Four different types of ecotoxicologically critical concentrations (**CC**) are discerned as input values for the calculation of risk quotients.

1. Ecotoxicological quality objectives for aquatic ecosystems in general (**CC_{ae}**).
   Since hardly any information is available on the sensitivity of groundwater organisms for pesticides, generic ecotoxicological quality objectives derived for aquatic ecosystems may serve as critical concentrations (CC_{ae}). As a generic objective the Maximum Permissible Concentration (MPC) is employed in the present study. This concentration is derived from laboratory toxicity data of aquatic species (often algae, fishes and crustaceans) and when available micro-organisms. The MPC plays an important role as technical basis for setting quality objectives in Dutch environmental policy (Kalf *et al.*, 1997).

   An argument to apply ecotoxicologically critical concentrations for surface water notwithstanding that they are less appropriate for groundwater ecosystems is that groundwater often comes back as surface water. When this occurs through springs or subsurface drainage into surface waters aquatic ecotoxicity data immediately gain relevance.

2. Toxicity data of groundwater species (**CC_{gs}**).
   More ecologically relevant appears the application of toxicity data of ground water inhabiting species. However, many practical reasons prevent the use of groundwater species in routine toxicity testing (Notenboom *et al.*, 1994). Few data on pesticides exist only for just one groundwater species, the crustacean *Parastenocaris germanica* (Notenboom and Boessenkool, 1994). They are applied in this study for setting ecologically critical concentrations for groundwater systems (CC_{gs}).

3. Toxicity data of crustaceans (**CC_{cr}**).
   Many invertebrate taxa occurring in ground water are crustaceans (see Chapter 2). Surface water representatives of this taxon have extensively been used in toxicity testing. Tests with *Daphnia* species, for example, are formalised in different international protocols and are required as basic information in pesticide risk assessments. Because of phylogenetic resemblance toxicity data of crustaceans could be considered more representative for groundwater invertebrates than aquatic toxicity data in general. Toxicity data on algae and fish, for example, are highly representative for many different surface water ecosystems but they are of little significance for groundwater ecosystems where photosynthetic primary production is lacking and vertebrates are absent. Therefore, in this study the hazardous concentration for 5% of the crustacean species only (van Straalen and Denneman, 1989; Wagner and Løkke, 1991; Aldenberg and Slob, 1993) is applied as a critical concentration for this group of organisms (CC_{cr}).

4. Toxicity data of micro-organisms (**CC_{mo}**).
   Micro-organisms are directly responsible for important ecological functions of groundwater ecosystems (biogeochemical cycles, degradation of organic substances, elimination of pathogens). Hence, it is obvious to use data on the inhibition of microbial processes by pesticides as a basis for deriving critical concentrations for groundwater ecosystems (CC_{mo}).

   Toxicity studies performed in aquifer material or with indigenous groundwater bacteria (Dippell *et al.*, 1991) are very scarce and they should be regarded with care because sample manipulations and experimental conditions make them less representative than intended (Health Council of the Netherlands, 1996).

   For the derivation of critical concentrations of pesticides for microbial processes two approximations appear feasible: (1) data from soil or sediment tests and a recalculation of solid phase effect concentrations to aqueous phase by means of partition coefficients; and (2) data from aquatic microbial tests. Preferably the process selected in the test should be such that it potentially also is performed by groundwater bacteria (e.g. denitrification, thymidine incorporation, mineralisation, enzyme activities).

   The response of many microbial tests performed in soil or sediment material depends in fact on the activity of the whole community (e.g., respiration, decomposition, and nitrification). Functional redundancy may mask in these tests the specific sensitivity of a particular functional group. Therefore, these kind of tests are generally considered as not very sensitive with a limited information content (van Beelen and Doelman, 1997). Recalculation of effect concentration from solid to aqueous phase by means of partition coefficients is an unavoidable additional source of uncertainty.

Hence, results of aqueous microbial tests are preferred for deriving critical pesticide concentrations in ground water. The most widely applied aqueous microbial test is the Microtox® test. This is a single-species (*Vibrio fisheri*), non-specific test, based on bioluminescence. For the Microtox® a large data base is available and test results appeared reproducible between different laboratories (Bulich, 1986). For 50 - 100 environmental pollutants (mainly with a nonreactive toxicant mechanism) fair to good correlation ($r = 0.70 - 0.85$) were found between results of the Microtox® test and tests with aerobic heterotrophs, methanogens and *Nitrosomonas*. Compared to aerobic heterotrophs and methanogens the Microtox® appeared to be more sensitive, for *Nitrosomonas* it was equally sensitive (Blum and Speece, 1991). In the present study Microtox® data are therefore considered as a rough approximation of the sensitivity of micro-organisms.

4. Data Collection and Treatment

4.1 Pesticide concentrations in ground water

4.1.1 Data selection

This study aims to collect data on the presence of pesticides in (shallow) ground water and present them in such a way that a comparison with ecotoxicological risk parameters is justified. Data on the presence of pesticides in ground water in the Netherlands, but also in other EU countries, are scattered amongst institutes, laboratories, drinking water companies and others. The emphasis of this study is on the Netherlands.

Two types of data were analysed and summarised. (1) Use related data that show a strong relation between pesticide application and their appearance in the upper ground water (0-10 m below soil surface). (2) Non-use related data for which direct relationships between application and observed concentrations could not be established. The latter includes data from observation filters and raw ground water of the drinking water extraction stations collected by drinking water companies (further indicated as VEWIN[1] database). The non use-related data are based on measurements all originating deeper than 10 m below soil surface (m-bss).

Data collected within the framework of the national monitoring program groundwater quality (Cornelese and van Maaren, 1992, 1993, 1994, Lagas *et al.*, 1988, 1989, Lagas *et al.*, 1990) served as starting point for the collection of use-related data. From other monitoring programs, collected by research institutes and governmental agencies, data were supplied:

- province of Noord-Brabant (van de Griendt, 1993);
- province of Groningen (Kuiper, 1995);
- Noordoostpolder (Zuiveringschap West-Overijssel, 1988);
- water catchment areas Helden and Valtherbos (Puijker *et al.*, 1994; Janssen and Puijker, 1991);
- experimental farm in Rolde (Fraters, 1991).

Only measurements between 1985 and 1995 and with certainty performed on groundwater samples originating from 0-10 m-bss (incl. drain water) were used for data analysis. The data were screened on reliability of the detection method and on relevance of the sample location i.e. whether the sample location is in agricultural area. Moreover, information on application and weather conditions was taken into account in order to link groundwater concentrations with pesticide use. The monitoring programs were mainly performed in agricultural areas with potatoes, maize and flower bulbs as most important land-use types. Pesticides used in non-crop areas such as railways or pathways were monitored at specific locations. Data from universities were not considered because too many uncertainties exist on analytical methods and quality assurance.

The non-use related data compiled from the VEWIN database contains 141 compounds and about 43,000 records measured between 1992 and 1995. Pesticides detected above detection

[1] VEWIN is the abbreviation for *Vereniging van Exploitanten van Waterleidingbedrijven In Nederland* (Association for proprietors of drinking water companies in the Netherlands).

limits were included in the non-use related table. The selected data were not screened with respect to reliability and relevance.

Use-related data for some other European countries were taken from a review prepared by the Soil Survey And Land Research Centre (SSLRC; Shardlow, UK) in collaboration with the European Crop Protection Agency and institutes in France, Germany, Italy, the Netherlands, Spain and Sweden. This study is certainly not a comprehensive review and not all EU countries are involved. The study summarises compounds based on information from national data banks only. It is not the purpose of the present study to give a complete overview of pesticides in ground water in Europe. The main purpose of involvement of other European countries was to get an indication of the extent of the problem at European scale. More pesticides were detected in ground water in European countries as reported by SSLRC (1997). The countries are difficult to compare with respect to depth of ground water and selection of pesticides that were analysed for. For the present study only data attributable to a specific crop or crop rotation were selected out of the SSLRC review.

4.1.2 Data handling

For the evaluation of pesticide concentrations in ground water, the following parameters have been derived:
- number of observations (n)
- limit of determination (LOD)
- number of positive observations (n>LOD)
- number of sample locations (m)
- number of locations with positive observations (m>LOD)
- median of positive observations (median+)
- 95% percentile interval of positive observations (95% perc+)
- maximum pesticide concentration (max)

The median value is preferred above the average because it is less affected by extreme observations. Reported 95% percentile values give information on the variation in the observations. To judge the relevance of the median and maximum values, the total number of observations as well as observations exceeding the limit of determination are listed. Both the total number of locations and the locations with positive findings are listed to indicate the (in)dependency of the observations.

4.1.3 Application of GIS to the modelling of pesticide leaching.

The number and distribution of pesticide observations in ground water are rather scarce and scattered respectively. They do neither provide a basis for a national overview of the presence of pesticides in shallow ground water nor indicate the potential of a compound to reach ground water at the national scale. One of the means to reveal a more complete overview of the potential occurrence of pesticides in ground water is the use of simulation models. Therefore model calculations, based on sorption and transformation characteristics of the pesticides and hydrological and meteorological properties of the environment, are made to estimate pesticide concentrations in ground water at 1-2 m-bss. GEOPESTRAS (Tiktak *et al.*, 1996) is used for these calculations. GEOPESTRAS combines model calculations and geographical information. The data on atrazine concentrations in ground water served for the

calibration of the model.

The PESTRAS model combines Freundlich adsorption, Darcy transport, temperature-, depth- and moisture-dependent first order biodegradation, plant uptake and volatilization (Boesten and van der Linden, 1991; Tiktak *et al.*, 1994). Digital maps of soil type, land-use, organic matter content and depth of ground water below soil surface are used as input to the calculation of the expected pesticide concentration in ground water between 1 and 2 m-bss.

Maps of the Netherlands for the potential leaching of atrazine, aldicarb and MITC to shallow ground water are generated by means of these model calculations. Selection of these compounds is based on the following considerations. Atrazine is widely applied as herbicide in maize and its presence in ground water shows a clear relationship with land-use patterns. The pesticide is furthermore regularly used as model compound. Aldicarb serves as an example of a widely applied nematicide in potatoes and beet for which a clear relationship with land-use is expected. MITC is chosen because it is frequently encountered in monitoring programs, and its toxicity for aquatic invertebrates appears high enough to expect considerable critical situations. Input parameters for GEOPESTRAS are given in Table 4.1.

Table 4.1. Input parameters for GEOPESTRAS. The %product column indicates the percentage of active substance converted to this metabolite.

Compound	Crop	Dose (kg/ha)	Method	Depth (m)	Mr (g/mol)	Henry (Pa)	DT50 (days)	Kom (l/kg)	%product
aldicarb	Potatoes	3	incorporated	0	190.3	2.21E-07	2.4	4.7	
aldicarb-sulfone		0		0	206.3	9.992E-07	47.8	0.5	50%
aldicar-bsulfoxide		0		0	222.3	8.344E-07	22	1.4	76%
atrazine	Maize	1	sprayed	0	215.7	1.181E-07	50	68	
desethyl-atrazine		0		0	201.7		45	21	21%
desisopropyl-atrazine		0		0	172.7		50*		4%
2-hydroxyatrazine		0		0	197.2		164	1287	33%
metam-Sodium	Potatoes	100	incorporated	0.2	129.2		<0.02	228	
MITC	Potatoes	0			73.1	6.80E-03	6	3	50%

A European map with potential atrazine leaching to groundwater is produced with a meta-model of the PESTRAS model, according to the methods used in the EUPHIDS model (Beinat and van den Berg, 1996). To this purpose 10 soil/climate scenarios have been defined differing in soil type and average annual precipitation and air temperature. Leaching for a specific area is then calculated in two steps. In the first step leaching is calculated off-line by the PESTRAS model for the defined soil/climate regions for a wide range of pesticides. In the second step leaching is calculated on-line by the meta-model, using differences in the soil characteristics within a soil/climate region and local load map as input. The results are then transferred to a map stating the amount leaching.

4.2 Ecotoxicological information

4.2.1 Data collection and evaluation.

For collecting toxicity data internal as well as external literature sources have been consulted. The internal literature sources were:

- the Cardbox Literature Database containing articles from open literature, which have been collected and evaluated within the projects 'Setting integrated environmental quality objectives' and 'Intervention Values';
- 'grey' literature, which is present in the documentation at RIVM-CSR.

The external literature sources were:

- on-line search in Biosis, ToxLine Plus and Aquire
- retrospective search based on public literature and reviews.

Studies are evaluated according to standard procedures of the quality assurance system of RIVM-CSR. For each substance separate tables for chronic and acute data for crustaceans and other aquatic species are given (Appendix 4). In these tables results of toxicity studies are presented together with the experimental conditions: species, whether or not the test substance is analysed, test type, purity of the test substance, test water, pH and hardness of the test water, duration of the experiment, the criterion (NOEC or LC50) and the reference. In a separate table studies are listed which deviate from international accepted tests. Results of those studies are used in case no other toxicity data were found.

Microtox® data are given in Appendix 5, with information on exposure time, criterion, test result and reference.

4.2.2 Derivation of ecotoxicologically critical concentrations

Aquatic ecosystems (CC_{ae})
For this approach the Dutch ecotoxicological risk limit of the Maximum Permissible Concentration (MPC) is applied. MPCs for aquatic ecosystems based on single species toxicity data are derived with the EPA method which uses assessment factors (OECD, 1992) or the statistical extrapolation method according to Aldenberg and Slob (1993).

The method that is used depends on the number and kind of available data. If four or more long term NOECs are available, the statistical extrapolation method is used. If less long term NOECs or only short term L(E)C50s are available the EPA method is used.
In the EPA method assessment factors are applied on toxicity data. The size of this factor depends on the number and kind of toxicity data available. In Table 4.2 the method is presented for aquatic organisms.

Table 4.2.EPA method for aquatic organisms (see Slooff, 1992).

Available information	Assessment factor
lowest acute L(E)C50-value or QSAR estimate for acute toxicity	1000
lowest acute L(E)C50-value or QSAR estimate for acute toxicity for minimal algae/crustacean/fish	100
lowest NOEC-value or QSAR estimate for chronic toxicity	10*
lowest NOEC-value or QSAR estimate for minimal algae/crustacean/fish	10

* value is subsequently compared to the calculated value based on the lowest L(E)C50, the lower is selected.

The principle of the statistical extrapolation method is that chronic toxicity data (NOECs) are log transformed and fitted according to a distribution function. Subsequently, a prescribed percentile of that distribution is used as criterion: the left-sided 95th percentile. At this concentration (the hazardous concentration 5 % or HC5) the NOEC may be exceeded for 5% of the species of the community (see OECD, 1992; Van Straalen and Denneman, 1989; Wagner and Løkke, 1991). Aldenberg and Slob (1993) refined the way to estimate the uncertainty of the 95th percentile by introducing confidence levels. They calculate the 95% protection level with a 50% and 95% confidence level. The MPC (= CC_{ae}) is than calculated as the former value, i.e. with 50% confidence (Slooff, 1992).

MPCs for pesticides were taken from Crommentuijn *et al.* (1997), Van de Plassche and Bockting (1993) and Van de Plassche (1994). If no MPCs were reported by these authors and if enough data were retrieved, they were derived in the context of the present study, according to one of the above mentioned methods.

Groundwater species (**CC_{gs}**)
By our knowledge the only available toxicity data of pesticides for groundwater organisms comes from Notenboom and Boessenkool (1994). They reported EC_{50} values of *Parastenocaris germanica* (stygobite crustacean) for some pesticides and metabolites. In order to deal with differences in species sensitivity and in acute and chronic toxicity an uncertainty factor of 100 is applied to derive critical concentrations for groundwater species (=CC_{gs}) according to the EPA-method (Table 4.2).

Crustaceans (**CC_{cr}**)
The number of different crustacean species for which toxicity data are available is generally limited; mostly data are available for fewer than four and often just one species (mostly a daphnid). The method of Luttik and Aldenberg (1997) is therefore applied for estimating the left-sided 95th percentile of the sensitivity distribution (HC5) dealing with small sample numbers. As input NOEC values from chronic toxicity studies are preferred. Since, however, most available data are LC50 or EC50 values coming from acute studies an acute-chronic ratio of 10 is applied for estimating a NOEC (see Appendix 5 for motivation). Experimentally established NOEC values completed with estimated values together are taken as input values for calculation of the HC5.

Toxicity data of at least 4 different freshwater species of crustaceans for 25 different pesticides are collected from Crommentuijn *et al.* (1997) and from the AQUIRE database (US-EPA, MED-Duluth, version April 23th, 1998). These data are used for calculation of an estimate of a pooled variance (S_p^2) of crustacean toxicity data for pesticides (formula (1) in Luttik and Aldenberg, 1997). The s_p is assumed to be an estimate of the standard deviation of crustacean species sensitivity for pesticides. According to Aldenberg and Slob (1993) the $\ln(HC5) = \mu - 1.62\sigma$. Hence, the standard deviation (σ) is given through the pooled estimate s_p and the mean (μ) by the mean of the sample (x). This ln(HC5) is a median estimate, it overestimates as well as underestimates the true ln(HC5) by 50%. The 5th percentile of this estimate is located at $\mu - 1.62\sigma + 1.64\sigma/\sqrt{n}$, with 1.64 being the Z-value of the standard normal distribution at the 5th percentile (Kooijman, 1987).

In the original concentration units the median and left confidence limit of the HC5 are calculated by:

$$HC5(50) = \exp(x - 1.62\sigma) \text{ and}$$

$$HC5(95) = \exp[x - (1.62\sigma + 1.64/\sqrt{n})\sigma]$$

The difference between HC5(50) and HC5(95) is determined by the number of toxicity data for different species. If for one single species and compound more data, either NOEC or NOECestimate, were available its geometric mean was applied. For the calculation of risk quotients the HC5(50) is applied as critical concentration for crustaceans (=CC_{cr}).

Micro-organisms (**CC_{mo}**)

Criteria reported in studies with Microtox® are EC10, EC20, and EC50 values at different exposure times (5 - 30 min.). EC20 and EC50 values are both extrapolated to EC10 values by dividing with 3, this factor is according to van Beelen and Doelman (1997). When more than one measured or extrapolated EC10 are available for a compound its geometric mean is calculated. The EC10 or their geometric means are applied as critical concentration for micro-organisms (=CC_{mo}). Differences in exposure times are not accounted for because they appear smaller than the differences found between different studies.

5. Results and Discussion

The chemicals discussed in this report, their application, mode of action and chemical group are listed in Appendix 2.

5.1 Pesticides in ground water

5.1.1 Monitoring data

Table 5.1 gives an overview of evaluated pesticide monitoring data in the upper ground water (0-10 m-bss). Interesting to compare is the total number of observations (n) with the number of different localities investigated (m). The fact that frequently n» m indicates large dependency between observations. The number of different locations with pesticides detected (m>LOD) is rather low (except for 1,2-dichloropropane this number is less than 10, mostly less than 5). Nevertheless, nine compounds were detected at all localities investigated (m = m>LOD). Of the total of 33 compounds detected, 26 exceed one or more times the standard of 0.1 µg/l. For 18 compounds the median of the positive observations (median+) exceeds this criterion. This is not surprising since the data of Table 5.1 are all collected at locations where pesticides have been applied.

Table 5.1. Summary table of pesticide concentrations in shallow Dutch ground water (0-10 m-bss). Represented in *italic* are pesticide metabolites. n = total number of observation, LOD = limit of detection, m = number of sample localities, median+ = median of positive samples, perc95+ = 95% percentile of positive samples, max = maximum pesticide concentration; land-use: major land use of sampled localities.

compound (µg/l)	n	n>LOD	M	m>LOD	median+	perc95+	max	land-use
aldicarb	98	4	20	1	0.2	0.3	0.3	potatoes,
aldicarb-sulfone	95	52	19	2	1.8	59	74	potatoes
aldicarb-sulfoxide	88	26	19	1	1.6	19	26	potatoes
amitrole	19	10	4	4	0.9	1.7	1.9	non-crop areas
atrazine	153	82	5	5	0.04	0.17	0.3	maize
desethyl-atrazine.	126	69	4	3	0.09	0.83	1.50	maize
desisopropyl-atrazine	130	42	4	3	0.07	0.41	0.98	maize
bentazone	249	93	21	7	0.08	0.55	1.1	maize
bentazone	4	4	1	1	19	30	31	flower bulbs
chlorpropham	13	0	1	0	<0.05	<0.05	<0.05	vegetables
2,4-D	71	3	20	1	0.10	0.19	0.2	agriculture
dichlobenil	14	12	4	4	0.05	0.48	0.83	non-crop-area
BAM	16	16	5	5	13	26	34	non-crop-area
1,3-dichloorpropene[a]	219	11	27	3	2.1	55	80	potatoes,beet
1,2-dichloropropane[b]	198	112	27	14	5.6	135	200	potatoes,beet
dimethoate	7	1	4	1			0.06	potatoes, leek
dinoseb[c]	158	23	23	3	0.5	5.0	9.2	potatoes, beet
dinoterb	47	2	21	1	0.04	0.05	0.05	potatoes, beet
diuron	22	14	4	4	0.15	1.9	2	non-crop-area
DNOC	47	2	21	1	0.07	0.09	0.09	potatoes
ethoprophos[d]	55	7	4	3	0.04	0.10	0.11	potatoes, beet
ETU[e]	174	14	23	4	0.15	13	30	potatoes, beet
ETU[e]	26	26	7	7	5.2	34	42	flower bulbs
fluazifop-butyl[f]	11	0	2	0	<0.05	<0.05	<0.05	potatoes
fluazifop	12	0	2	0	<0.03	<0.03	<0.03	potatoes

Table 5.1 (continued)

Compound (µg/l)	n	n>LOD	m	m>LOD	median+	perc95+	max	land-use
glyphosate[g]	12	1	3	1			0.5	potatoes, maize
AMPA[g]	12	2	3	2	0.35	0.40	0.40	potatoes, maize
linuron	49	1	21	1			0.09	potatoes, cereals, asparagus
MCPA	93	1	21	1			0.3	cereals, grass
mecoprop	119	4	23	2	0.3	1.8	2	cereals, grass
metamitron	133	16	23	3	0.19	0.57	0.73	maize, beet
MITC[h]	117	3	22	3	1.5	2.4	2.5	potatoes, beet
MITC[h]	9	8	5	5	0.05	0.42	0.59	flower bulbs
metribuzin	69	16	20	2	0.4	5.7	19	potatoes, maize, cereals, asparagus
pirimicarb	13	0	1	0	<0.05	<0.05	<0.05	potatoes
propachlor	21	8	1	1	0.2	0.37	0.4	vegetables

a Sum of *cis*- and *trans*-dichloropropene.
b Some positive samples are due to application of 1,3-dichloropropene with 1,2-dichloropropane as a formulation additive (30% or 5% 1,2-dichloropropane). Nowadays 1,2-dichloropropane is an impurity of 1,3-dichloropropene (<0.1-0.5%).
c Dinoseb has not been used since 1990.
d Ethoprophos concentrations are indicative, because all positive samples were detected by NPD. Only recently it was shown that this method is not selective enough and may overestimate ethoprophos-concentrations (RIZA, 1997).
e ETU (ethylenethioureum) is a metabolite of bis-dithiocarbamates (maneb, zineb, mancozeb and metiram); all fungicides. ETU concentrations are indicative, but are confirmed by confidential research (Boland et al, 1995). Confidential research revealed some analytical problems, which may have influenced the data presented here (resulting in overestimation).
f After application, fluazifop-butyl hydrolyses to fluazifop, which is the actual active compound.
g Glyphosate and AMPA (aminoethyl-phosphonic acid) concentrations are indicative because the analytical method is not selective enough for the separation and detection of these polair compounds at such low levels.
h After application, metam-sodium decomposes to MITC (methylisothiocyanate), which is the actual active compound.

Table 5.2. Pesticide concentrations in Dutch ground water deeper than 10 m b.s.s. in aquifers used for drinking water production (VEWIN database, 1992-1995). Represented in *italic* are pesticide metabolites. n = total number of observations, m = number of locations, LOD = limits of detection, median+ = median of positive observations, 95%perc+. = 95% percentile of positive observations, max = maximum pesticide concentration.

compound (µg/l)	n	n>LOD	m	m>LOD	LOD min	LOD max	median+	95% perc+	max
atrazine	1283	13	192	10	0.003	1	0.05	0.11	0.13
desethyl-atrazine	1106	1	165	1	0.003	0.1			0.05
bentazone	303	15	78	10	0.01	0.29	0.05	0.20	0.29
2,4-D	90	1	13	1	0.03	0.07			0.06
dichlobenil	526	2	60	1	0.005	0.03	0.16	0.22	0.23
1,2-dichloropropane[a]	645	251	14	12	0.01	2.39	0.36	2.9	3.5
dinoterb	181	1	25	1	0.03	0.05			0.07
diuron	134	1	16	1	0.02	0.1			3.3
DNOC	193	1	26	1	0.02	0.05			0.28
ETU	69	30	2	1	0.05	0.5	0.05	0.29	0.8
MCPA	105	2	13	2	0.03	0.07	0.14	0.21	0.22
mecoprop	105	3	14	3	0.03	0.07	0.07	0.80	0.88
bromacil	935	25	111	5	0.005	0.5	0.03	0.148	0.15
chlorobromuron	79	1	11	1	0.02	0.1			0.14
dikegulac-sodium	40	4	19	2	0.01	0.05	0.09	0.29	0.33
beta-endosulfan	409	2	93	1	0.005	0.1			0.14
heptachlor	1241	1	189	1	0.009	0.1			0.13
isoproturon	119	1	15	1	0.01	0.1			0.05
lindane	1291	1	203	1	0.0007	0.1			0.002
parathion-ethyl	1141	12	29	1	0.005	0.05			0.01
simazine	1171	7	169	2	0.006	1			0.04
tetrachlorovinphos	307	8	10	3	0.01	0.05			0.09

a See note b Table 5.1.

The VEWIN database contains altogether 140 compounds, those encountered above detection limits are summarised in Table 5.2. These data cannot be linked with land-use practices, it concerns data from water catchment areas and from aquifers exploited for drinking water production. Of the 22 compounds in this table, 14 sometimes exceed the 0.1 µg/l criterion. Maximum concentrations exceed 1 µg/l only twice (1,2-dichloropropane and diuron), and never reached concentrations higher than 10 µg/l as in the use-related database. In comparison with Table 5.1 the number of different locations investigated is much larger. Again 1,2-dichloropropane shows up as the compound present at the largest number of locations (m>LOD = 12). Proportionally the number of observations and locations where pesticides have been demonstrated is lower in deeper ground water (Table 5.2) than in shallow ground water (Table 5.1). Though, their deeper occurrence may indicate the presence in larger water bodies. Five compounds demonstrated in shallow ground water, some at rather high level (BAM), are not present in the VEWIN database. Ten compounds are detected in deeper ground water while there are no data available on their presence in shallow ground water, related to agricultural applications. These compounds are given at the end of Table 5.2. These compounds were not included in the monitoring programmes concerning shallow ground water. Compounds analyzed for but not detected by VEWIN are listed in Appendix 3.

Table 5.3. Use-related pesticide concentrations in ground water of some European countries. n = number of samples, LOD = limit of detection, avg = average concentration, max = maximum concentration.

compound (µg/l)	date	n	n>LOD	LOD	avg	max	crop
France							
2,4-D	1992-1995	250	6	0.05	0.09	0.14	
MCPA	1992-1995	250	0	0.05	0		
mecoprop	1992-1995	250	9	0.05	0.06	0.14	
Germany							
atrazine	1990	3	1			0.082	wheat
desisopropyl-atrazine	1994	1	1			0.06	wheat
mecoprop	1993	4	3	0 .05	0.09	0.2	wheat
metribuzin	1990	3	1			0.02	wheat
Italy							
atrazine	1995	1326	824	0.02			wine
desethyl-atrazine	1994-1995	1294	929	0.02			wine
Spain							
atrazine	1994				1.2	1.2	citrus
diuron	1994				<0.4		citrus
Sweden							
atrazine	1990-1995	82	23		2	14	wheat
desethyl-atrazine	1990-1995	77	20		1.7	14	wheat
BAM	1990-1995	10	6		0.4	1	wheat
bentazone	1990-1995	78	7		8.3	26	wheat
MCPA	1990-1995	100	1			0.2	wheat
mecoprop	1990-1995	80	4		0.1	0.2	wheat
metribuzin	1990-1995	100	1			0.2	wheat
United Kingdom							
dimethoate	1993	26	1			0.01	wheat
MCPA	1993	25	0	0.1			wheat
pirimicarb	1993	25	0	0.03			wheat

Pesticides of Table 5.1 for which the SSLRC (1997) study gives data from other European countries are summarised in Table 5.3. The number of pesticides reported above detection limits is much lower than the 33 of Table 5.1. Atrazine, BAM, bentazone, 2,4-D, MCPA, mecoprop and metribuzine are demonstrated to occur above detection limits both in the Netherlands and in France, Germany, Sweden, Italy or Spain. Comparison between countries is hindered by large differences in data availability and design and objectives of the various monitoring programs. The data, however, illustrate that the presence of detectable pesticides levels in ground water, also above environmental quality objectives, is a European wide problem.

The most seriously groundwater contaminating pesticides apparently are atrazine (and its metabolite desethyl-atrazine), mecoprop, bentazone and MCPA; they exceed the environmental standard of 0.1 µg/l in each of the Tables 5.1 through 5.3. However, such a conclusion should be drawn carefully because the tables summarise very heterogeneous data. The data originate from monitoring programmes of several institutes, with different objectives and different numbers of samples. It turns out that these five compounds are more often included in the monitoring programmes compared to other compounds. The use of these compounds was (and in the Netherlands still is) widespread, but the sampling points not necessarily do represent all the areas on which the compounds are used; vulnerable areas may be over-represented in the tables.

Nevertheless, the tables show that groundwater is not coincidentally contaminated with pesticides. The tables alone give just a deficient overview of the concentrations one can expect in shallow ground water. A better overview can be obtained if an additional frequency distribution graph is given. Figure 5.1 shows frequency distributions for six of the more regularly observed compounds in shallow ground water (0-10 m-bss). Nearly 50% of all aldicarb-sulfone measurements is above the standard of 0.1 µg/l. Approximately 15% of all measurements exceed the standard more than 100 times. For atrazine and its metabolite desethyl-atrazine the number of values exceeding the 0.1 µg/l is approximately 50%, but to a lesser degree than for aldicarb-sulfone. For the other pesticides or metabolites shown in Figure 5.1 both the percentage of values exceeding 0.1 µg/l and the degree of exceeding are lower. The formulation additive 1,2-dichloropropane is found in most of the samples when this compound is included in a monitoring programme. Most of the samples show a concentration that is 10 to 100 times the standard. Approximately 15% of the samples have a concentration of more than 1000 times the standard of 0.1 µg/l.

Table 5.1 illustrates that the pesticide concentrations in ground water are strongly related to land-use. In case of ETU and bentazone, concentrations in flower bulb cultivation areas differ significantly from concentrations found in areas with potatoes as main culture. This is at least partly caused by a combination of higher dosages applied and more vulnerable soil types in flower bulb cultivation areas. Remarkable is that amitrole, dichlobenil, BAM, and diuron, compounds with non-agricultural applications may exceed the standard of 0.1 µg/l, as well.

Furthermore Table 5.1 shows application of nematicides, fungicides and soil fumigants in potato, beet and flower bulb cultures may induce very high (>10 µg/l) pesticide concentrations in shallow ground water. Metabolites (aldicarb-sulfone and -sulfoxide, BAM and ETU) and formulation additives (1,2-dichloropropane) apparently are amongst the most critical compounds. In the non-use related database (Table 5.2) herbicides appear the most critical compounds, but their highest detected concentrations are 1-2 magnitudes lower than in the use-related database. One should keep in mind however that the distribution of

analyses is biased towards herbicides; in monitoring programmes much more attention has been given to herbicides than to other pesticides.

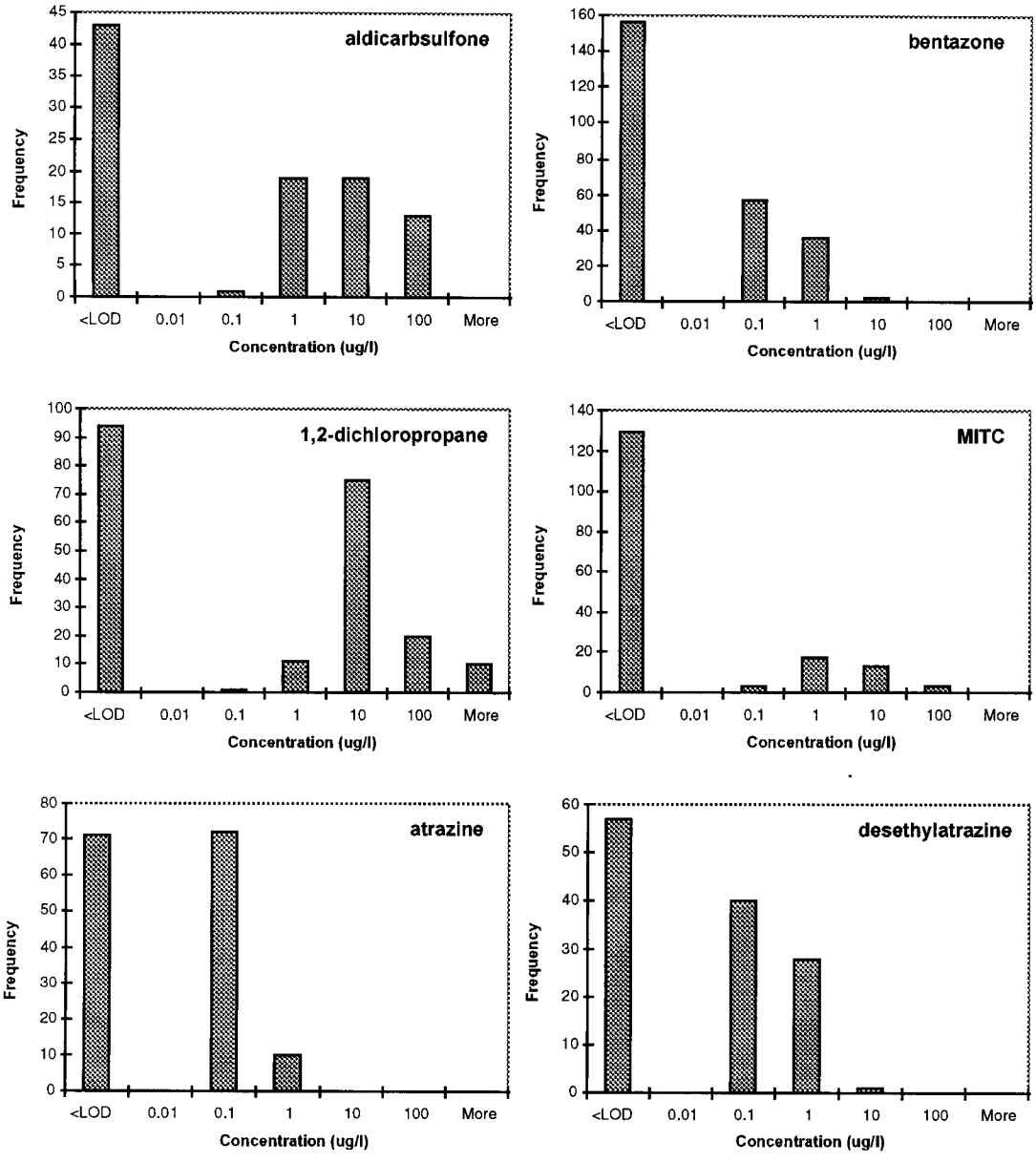

Figure 5.1. Frequency distribution of pesticide concentrations in shallow ground water, samples taken between 0 and 10 m-bss. Classes are <LOD, <0.001, 0.01-1, 1-10, 10-100, and >100 µg/l.

The extent of contamination is not only judged by the **concentration** of the pesticides but also by the **frequency** of detection in relation to the **number of sampling locations**. To quantify the latter, the number of locations with positive findings (m>LOD) is compared with the total number of locations sampled (m). As a measure of the extent of contamination, pesticides with 10% or more of the sampled locations with positive findings have been counted. In Table 5.1, 21 out of 33 pesticides have more than 10% contaminated locations (average 41%, min. 0% - max. 100%). In Table 5.2, 5 of the 22 detected pesticides have more than 10% contaminated locations (average 8%, min. 0% - max. 86%). Three factors cause the differences between these tables: time, depth and the sampling program. Table 5.1 mainly contains data of measurements on samples aimed to have been taken in a period following agricultural applications of pesticides, whereas Table 5.2 contains data of routine

monitoring programs in observation filters of drinking water companies. In the latter case a relation with pesticide use is not obvious and reported pesticide concentrations are consequently lower. The comparison between both tables is summarised below (Table 5.4).

Table 5.4. Comparison between above given tables 5.1 and 5.2.

Source	groundwater type	sampling type	%locations with samples >LOD
Table 5.1 (use-related)	shallow	aimed sampling after pesticide application	41%
Table 5.2 (no-use related)	deep	monitoring	8%

It must be emphasised that the number of "contaminated" sites is not a direct measure for the contaminated area. The area of the contaminated site is very dependent on groundwater flows. Moreover contamination is a time-dependent phenomenon. The concentration of a pesticide in a groundwater sample is a "snapshot". When pesticides have been applied the concentration front will move downwards into the soil. The rate of this vertical transport depends on adsorption characteristics of the soil and the pesticide, precipitation and soil structure.

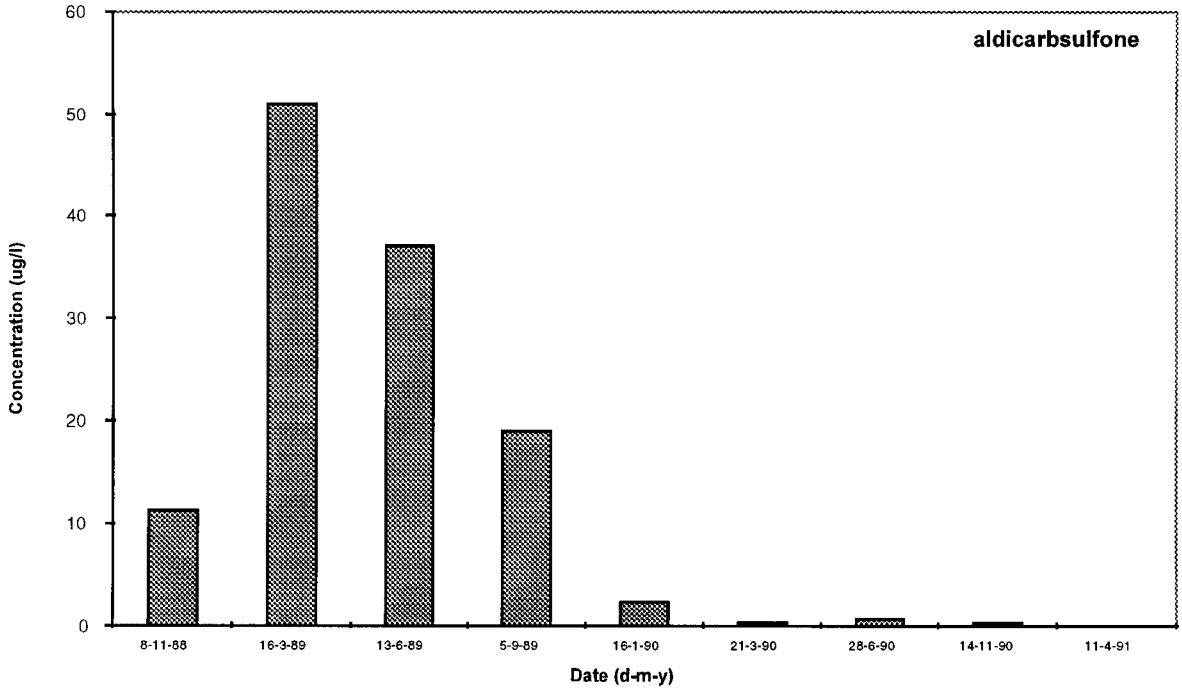

Figure 5.2. Aldicarb-sulfone concentrations in ground water at 1.5 m-bss after aldicarb application (3 kg/ha) in March 1988.

This effect is illustrated with aldicarb-sulfone (Figure 5.2), 6 months after aldicarb application in potatoes, the peak of the major mobile metabolite aldicarb-sulfone appears. It takes 2 years before the concentration drops to below the detection limit. For pesticides less mobile than aldicarb-sulfone (Kom =0.5 l/kg) the downward movement of the pesticide front will be much slower. This could result in a longer residence time in the plough layer and in more favourable conditions for (bio)degradation. So large variations in pesticide concentrations are normal, caused by the choice of the sampling time after pesticide application, sampling depth, soil characteristics, and hydrology.

The observed difference between Table 5.2 and Table 5.1 (Table 5.2 contains more data below the detection limit than Table 5.1) could therefore at least partly be caused by the fact that fronts of pesticides and their metabolites have not yet moved deep enough. In that case the problem of pesticide contamination in deeper ground water will increase in the future even if pesticide use will be reduced.

Table 5.5. Properties of pesticides frequently detected in deeper ground water.

compound	DT50 (day)	Kom (l/kg)	DT50/Kom
atrazine	50	68	0.74
bentazone	16	4	4
bromacil	371	71	5.2
1,2-dichloropropane	800	11	72.7
ETU	0.08 - 0.16	2	0.04 - 0.08

Considering the substances that are frequently found in deeper ground water a general profile of physico-chemical characteristics of potential hazardous compounds is not clear. As can be seen in Table 5.5 substances characterised as mobile to slightly mobile and readily degradable to very slightly degradable are frequently found in deeper ground water. It is the ratio between DT50 and Kom that is important to estimate the leaching potential: a large DT50/Kom ratio is favourable for leaching. The leaching of bentazone, bromacil and 1,2-dichloropropane is therefore obvious, as the DT50/Kom ratio is large. The data of ETU, however, can not be explained in this way. Apparently there are other conditions (e.g. redox-potential, pesticide history) that overrule a general behavioural pattern.

5.1.2 Geographical modelling.

Modelling in combination with GIS is used to generate a national and an European overview of the threats posed on ground water. For the national overview atrazine, MITC and aldicarb are selected. For Europe calculations are performed for atrazine.

Atrazine (Figure 5.3) is used (sprayed) in the Netherlands for the control of weeds in maize. Depending on the composition of the formulation applied, the amounts of active ingredient on maize fields range in the Netherlands from 0.5 to 1.0 kg/ha. If applied on agricultural fields, atrazine and its metabolite desethyl-atrazine (the only metabolite considered in the calculation) may leach to ground water. The organic matter content of the soil appears the most determining factor causing differentiation in the amounts leached. Leaching is expected to be lowest in the peat and peaty clay areas of the Netherlands (leaching below 0.1 µg/l at 1-2 m-bss) and highest in areas with soils poor in organic matter (old dune areas and excavated peat areas). In the latter total leached concentrations above 1 and sometimes even above 10 µg/l at 1-2 m-bss are expected. Maize cultivation is mostly found in the sandy areas of the southern and eastern part of the country. In these areas pesticide concentrations in the uppermost groundwater above 0.1 µg/l are expected to occur below more than 5% and sometimes even over 25% of the agricultural fields. Fortunately the soils in these maize cultivation areas belong not to the most vulnerable ones in the Netherlands.

Metam-sodium is used (incorporated) as a soil fumigant mainly in the cultivation of potatoes, bulbs and beets. Metam-sodium quickly transforms into MITC (methylisothiocyanate) (Figure 5.4), a compound with a relatively high vapour pressure and Henry coefficient (Buckman, 1993). Part of the transport of MITC therefore occurs in the gas-phase of the soil. As with atrazine, the organic matter of the soil appears an important factor influencing the vertical transport of MITC, but now also the soil texture and the groundwater depth are

important. These two factors determine whether transport in the gas-phase is possible as they influence the occurrence of larger pores and their connectivity (a higher water level and therefore a higher water content limits gas transport). Applications of metam-sodium usually occur in autumn with rates of 100 kg/ha or more. Potential concentrations in ground water in most soils are expected to be above 10 µg/l at 1-2 m-bss, except for soils very rich in organic matter and with a high groundwater table. The fact that the compound is applied in autumn contributes to a large extent to the groundwater contamination. As the percentage of area on which the compound is applied is rather low, the 0.1 µg/l concentration is exceeded in shallow ground water only on a small percentage of the agricultural area (mainly in the potato growing areas) of the Netherlands.

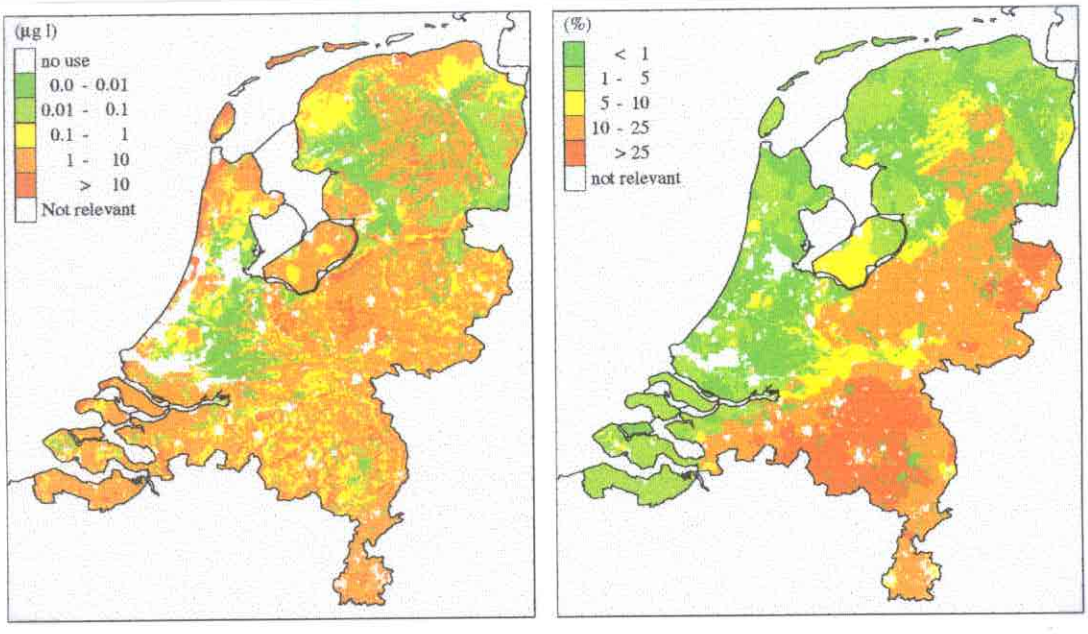

Figure 5.3. (a) Average atrazine concentration at 1-2 m-bss at actually used dosage rates. (b) Percentage of cultivated area with an atrazine concentration 1-2 m-bss above the standard of 0.1 µg/l.

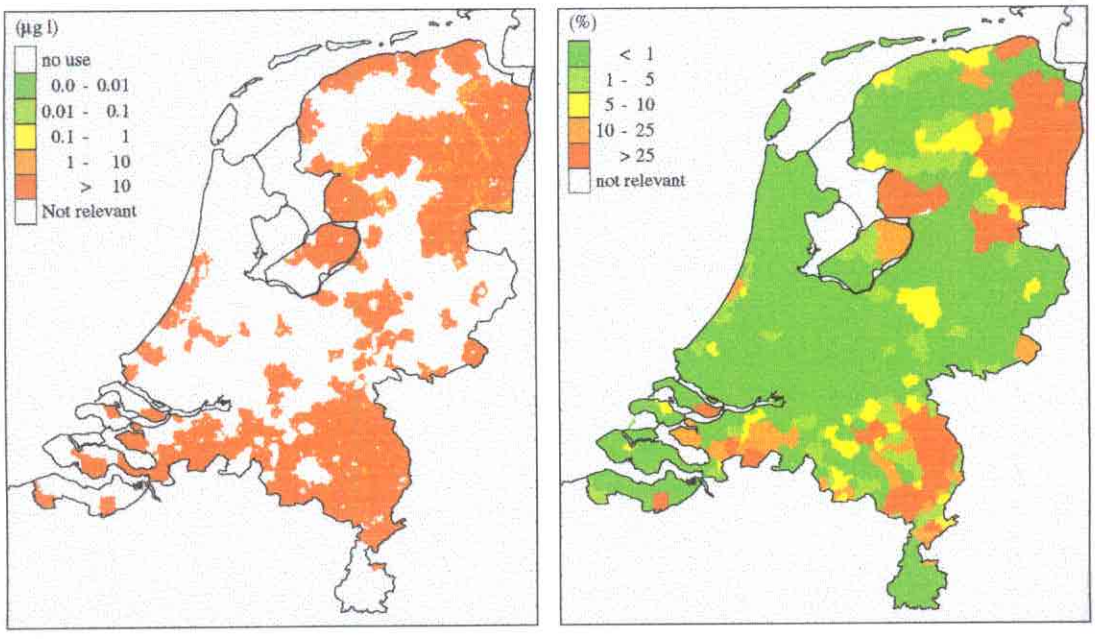

Figure 5.4. (a) Average MITC concentration at 1-2 m-bss at actually used metam-sodium dosage rates. (b) Percentage of cultivated area with a MITC concentration 1-2 m-bss above the standard of 0.1 µg/l.

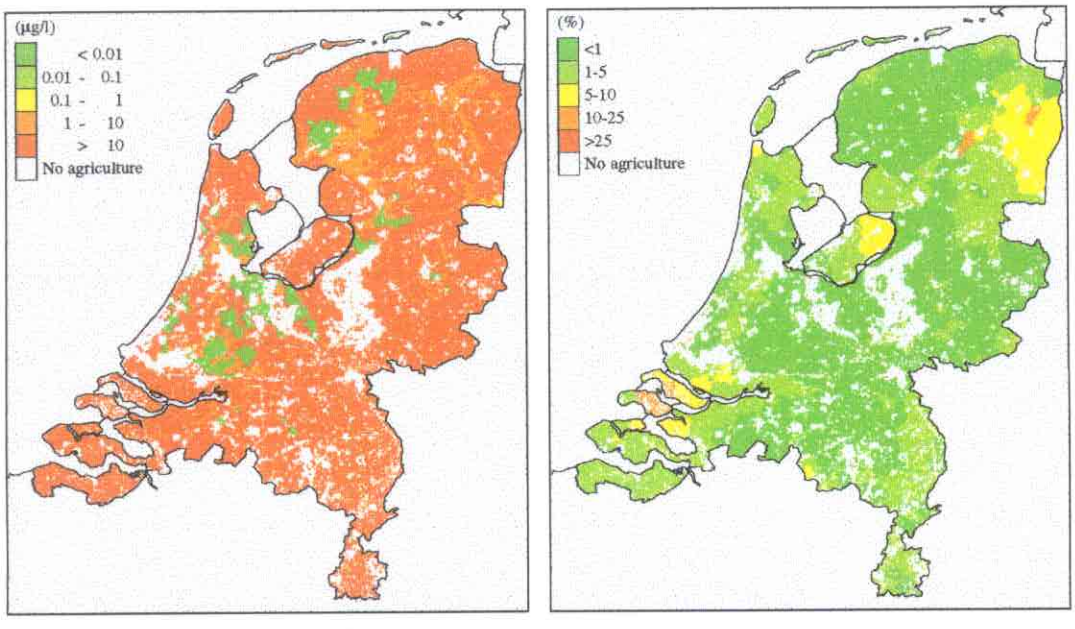

Figure 5.5. (a) Average aldicarb concentration at 1-2 m-bss at actually used dosage rates. (b) Percentage of cultivated area with an aldicarb concentration 1-2 m-bss above the standard of 0.1 µg/l.

Aldicarb (Figure 5.5) is used (incorporated) as a soil nematicide/insecticide mainly in the cultivation of potatoes at a rate of 3 kg/ha and in tree nurseries at a rate of 30 kg/ha. The latter application usually is to tubs and therefore not directly posing a threat to ground water. Aldicarb relatively quickly transforms into its sulphoxide and subsequently into its sulphone. The latter two metabolites are more persistent and more mobile than the parent compound. The soil hydraulic conductivity and the precipitation excess mainly determine the leaching of aldicarb and its metabolites. Potentially the total concentration of the compounds is expected to be above 1 µg/l at 1-2 m-bss. Considering the areas where the compound is actually used, aldicarb poses a threat to ground water mainly in the excavated peat areas in the north of the Netherlands as well as in the reclaimed polders.

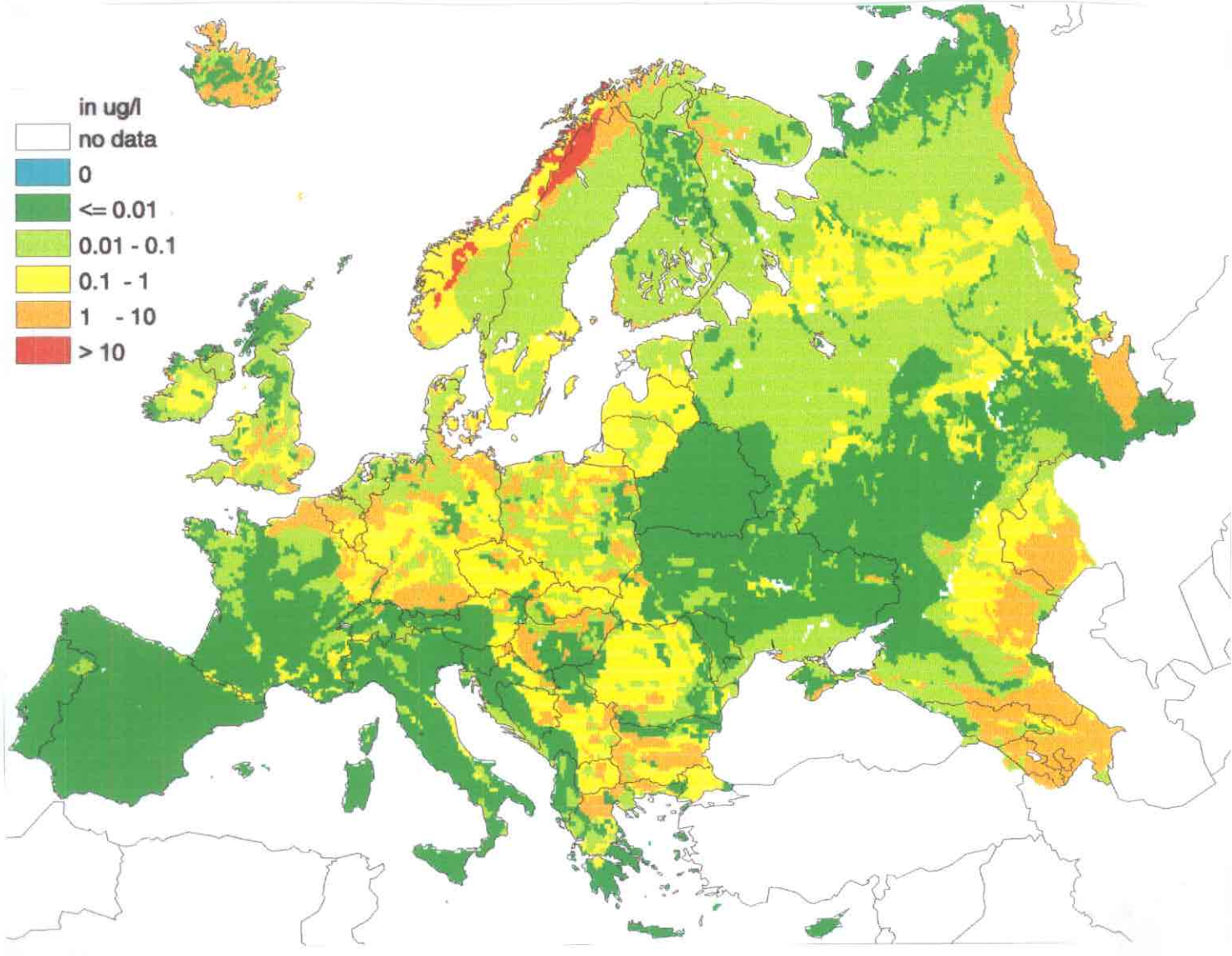

Figure 5.6 Potential leaching of atrazine and its metabolite desethyl-atrazine in Europe. Calculations performed with a meta-model of PESTRAS analogous to the method described by Beinat and Van den Berg (1996).

A map of Europe has been generated for potential leaching of atrazine (Figure 5.6). This map shows that there are large areas in Europe, which are vulnerable for leaching of pesticides with properties comparable to atrazine. Large areas that show a high leaching potential

though are not in use as agricultural land because of poor soil or climate conditions. This is the case for Norway and mountainous regions in Russia (Ural, Caucasus). Although the potential leaching in these areas is high, the actual leaching will be negligible because there is no pesticide use in these areas. Although Germany, Italy and the United Kingdom show a high potential leaching of atrazine, the actual leaching of atrazine is zero because atrazine is not admitted in these countries.

The number of samples recorded in Table 5.3 is far too low to judge on the accuracy of the map. They, however, do indicate that leaching of atrazine occurs and that the calculated concentrations are in the range of the observed concentrations. The calculations indicate that desethyl-atrazine is likely to leach to a greater extent than atrazine itself. Unfortunately it cannot be concluded from the measurements whether this also occurs in reality.

5.2 Ecotoxicologically critical concentrations

For the pesticides mentioned in part 5.1 available MPC values are given in Table 5.6; the MPC_{water} is used as critical concentration (CC_{ae}). By lack of data not for all compounds MPC values are available or could additionally derived. Some compounds have MPC values lower than the actual standard for pesticides in ground water of 0.1 µg/l: aldicarb, aldicarb-sulfoxide, dinoseb, dinoterb, ethoprofos, MITC, parathion-ethyl, pirimicarb and trifluralin. For these compounds ecotoxicological effects cannot be excluded at the actual standard for pesticides in ground water. For some other compounds MPC values are close to actual criterion (between 0.1 and 1 µg/l): carbendazim, diuron, isoproturon, lindane, linuron, metolachlor and simazine.

Table 5.6. Available maximum permissible concentrations (MPC) of pesticides for (fresh)water ecosystems. MPC_{water} based on Van de Plassche and Bockting (1993), Van de Plassche (1994) and Crommentuijn *et al.* (1997) or additionally derived with standard methods.

substance (µg/l)	MPC_{water}	substance	MPC_{water}
1,2-dichloropropane	76	ethoprophos	0.063
1,3-dichloropropene	8	ETU	260
2,4-D	9.9	heptachlor	0.0005
aldicarb	0.098	isoproturon	0.32
aldicarb-sulfone	-	lindane	0.77
aldicarb-sulfoxide	-	linuron	0.25
atrazine	2.9	MCPA	1.7
bentazone	64	mecoprop	3.9
chlorpropham	-	metamitron	10
dimethoate	23	MITC[a]	0.035
dinoseb	0.025	parathion-ethyl	0.0019
dinoterb	0.034	pirimicarb	0.09
diuron	0.43	simazine	0.14
DNOC	21		

The few existing EC50 values of pesticides for a stygobitic crustacean (*Parastenocaris germanica*) and the derived critical concentration CC_{gs} are all summarised in Table 5.7. These data indicate that effects cannot be excluded at the 0.1 µg/l level for aldicarb-sulfoxide, cypermethrin, fenpropathrin and thiram; only the first compound, however, is demonstrated in Dutch groundwater monitoring programs.

Table 5.7. Available acute toxicity data for the groundwater crustacean *Parastenocaris germanica* and the from these data derived critical concentrations (CC_{gs}) for groundwater ecosystems.

substance (µg/l)	EC_{50} (96 hr)	CC_{gs}
aldicarb-sulfoxide	<10	<0.1
aldicarb-sulfone	<180	<1.8
cypermethrin	0.02	0.0002
ethoprofos	450	4.5
ETU	2330	23.3
fenpropathrin	0.006	0.00006
MITC	32	0.32
thiram	2.3	0.023

Table 5.8. Summary table of available HC5 estimates as critical concentration for crustaceans derived according to Luttik and Aldenberg (1997). HC5(50) is the median estimate, HC5(95) is the left confidence limit; the difference between both estimates indicates the uncertainty which is related to the number of data. The applied estimated pooled variance (S_p^2) based on 25 pesticides with toxicity data for 4 or more different species was 6.84.

substance (µg/l)	nr of species	concentration range	HC5(50) = CC_{cr}	HC5(95)
1,2-dichloropropane	1	48000	69	0.95
1,3-dichloropropene	1	6200	8.95	0.12
2,4-D	4	320 - 47000	61	7.2
aldicarb	1	84	0.12	0.002
aldicarb-sulfon	1	670	0.97	0.01
aldicarb-sulfoxide	1	67	0.10	0.001
AMPA	1	690000	996	13.6
atrazine	4	140 - 2500	7.6	0.88
bentazone	1	64000	92	1.3
dichlobenil	5	7800 - 34000	19	2.8
dimethoate	1	108	1.6	0.02
dinoseb	2	240 - 2100	1.0	0.05
dinoterb	1	470	0.68	0.01
diuron	6	16 - 200	1.1	0.19
DNOC	3	83 - 538.8	2.5	0.21
ethoprophos	1	50	0.07	0.001
ETU	1	26000	38	0.51
fluazifop	1	323000	466	6.4
fluazifop-butyl	1	> 1000	>1.44	>0.020
glyphosate	2	5300 - 47000	23	1.1
isoproturon	1	4400	64	0.87
lindane	3	1.8 - 22.8	0.09	0.01
linuron	1	122.6	1.8	0.02
MCPA	1	65950	952	13
mecoprop	1	11770	170	2.3
metamitron	1	100000	144	2.0
MITC[a]	1	35	0.05	0.001
parathion-ethyl	4	0.02 - 0.5	0.002	0.0002
pirimicarb	2	0.9 - 90	0.13	0.01
propachlor	1	266	3.8	0.05
simazine	3	1000 - 13000	5.1	0.43

a data on metam-sodium are applied because this substance is immediately transformed into MITC in water

For five of 31 considered compounds median estimates of HC5 for crustaceans are 0.1 µg/l or lower: aldicarb-sulfoxide, ethoprophos, lindane, MITC and parathion-ethyl (Table 5.8). For an additional group of 8 compounds the left confidence limit of the HC5 is lower than 0.1 µg/l: aldicarb, aldicarb-sulfone, dimethoate, dinoseb, dinoterb, linuron, pirimicarb, and propachlor. Because most HC5 estimates are based on data for very few different species large uncertainties exist, resulting in a large difference between HC5(50) and HC5(95). For the calculation of risk quotients (part 5.3) the HC50(50) is applied as ecotoxicological critical concentration (CC_{cr}).

Some comments on the application of the HC50(50) as an estimate of a critical concentration for groundwater crustaceans is requisite. The uncertainty of sensitivity estimates caused by

the lack of sufficient toxicity data in general is already mentioned. Another source of uncertainty is that only data for surface water crustaceans are available, strongly dominated by very few daphnid species, and that these may deviate strongly in physiology from groundwater crustaceans. Physiological adaptations as a result of groundwater life may structurally cause differences in sensitivity patterns between surface and groundwater crustaceans. Due to the lack of knowledge of the physiology and toxicology of groundwater organisms the extent of this source of uncertainty is hard to elucidate.

Table 5.9. Summary table of EC10 Microtox values.

compound (µg/l)	nr of values	EC10
atrazine	7	10200
bentazone	2	9700
2,4-D	9	7200
1,2-dichloropropane	1	37000
DNOC	1	2200
ETU	1	700
glyphosate	1	2600
lindane	7	19200
MCPA	2	57700

Table 5.9 summarises available Microtox® values. For 9 compounds EC10 values could be derived, further treated as the ecotoxicologically critical concentrations for micro-organisms (CC_{mo}). In comparison with critical concentrations derived from plant, vertebrate and/or invertebrate toxicity data, CC_{mo} values are high. This suggests that micro-organisms are relatively insensitive to the pesticides. This is understandable since most pesticides have a specific mode of action, many of them are cholinesterase inhibitors, associated with the function of the animal nervous system. None of the critical concentration for micro-organisms are lower than 0.1 µg/l this might indicate that the actual standard of 0.1 µg/l do not pose threats to the microbial function of aquifers.

5.3 Pesticide risks based on monitoring data

Table 5.10 gives risk quotients (RQs), the median and 95-percentile levels of positive pesticide records as environmental concentrations divided by the various critical concentrations. Not for all compounds detected in monitoring programs toxicity data are available, for some compounds no ecotoxicological critical concentration could be found or derived at all (viz., desethyl-atrazine, desisopropyl-atrazine, BAM, fluazifop-butyl). In particularly BAM revealed to occur at relatively high levels in shallow ground water (Table 5.1).

The risk quotients based on CC_{ae} show that for aldicarb, 1,2-dichloropropane, 1,3-dichloropropene, dinoseb, dinoterb, diuron, ethoprofos, and MITC environmental concentrations exceed the critical concentration. So, on the basis of generic CC_{ae} values toxicological impact of these compounds on groundwater ecosystems is to be expected. Except dinoterb and diuron these compounds have a rather wide mode of action. Most severe impact (RQ > 10) do probably have dinoseb and MITC.

Comparison between summary values of environmental concentrations and critical concentrations for groundwater species (CC_{gs}) is possible only for a few compounds (Table 5.7). Risk quotients for aldicarb-sulfone, aldicarb-sulfoxide, ETU and MITC are larger than one unity.

Table 5.10. Various risk quotients for pesticides in shallow ground water (use related). Two summary values of environmental concentration (median (med) and 95-percentile (95+) of positive pestide records) are combined with the four ecotoxicologically critical concentrations (CC_{ae}, CC_{gs}, CC_{cr} and CC_{mo}). In **bold** risk quotients that exceed 1. Not for all compound detected in shallow groundwater critical concentrations are available.

compound	med/CC_{ae}	95+/CC_{ae}	med/CC_{gs}	95+/CC_{gs}	med/CC_{cr}	95+/CC_{cr}	med/CC_{mo}	95+/CC_{mo}
aldicarb	**2.04**	**3.06**			**1.65**	**2.47**		
aldicarb-sulfone			**>18**	**>594**	**1.86**	**61.4**		
aldicarb-sulfoxide			>0.9	**>11**	**16.5**	**196**		
amitrole					0.32	0.59		
atrazine	0.01	0.06			0.01	0.02	0.00	0.00
desethyl-atrazine.								
desisopropyl-atrazine								
bentazone (a)	0.00	0.01			0.00	0.01	0.00	0.00
bentazone (b)	0.29	0.47			0.20	0.32	0.00	0.00
chloropropham					<0.00	<0.00		
2,4-D	0.01	0.02			0.00	0.00	0.00	0.00
dichlobenil					0.00	0.03		
BAM								
1,3-dichloropropene	0.26	**6.88**			0.23	**6.14**	0.00	0.00
1,2-dichloropropane	0.07	**1.77**			0.08	**1.94**		
dimethoate	0.00	0.00			0.04	0.04		
dinoseb	**20.00**	**198**			0.49	**4.84**		
dinoterb	**1.18**	**1.44**			0.06	0.07		
diuron	0.35	**4.35**			0.3	**1.68**		
DNOC	0.00	0.00			0.03	0.04	0.00	0.00
ethoprophos	0.63	**1.51**	0.01	0.02	0.55	**1.32**		
ETU (a)	0.00	0.05	0.01	0.56	0.00	0.35	0.00	0.00
ETU (b)	0.02	0.13	0.22	**1.46**	0.14	0.91	0.00	0.00
fluazifop-buthyl								
fluazifop					<0.00	<0.00		
glyphosate					0.02	0.07	0.00	0.00
AMPA					0.00	0.00		
linuron	0.36	0.36			0.05	0.05		
MCPA	0.18	0.18			0.00	0.00	0.00	0.00
mecoprop	0.08	0.45			0.00	0.01		
metamitron	0.02	0.06			0.00	0.00		
MITC (a)	**42.86**	**68.57**	**4.69**	**7.50**	**29.7**	**47.5**		
MITC (b)	**1.29**	**12.06**	0.14	**1.32**	0.89	**8.35**		
metribuzin					0.00	0.02		
pirimicarb					<0.4	<0.4		
propachlor					0.05	0.10		

As far as the available data enable comparison it seems that RQs based on CC_{cr} and CC_{ae} values show very similar patterns.

Our approach revealed that for the few compounds, for which data are available, the monitored concentrations in ground water do not pose any risk to micro-organisms, as is judged from data of the Microtox® test.

Summarising, pesticides reported at ecologically hazardous concentrations in shallow ground water as indicated by exceeding one or more of the applied risk quotients are: aldicarb, carb-sulfone, aldicarb-sulfoxide, 1,3-dichloropropene, 1,2-dichloropropane, dinoseb, dinoterb, diuron, ethoprofos, ETU, and MITC.

For 20 of the 22 compounds detected in deeper ground water (> 10 m-bss) one or more eco-toxicologically critical concentrations are available (Table 5.2). None of the calculated RQs with the median and 95-percentile levels of positive records as environmental concentration, however, exceed one unity. Only if maximum recorded concentrations are applied, RQs for dinoterb, diuron, heptachlor, and parathion-ethyl are larger than one. Although the presence of pesticides in deeper ground water is a severe problem in particularly because measurements originate often from water catchment areas and aquifers exploited for drinking water production there are hardly indications that it poses ecotoxicological risks.

5.4 Pesticide risks based on extrapolated data

Results of geographic modelling for atrazine, MITC and aldicarb in the Netherlands are presented in Figures 5.3 to 5.5. For Europe Figure 5.6 shows the modelling results of atrazine and desethyl-atrazine. What do these maps mean in terms of risks for groundwater ecosystems? For atrazine ecotoxicologically critical concentrations (CC_{ae} and CC_{cr}) are between 1-10 µg/l. The map of Figure 5.3 indicates that such concentrations are reached at 1-2 m -bss mainly in the southern and eastern part of the country. The metabolite desethyl-atrazine contributes most to these concentrations. It appears that exceeding of critical concentrations is linked to agricultural fields with maize culture. Deeper below surface concentrations decrease and critical concentration will be less frequently exceeded, although dilution along the flow path is rather small if the compound is used each year and on a substantial part of arable land.

Figure 5.6 roughly indicates that in large parts of Europe potential atrazine leaching is considerable and that groundwater concentrations may reach ecotoxicologically critical concentrations. However, the actual threat will less extended than the potential leaching map suggests because not all areas of high potential leaching are in use for agriculture and in several European countries application of atrazine in agriculture is not allowed. The main lesson to be learned from Figure 5.6 is that for compounds with properties comparable to atrazine large areas are vulnerable for leaching and that this can lead to groundwater concentrations that may be hazardous for groundwater ecosystems. More specific analysis of pesticides, agricultural use, soil conditions and regional hydrology are needed to prove the seriousness of such problems.

Critical concentrations (CC_{ae} and CC_{cr}) for MITC are low and ecotoxicological effects are to be expected above 0.01 µg/l. These concentrations may be exceeded at 1-2 m -bss only on a relatively small percentage of the agricultural area, mainly with potatoes in excavated peat areas (Figure 5.4) and on areas with flowerbulb cultivation, where soils are disinfected with metam-sodium. In these areas exceeding of critical concentrations can be severe because of the very high dosage rate of metam-sodium (> 100 kg/ha). Vertical transport of MITC depends on the extension of the gas-phase and is favourable at low groundwater levels and when pores are large and well connected. The latter features are also favourable for the occurrence multicellular organisms in the subsurface.

Potentially aldicarb metabolites can reach critical concentration (CC_{ae} and CC_{cr}) at 1-2 m -bss over large agricultural surfaces in the Netherlands. Since the compound is applied mainly in potato culture in the excavated peat areas in the north of the Netherlands and reclaimed polders the actual threat appears small (Figure 5.5). Under anoxic conditions these

compounds are transformed relatively fast and therefore the threat may be attenuated at greater depth.

5.5 Representativeness of pesticide concentrations in ground water

5.5.1 Importance of sampling strategy and sampling method

The presence of a pesticide at a certain depth is not a static situation. Pesticide concentrations will increase after application and decrease after having reached a maximum concentration (see Figure 5.2). The time span in which a pesticide can be observed at a certain depth depends on precipitation, adsorption and transformation rates. Even if compounds are rather immobile they may reach deeper layers in case of heavy rainfall shortly after utilisation and transport through preferential flow-paths like clay-cracks.

The design of a monitoring study strongly affects the type of result that comes out of it. Studies that have been set up to demonstrate the potential leaching of a pesticide are likely to produce higher pesticide concentrations in shallow ground water than monitoring programmes to assess groundwater quality in a region. This is due to the selection of sites which are relatively vulnerable for pesticide leaching, measurements right below application areas, and the known moment and quantity of application. In Table 5.1 those vulnerable study sites are included. Furthermore it is important to assess whether 0-observations and unexplainable, extreme observations were reported. This is done for Table 5.1 and Table 5.2. However, in general this information is often not presented and that may give rise to a partial view of the situation.

Sampling techniques should ensure the collection of samples in an undisturbed and exact manner, preventing the occurrence of bypass flow and changes of concentrations due to the sampling procedure. Bypass flow may change concentrations in two directions: concentrations may become higher if contaminated water flows to the sampling point without passing an active layer of the soil or aquifer, but concentration may become smaller if samples are diluted with not contaminated water. Changes in concentrations in collected water samples might occur due to evaporation, volatilisation and/or precipitation during or after sampling. Precipitation might occur due to changes in physicochemical conditions during processing and storage. Both the sampling strategy and the sampling methods require a good knowledge of the hydrological situation of the sites investigated.

In many studies, only maximum concentrations or positive observations results were recorded. Frequently, when negative results were obtained, the subsequent report failed to mention whether or not the agent had ever been used at the location in question. Many agents were never investigated at all, partly because appropriate analytical protocols are lacking. These include also substances that have been found to occur in the ground water of other European Union member states or which, according to model calculations, can easily leach into ground water. Teunissen-Ordelman and Schrap (1996) estimate that the presence of just 50% of the pesticides which can be expected in ground water is investigated.

This illustrates that information on the scope of a study, sampling strategy and data treatment is essential for an accurate judgement of the relevance of reported data. Only with additional

background information the relevance and meaning of reported pesticide concentrations in ground water could be appreciated. Altogether this makes that existing monitoring data of pesticides in ground water contribute to a rather incomplete and perhaps distorted picture of the entire problem.

5.5.2 Dependency of observations

In the databases dependent observations are abundant. Dependency occurs if, for example, from a field samples are taken every 3 months at 6 depths for 3 years (n = 72). Each individual measurement is included in the databases consulted. In the case of aldicarb all positive observations in shallow ground water come from one single location (Table 5.1). Aldicarb-sulfone has 52 positive observations but a closer look of these data reveals that 51 of these findings originate from just one location. This location is therefore very influential.

For assessing ecotoxicological risks individual data should be considered because averages in time or depth flatten concentration peaks and critical situations would be underestimated.

Investigations limited to localities where application of pesticides take place give not a representative picture of the occurrence of pesticides in ground water. Variations in sampling technique and in the sensitivity of detection methods lead to further inconsistencies in the quality and interpretation of the measurements.

5.5.3 Fate of pesticides in the saturated zone

In the saturated zone pesticides are liable to further dissipation and sorption processes dependent on prevailing environmental conditions. As in general the organic matter content of aquifers is rather low, usually smaller than 0.1 %, sorption to mineral constituents becomes relatively more important. As the mineral particles in aquifers are course to very course and, therefore, the surface area of the particles is quite small, sorption is a relatively unimportant process. Van de Weerd and van der Linden (1991) found retardation factors of 1(no sorption) to 1.3 (little sorption) for a total of five compounds in an in situ experiment.

Van den Berg *et al.* (1992) reported that transformation of pesticides in ground water occasionally occurs depending on prevailing environmental conditions. For some compounds transformation could not be demonstrated, although it cannot be excluded that subsurface environmental conditions could be preserved in the tests. In situ transformation experiments performed so far were only able to distinguish whether a compound showed rapid transformation or not (Van de Weerd and van der Linden, 1991).

Transformation and sorption are not the only processes that lead to a decline of pesticide concentrations in the saturated zone also dilution by dispersion contributes to this. Uffink and van der Linden (1998) studied the importance of the dispersion process in some detail in a phreatic aquifer in the Netherlands. They performed computer simulations of the transport of a non-reactive (conservative) compound in a 10 by 10 km area around a drinking water pumping station. As such they studied how fast concentration peaks fade out due to dispersion processes in the saturated zone under realistic conditions of land use (pesticide load to the aquifer).

Although variability in groundwater recharge in course of time exists and consequently there is variability in hydraulic heads and groundwater flow, the flow paths appear not very variable. This means that the flow path between the point of infiltration and the pumping well is rather constant. Decrease in concentration is the result of mixing of contaminated water with water from surrounding areas containing lower pesticide concentrations. Main conclusions of this research are:

- there is a general decrease in concentration with depth, but the rate of reduction is not systematic and variable throughout the region;
- changes in concentrations are highest on the boundaries between areas having differences in infiltrating concentrations;
- in certain areas hardly any reduction in concentration occurs because of infiltrating water shows almost no variability in concentrations;
- a crop rotation scheme results in a time dependent load of the ground water, but the variability at the groundwater level is only partly attenuated at a depth of 10 m below groundwater level; full attenuation is only reached at the pumping well where water of different origins is completely mixed.

The study of Uffink and van der Linden (1998) also shows that, in the absence of transformation in the saturated zone, compounds may reside in the groundwater for prolonged periods above critical levels. In several observation points in the study the calculated concentrations were around 0.04 µg/l for over 15 years. Biota in aquifers may therefore be exposed for rather long periods of time.

5.5.4 Transformation in subsurface materials

Both *in vitro* and *in situ* methods for the determination of transformation of pesticides in aquifer materials exist (Van den Berg (1990), Van den Berg (1992), Van der Linden (in prep.)). *In vitro* methods have the disadvantage that samples are taken out of the natural situation. It is difficult, if at all possible, to preserve environmental conditions after sampling. It is very important to prevent such samples from being contaminated with (micro)organisms from other layers. In general, these type of studies give an indication of the potential transformation of compounds under prevailing aquifer conditions. Often this information is enough to quantify the risk of exceeding drinking water limits in drinking water abstraction wells. This information might be insufficient to estimate exposure concentration for biota in groundwater aquifers.

In situ experiments do not have the drawback that materials are removed from the natural situation, but they have other disadvantages. Small-scale in situ experiments have the disadvantage that only relatively fast transformation rates can be established. Slow transformations cannot be detected because of the small differences between initial or ingoing concentrations and final or outgoing concentrations (van de Weerd and van der Linden, 1991). Moreover, such small-scale experiments usually do not last for more than one month. Large-scale *in situ* experiments suffer from enormous costs because of the huge number of samples to be taken. Such experiments can not be run on a routine basis to identify the transformation potential of all pesticides.

5.6 Recovery of groundwater ecosystems

In this study ecotoxicological risk levels based on aquatic toxicity data are applied to judge the risks of pesticides for groundwater systems. The majority of underlying data comes from toxicity studies with organisms from surface waters, which can be cultured and handled in the laboratory. With exception of the few available data of *Parastenocaris,* a stygobitic crustacean, the data used are not explicit for groundwater systems. In view of the ecological relevance of this approach it is worth to consider important differences between ground and surface water ecosystems (ponds, lakes, rivers etc.).

In contrast to many surface waters, habitats in ground water are generally constrained by the scarcity of food resources and oxygen. Energy resources are therefore limited with consequences for growth and reproduction rates, and the structure of food webs. Moreover, in the heterogeneous, interstitial environment of geological strata dispersal possibilities for multicellular organisms are seemingly physically restricted. These aspects should be considered in relation to the potential for ecological recovery, viz., the ability of an ecosystem to recover from toxic effects after toxicants are disappeared.

Multicellular organisms in ground water are limited to the presence of oxygen. But many groundwater species may occur under very low oxygen conditions (Danielopol *et al.* 1994; Malard and Hervant, 1999). It seems that ambient oxygen levels hardly influence the intrinsic sensitivity of stygobitic species (Notenboom *et al.,* 1992). Under anaerobic conditions bacteria almost exclusively perform ecological functions. As such it seems relevant to consider that under such conditions microbial processes might be more severely inhibited by certain toxic compounds than under aerobic conditions (van Beelen and Doelman, 1997).

The question if there exists a structural difference in intrinsic sensitivity to toxicants between ground and surface water organisms can not be analysed at the moment in a statistically appropriate way. The few comparisons made between both groups, based on only a limited number of acute toxicity data (Notenboom and Boessenkool, 1994; Notenboom *et al.*, 1994; Mösslacher and Notenboom, in press), do not reveal any clear relationship or trend. In fact the best hypothesis to accept is that no intrinsic sensitivity differences between both groups exist.

From an ecological point of view population growth rates after long periods of exposure to pesticides are more relevant to consider than just toxicity. Experimental data on the impact of pesticides on the population dynamics of groundwater species are lacking and are very scarce in general for other ecosystems. Theoretically, however, one can, given equal intrinsic sensitivity of surface and groundwater organisms, deduce a higher vulnerability of groundwater populations. Their life-history characteristics follow that of k-selection in contrast to that of species used in standard laboratory tests which better fit the r-selection model. So, the fact that many groundwater organisms grow and develop slowly, and produce few eggs in small clutch sizes make that when part of a population is wiped away replacement will be very slow. Moreover, in combination with low migration rates in ground water this lead to low recovery rates of populations (Maund *et al.* 1997).

From an analysis of population studies in soil ecotoxicology similar conclusions are drawn. Animals with long life-spans, low reproductive output, and genetically isolated populations exhibit high ecotoxicological risk profiles (Posthuma and Van Straalen, 1993). Which means that their populations are relatively vulnerable for disturbance. This ecological risk profile

seems almost a rule for populations in groundwater ecosystems. Data are, however, limited to test the vulnerability hypothesis for groundwater adapted populations appropriately.

Communities in ground water have simple structures as another result of the generally energy poor conditions. Although quantitative analysis of groundwater food webs has hardly been performed it is postulated that they consist of few trophic levels with a limited number of functional groups (Gibert *et al.*, 1994). Given the generally low species number of groundwater communities, their functional groups will consist of few species. This rough characterisation might imply that the functional redundancy and resilience of food webs in energy poor groundwater systems is low.

For animal populations and communities it is concluded that due to adaptations to a constraining environment recovery after disturbance is likely to be more slowly than in many surface water ecosystems. Furthermore, since anaerobic conditions widely occur in ground water it is worth to mention that under such conditions microbial processes might be affected more severely than under aerobic conditions.

6. Conclusions and Recommendations

6.1 Pesticide monitoring data

1. Existing Dutch and European pesticide monitoring data in ground water are very heterogeneous. The data originate from various programs differing in objectives, study design, sampling and analytical techniques, and data treatment. Moreover, zero observations and background information on land-use, soil characteristics and hydrology are not consistently reported. In the present study heterogeneity is reduced by distinction of shallow (0-10 m-bss) and deep ground water (>10 m-bss) data and thorough screening of reliability of analytical methods.

2. Monitoring data demonstrate that pesticides are widely present beneath agricultural and non-agricultural settings. Leaching is determined by multiple factors: application rates, precipitation, soil organic matter, and pesticide properties with Kom and DT50 apparently as most important ones. A relationship between physicochemical properties of the chemical and its presence in ground water is not unequivocally demonstrated.

3. About 800 pesticides are registered in Europe, of which approximately 280 in the Netherlands. Only about 125 compounds have been included in groundwater monitoring programmes so far. The Tables 5.1 through 5.3 therefore probably indicate only a part of the real threat posed on ground water. Some of the non-examined compounds have a potential to leach to ground water as judged from their sorption and transformation ratios.

4. Interdependency between observations within the reported data sets is large. Many observations come from repetitive sampling or from different depths at one site. Therefore, the extension of pesticide contamination should not be judged just by considering the total number of observations. Another aspect to be considered is that observations are based on one-off sampling of a dynamic pattern of pesticide occurrence in space and time. In addition, the monitoring programmes in the different countries are not independent from each other. Several pesticides included in the monitoring programmes are recommended to be included in the programmes as they appear on international priority lists.

5. The number of independent localities where a given pesticide has been detected is rather low, mostly five or less. An exception is 1,2-dichloropropane with 112 out of 198 positive observations; it is found at 14 of 27 investigated localities. About 75% of the compounds (active substances, additives, metabolites) in shallow ground water have maximum levels of 0.1 µg/l or higher. The median of positive findings exceeds the 0.1 µg/l for some 50% of the compounds. A few compounds have maximum concentrations in shallow ground water exceeding 10 µg/l: aldicarb-sulfone, aldicarb-sulfoxide, bentazone, BAM, 1,3-dichloropropene, 1,2-dichloropropane, ETU and metribuzin. Such high levels are associated with agricultural land-use where high doses are applied on vulnerable soils (low in organic matter).

6. A modelling exercise with some selected compounds reveals that there is a leaching potential for these pesticides in the Netherlands. The percentage of the area where these compounds are expected to exceed the 0.1 µg/l level (the drinking water standard) regularly is above 5% and may be up to 25%. As mentioned above, the number of obser-

vations in combination with the different objectives of the monitoring programmes do not allow a validation of the calculation methods. The observations are however in the same order of magnitude as the calculations. A modelling exercise for the compound atrazine and its metabolite desethyl-atrazine indicates that groundwater contamination is not restricted to the Netherlands. Problems in other European countries are expected to have the same order of magnitude.

7. In deeper Dutch ground water (> 10 m-bss) the presence of 10 % of the investigated compounds (ca. 140) is demonstrated at concentrations > 0.1 µg/l. Although contaminant levels in deeper ground water are much lower than in shallow ground water their deeper occurrence may indicate larger contaminated volumes. Considering concentration and the number of localities, 1,2-dichloropropane was the most frequently occurring compound in deeper ground water.

8. Comparison of groundwater pesticide monitoring data between European countries is hardly feasible due to large inconsistencies in available datasets. Occurrence of pesticides beneath agricultural areas evidently is a European wide environmental problem. European wide atrazine and its metabolites are the most frequently reported compounds in ground water.

9. Available information seems to indicate that herbicides are more likely to be found in ground water than other pesticides. This however might not be true. It appears that herbicides are over-represented in the monitoring programmes. Reasons for this might be:
   - the application of herbicides during more vulnerable periods in the growing cycle of the plants and therefore expected higher leaching rate;
   - the higher fraction of compound reaching the soil as compared to insecticides and fungicides (less interception by the crops), also leading to a higher expected leaching rate;
   - the occurrence on international priority lists.

10. Based on available monitoring data, national and international mapping of pesticides in ground water is not feasible. Available data give snapshot information only for selected, mostly agriculture, areas. Combined application of models and GIS appears the only way to construct geographic information. The success of that approach depends however on availability of necessary basic data (application rates, soil characteristics, precipitation) and model reliability.

6.2 Ecotoxicological risks

1. Risk assessment of pesticides for groundwater ecosystems is preferably based on system specific information about exposure, species sensitivity, population and community effects, and ecological recovery. This information however is hardly available and no signs exist that applicable data and methods become available in nearby future. The philosophy is therefore adapted that risk levels derived from the base set of aquatic toxicity data are applicable to groundwater ecosystems for first problem recognition.

2. Four types of ecotoxicological critical concentrations are compared with the EU standard of 0.1µg/l and with pesticide monitoring data. These critical levels are based on the few available acute toxicity data for a groundwater species (hardly any data), generic

Maximum Permissible Concentration for aquatic ecosystems, Hazardous Concentration for 5% (HC5) of the species based on crustacean toxicity data only, or Microtox® data. In these approaches emphasis is on crustaceans and micro-organisms because they are, respectively, the most important facies of groundwater inhabiting fauna and the most important functional component of groundwater ecosystems.

3. The Maximum Permissible Concentration and the HC5 for crustaceans are in the same order of magnitude. Microtox® toxicity data are systematically much higher, an indication for the relative insensitivity of micro-organisms to pesticides. Not for all relevant pesticides risk quotients could be calculated. Main problem is the lack of data for desethyl-atrazine, desisopropyl-atrazine, and BAM, metabolites of respectively atrazine and dichlobenil. The reliability of many HC5 values derived for crustaceans is low due to the scarcity of data, mostly only one figure is available. This implies an over or under estimation of risks.

4. Risk quotients for pesticides in shallow ground water with the median and 95-percentile of positive records as environmental concentration showed that aldicarb and metabolites, 1,3-dichloropropene, 1,2-dichloropropane, dinoseb, dinoterb, ethoprophos, and MITC occur at ecotoxicologically hazardous concentrations. Most hazardous contaminants appear aldicarb-sulfoxide, dinoseb, and MITC; the latter when applied in potatoes and beet cultivation areas.

5. In deep ground water none of the calculated risk quotients exceed ecotoxicologically critical concentrations (yet). Point of concern remains that low levels of pesticides contaminate large bodies of water exploited for drinking water production.

6. Geographic modelling helps to determine the extent of groundwater contamination exceeding ecotoxicologically critical concentrations. If appropriate data are available groundwater areas with hazardous concentrations can be calculated and regions can be located with the largest problems. This can be verified with monitoring data.

7. The standard of 0.1 µg/l for individual pesticides in ground water is not for all compounds a guarantee for ecosystem protection. Compounds that reveal to be hazardous for ecosystems at concentrations lower than 0.1 µg/l are, among others, aldicarb and aldicarb-sulfoxide, cypermethrin, ethoprophos, fenpropathrin, heptachlor, metam-sodium (MITC), parathion-ethyl, and thiram. Most of them are insecticides.

8. Almost as a rule pesticide contamination of ground water consists of a mixture of compounds. In this exploratory study the simultaneous exposure to two or more compounds with possible different modes of toxic action has not been taken into account. Nor the occurrence of pesticide compounds in combination with other types of contaminants. Combined exposure may lead to the occurrence of toxic effects at lower concentrations than expected from a single substance approach and thus to an underestimation of risks.

9. According to Dutch regulation pesticides should fulfil the 0.1 µg/l criterion at 10 m-bss. Consequently higher concentrations are allowed in shallow ground water if it is shown that physical, chemical or biochemical processes in shallow ground water quarantee that the criterion is met at 10m-bss. This may pose considerable toxic stress on this part of the

subsurface ecosystem. It is just that part of the subsurface with presumably the highest biodiversity.

10. With regard to system properties in relation to ecotoxicological risks some specific uncertainties exist. Exposure is typically long-lasting to rather low concentrations; the consequences might be underestimated when laboratory toxicity data with completely different exposure regimes are used in risk assessments. The potential for ecological recovery is low in ground water; small effects might therefore have long-lasting consequences. Mechanisms of toxicity to micro-organisms under anaerobic conditions might deviate strongly from aerobic conditions. For the moment the importance of these features is not clear.

6.3 Recommendations

1. Due to the inaccessibility of the ground water and the high costs involved in the monitoring of pesticides it will be impossible to establish the full extent of groundwater contamination by monitoring alone. Moreover, the groundwater system is not static and groundwater contamination at a certain spot is therefore transient. It is therefore recommended to use a combination of monitoring and modelling to establish the threat pesticides pose to ground water. Only little experience in this area exists at this moment and furthermore the information necessary for the calculations – especially the spatial information on the use of pesticides – is hardly available.

2. Strategies for the elucidation of groundwater contamination with pesticides should be developed further. Points of special interest are the availability of use data at least at regional scales, for instance watersheds, and information on application and weather conditions. Better results will be obtained when the validation status of the available models rises.

3. Registrations and use of compounds may be very different in the various countries of the EU. Before inclusion in a monitoring programme, a pre-evaluation of the leaching potential of compounds appearing on international priority lists is recommended. The evaluation should recognise the physical and chemical properties of the pesticide, the (proposed) use of the compound, environmental conditions and management practices.

4. For assessing potential risk levels of pesticides for groundwater ecosystems generic risk levels for aquatic ecosystems appear applicable. Preferably these are based on toxicity data for taxonomic groups which are also represented in groundwater. The HC5 for crustaceans as applied in this study is an example of such an approach. It has the advantage that toxicity for Daphnids is basic information wanted in legislation procedures. Further improvements are possible if toxicity data are available for more different species than just Daphnids and if differences in toxic mode of action are accounted for in extrapolation methods.

5. Risks of pesticides for groundwater ecosystems should be incorporated in ongoing political discussions in the EU on the effect of pesticides on non-target organisms and ecosystems. Although the present report deals mainly with the risk of pesticides in ground water in the Netherlands it aims also to contribute to EU discussions on this. Technically the approaches elaborated follow current Dutch risk assessment methodologies (HC5,

MPC, and extrapolation factors) and less methodologies followed within EU. Discussion on risk assessment approaches for groundwater and technical guidance should preferably be provided within existing community frameworks, viz., the Uniform Principles and the water framework directive.

6. Development of ecotoxicity tests for routine testing with specific groundwater organisms appears no realistic route to follow. Relevant is information on the effects of pesticides on population growth parameters in chronic exposure experiments. This requires large laboratory cultures and reproducing animals in test systems. Because ground water adapted organisms are very difficult to culture and their reproductive rates are very low, test development is not feasible for routine toxicity testing.

7. If derivation of ecotoxicological risk levels for ground water is persuade it is recommended to apply aquatic toxicity data and to extrapolate these to groundwater ecosystems. Extrapolation methods should account for the particularities of groundwater ecosystems with regard to exposure regime, types of organisms, population dynamics and community structure. In a next step methods can be validated or calibrated in some well-designed groundwater ecosystem studies.

8. If a risk approach as foundation for environmental criteria for pesticides in ground water is accepted it should consistently be applied to the whole groundwater or subsoil system. This might have as a consequence that for some compounds lower percentages of leaching are accepted than for others.

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Appendix 1: Mailing list

1. Directoraat-Generaal Milieubeheer, Directeur Drinkwater, Water en Landbouw, t.a.v. Mr A.B. Holtkamp, wnd directeur
2. Plv. Directeur-Generaal Milieubeheer
3. Directoraat Generaal Milieubeheer, Directie Stoffen, Veiligheid en Straling, Dr C.M. Plug
4. Directoraat Generaal Milieubeheer, Directie Bodem, Mr A.B. Holtkamp
5. Ir J.H. de Rijk, DGM-DWL
6. Ir A.C.M. van Straaten, LNV-Dir L
7. Dr ir H. de Heer, LNV-Dir L
8. Dr ir H.E. van de Baan, LNV-Dir L
9. Drs M.A. van der Gaag, IPO
10. Dr M. Herrchen, FhG/IUCT, Schmallenberg
11. Dr L. Smeets, DG VI, Brussels
12. Dr W-M. Maier, DG VI, Brussels

13-16. Prof H-G. Nolting, BBA, Braunschweig

17. Prof dr. D.L. Danielopol, Austrian Academy of Sciences, Institute of
18. Limnology, Mondsee
19. Prof Dr J. Gibert, Université Claude Bernard – Lyon I, France
20. Dr H. Koepp, BBA, Braunschweig, Germany
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22. Dr G. Bennekou, Danish Environmental Protection Agency, Copenhagen
23. Dr J. Hopkins, US Environmental Protection Agency, Washington
24. Dr A. Riggenbach, Swiss Federal Office of Agriculture, Bern
25. Dr A.-B. Delmas, INRA, Paris, France
26. Dr O. Stig Jacobson, GEUS, Copenhagen, Denmark
27. Dr J. Aamand, GEUS, Copenhagen, Denmark
28. Dr ir T.C.J. Feijtel, Procter & Gamble, ECETOC, Belgium
29. Dr F.M. Carpanini, ECETOC, Brussels, Belgium
30. Dr J.S.M. Boleij, CTB
31. Ing R. Faassen, RIZA
32. Dr H. van Dijk, Gezondheidsraad
33. Dr K. Verloop, TCB
34. Dr. J.J. Vegter, TCB
35. Prof Dr Ir C. van den Akker, TUD
36. Prof Dr Ir F.A.M. de Haan, LUW
37. Dr ir J.J.T.I. Boesten, SC-DLO
38. Dr Th. Brock, SC-DLO
39. Dr P. Doelman, IWACO
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42. Dr M. Schrap, RIZA
43. Ir C. van den Brink, IWACO
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53. Sectordirecteur Milieuonderzoek
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55. Hoofd Centrum voor Stoffen en Risicobeoordeling
56. Hoofd Laboratorium voor Ecotoxicologie
57. Hoofd Laboratorium voor Water- en Drinkwateronderzoek
58. Hoofd Afdeling Voorlichting en Public Relations
59. Dr W. Slooff, RIVM/CSR
60. Drs J.A. Janus, RIVM/CSR
61. Dr A.P. van Wezel, RIVM/CSR
62. Dr ir J.E. van Engelen, RIVM/CSR
63. Drs M.H.M.M. Montforts, RIVM/CSR
64. Dr J.H.M. de Bruijn, RIVM/CSR
65. Drs T.G. Vermeire, RIVM/CSR
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73. Dr P. van Beelen, RIVM/ECO
74. Dr R.A. Baumann, RIVM/LOC
75-85. Auteurs
86. SBD/Voorlichting & Public
87. Bureau Rapportenregistratie
88. Bibliotheek RIVM
89-110. Bureau Rapportenbeheer
111-125.Reserve-exemplaren

Appendix 2: Pesticides mentioned

List of pesticides, together with the chemical group and mode of action.

substance	chemical group	pesticide	mode of action
1,2-dichloropropane	halogenated hydrocarbon; impurity of 1,3-dichloropropene	NA	NA
1,3-dichloropropene	halogenated hydrocarbon	nematicide	soil fumigant nematicide
2,4-D	phenoxy carbonic acid	herbicide	growth inhibitor
2,6-dichlorobenzamide	amid; metabolite of dichlobenil	NA	NA
aldicarb	carbamate	insecticide, acaricide, nematicide[b]	cholinesterase inhibitor
aldicarb-sulfone	metabolite of aldicarb	NA	NA
aldicarb-sulfoxide	metabolite of aldicarb	NA	NA
atrazine	triazine	herbicide	photosynthesis inhibitor; inter-ference with enzym. proceses
desethyl-atrazine	metabolite of atrazine	NA	NA
desisopropyl-atrazine	metabolite of atrazine	NA	NA
bentazone	benzothiadiazole	herbicide	photosynthesis inhibitor
bromacil[a]	uracils	herbicide	photosynthesis inhibitor
carbendazim	benzimidazole; MBC	fungicide	systemic fungicide
chloridazon	pyridazine	herbicide	photosynthesis inhibitor
chlorothalonil	phthalimid	fungicide	non-systemic foliar fungicide
chlorotoluron	urea	herbicide	photosynthesis inhibitor
chlorpropham	carbamate	herbicide	growth regulator
clopyralid	pyridine	?	?
dicamba	benzoic	herbicide	auxine-like growth regulator
dichlorprop	phenoxy	herbicide	growth regulator
dimethoate	organophosphorous	insecticide, acaricide	cholinesterase inhibitor
dinoseb[a]	nitro compound	herbicide[b], insecticide	phosphorylation inhibitor
dinoterb	nitro compound	herbicide	selective contact herbidide
diuron	urea	herbicide	photosynthesis inhibitior
DNOC	nitro compound	insecticide, herbicide[b], acaricide, fungicide	non-syst. herbicide; contact herbicide; fungicide
ethoprophos	organophosphorous	nematicide[b], insecticide	cholinesterase inhibitor
ETU	metabolite of ethylene bisdithio-carbamates	NA	NA
fluazifop-butyl	phenoxy; trifluoromethyl; pyridine	herbicide	interference ATP-production
fluazifop-P-butyl	phenoxy; trifluoromethyl;	herbicide	interference ATP-

	pyridine		production
fluazifop	metabolite of fluazifop-butyl, fluazifop-P-butyl	NA	NA
furalaxyl	acylalanine	fungicide	systemic fungicide
glyphosate	organophosphorous	herbicide	interference enzym. proceses
AMPA	metabolite of glyphosate	NA	NA
isoproturon	urea	herbicide	photosynthesis inhibitor
lindane	organochlorine	insecticide	contact, stomach and respiratory action
linuron	urea	herbicide	photosynthesis inhibitor
MCPA	phenoxy carbonic acid	herbicide	growth inhibitor
mecoprop	phenoxy carbonic acid	herbicide	hormon-type herbicide
metam-sodium	carbamate	soil fumigant	
metamitron	triazine	herbicide	photosynthesis inhibitor
metazachlor	acetamide; pyrazole	herbicide	germination inhibitor
methabenzthiazuron	urea; benzothiazole	herbicide	photosynthesis inhibitor
metolachlor	acetamide	herbicide	germination inhibitor
metoxuron	urea	herbicide	photosynthesis inhibitor
metribuzin	triazine	herbicide	photosynthesis inhibitor
MITC[d]	isothiocyanate	soil fumigant	-
parathion-ethyl	organophosphorous	insecticide[b], acaricide	cholinesterase inhibitor
pirimicarb	carbamate; pyrimidine	insecticide	cholinesterase inhibitor
simazine	triazine	herbicide	photosynthesis inhibitor
terbumeton[c]	triazine	herbicide	photosynthesis inhibitor
terbuthylazine[a]	triazine	herbicide	inhibitor of photosynthesis and enzymatic proceses
trifluralin[a]	trifluoromethyl; dinitroaniline	herbicide	lethal effects during germination

- no data available
a banned in the Netherlands
b most important application in the Netherlands
c not registered in the Netherlands
d also occuring as a metabolite of metam-Na

Appendix 3: VEWIN list

List of compounds (pesticides, metabolites and assmed metabolites) analyzed by drinking water companies in the period 1992-1995, but not detected.

alachlor	dicofol	metoxuron
aldicarb	dieldrin	metribuzin
aldicarb-sulfon	dimethoate	mevinfos
aldicarb-sulfoxide	2,4-dinitrophenol	mirex
aldrin	dinoseb (2-sec.butyl-4,6-dinitrofenol)	monolinuron
ametryn	disulfoton	monuron
anthranilic acid-isopropylamide	alfa-endosulfan	naphtalene
azinfos-ethyl	beta-endosulfan	2-nitrophenol
azinfos-methyl	endrin	4-nitrophenol
benazolin-ethyl	ethion	oxadixyl
bromofos-methyl	ethofumesate	paraoxon-ethyl
bromofos-ethyl	ethoprophos	paraoxon-methyl
carbendazim	fenchlorvos (ronnel)	parathion-methyl
chlordane	fonofos	penconazole
2-chlorophenol	forate	pentachloroaniline
4-chlorophenoxyacetic acid	fosfamidon	pentachlorophenol
chlorofenvinfos	glyphosate	permethrin
chlorotoluron	haloxyfop-ethoxyethyl	pirimicarb
cyanazine	heptachlorepoxide	prometryn
cyclohexene	cis-heptachlorepoxide	propachlor
2,4-DB (4-(2,4-dichlorophenoxy)butiricacid)	trans-heptachlorepoxide	propazin
o,p-DDD	heptenofos	propiconazole
p,p-DDD	hexachloorbenzene (HCB)	pyrazofos
o,p-DDE	alfa-HCH (alfa-hexachlorcyclohexane)	quintoceen
p,p-DDE	beta-HCH (beta-hexachloorcyclohexane)	sulfotep
o,p-DDT	delta-HCH (delta-hexachlorocyclohexane)	2,4,5-T (2,4,5-trichlorophenoxyacetic acid)
p,p-DDT	hexazinon	tecnazene
DEET	isodrin	telodrin
desisopropyl-atrazine	linuron	terbutryn
demeton-S-methyl	malathion	terbutylazine
desmetryn	MCPB (4-(4-chloor-2-methylphenoxy)butiric acid)	2,4,5-TP (2-(2,4,5-trichlorophenoxy)propionic acid)
diazinon	metamitron	triadimefon
dibromomethane	metazachlor	triadimenol
dicamba	methabenzthiazuron	2,4,5-trichlorophenol
2,4-dichlorophenol	methidathion	2,4,6-trichlorophenol
dichlorprop (2,4-DP)	methoprene	trichloronate
1,3-dichloorpropane	metoxychlor	trietazin
1,3-dichloorpropene	methylisothiocyanate (MITC)	vinchlozolin
dichlorvos	metobromuron	chloorprofam
dichloran	metolachlor	

Appendix 4: Toxicity data, collected for this study

Legend

organisms	Species used in the test, if available followed by: age, size, weight or life stage	
A	Y	test substance analysed in test solution
	N	test substance not analysed in solution or no data
test type	S	static
	R	renewal
	CF	continuous flow
test water	am	artificial medium
	tw	tap water
	nw	natural water
	rw	reconstituted water
test substance purity	percentage active ingredient (%)	
	anal	analytical grade
	tech	technical grade
	high	high but unknown purity
exposure time	h	hour(s)
	d	day(s)
	w	week(s)
	m	month(s)
	CLC	complete life cycle
results	> and [3] value indicated highest concentration used in the test.	
	< and ≤ value indicated lowest concentration used in the test.	
A	given value based on measured concentrations	
-	no information available	

Toxicity data are listed in the following order:

- Freshwater toxicity: chronic and acute data
- Freshwater toxicity to other organisms.
- Data from deviating tests
- Microtox® data

Freshwater toxicity: crustaceans

Chronic data

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
2,4-D											
Ceriodaphnia dubia, < 12 h	Y	R	>99	rw	8.2	57	7 d	NOEC	24[a]	α	Oris *et al.*, 1991
Daphnia magna	-	-	-	-	-	-	-	NOEC	79[b]		IRC, 1997
Daphnia magna	-	-	-	-	-	-	-	NOEC	28[b]		IRC, 1997
amitrole											
Daphnia magna	Y	SS	-	-	-	-	21 d	NOEC	0.2		IPCS, 1994
Daphnia magna	-	SS	-	-	-	-	21 d	NOEC	0.32		IPCS, 1994
atrazine											
Ceriodaphnia dubia, < 12 h	Y	R	>99	am	8.2	57	7 d	NOEC	2.5[c]	α	Oris *et al.*, 1991
Daphnia magna, ≤ 24 h, 3 gen.	Y	CF	94	nw	6.3-7.5	32	9 w	NOEC	0.14[d]	α	Macek *et al.*, 1976
Daphnia pulex, ≤ 15 h	N	R	99.2	nw	-	-	28 d	NOEC	1.0[e]		Schober and Lampert, 1977
Daphnia pulex, ≤ 15 h	N	R	99.2	nw	-	-	28 d	NOEC	2.0[f]		Schober and Lampert, 1977
Daphnia pulex, ≤ 15 h	N	R	99.2	nw	-	-	28 d	NOEC	1.0[g]		Schober and Lampert, 1977
Gammarus fasciatus, 1-22 d	Y	CF	94	nw	6.4-7.2	35	17 w	NOEC	0.49[h]	α	Macek *et al.*, 1976
Gammarus fasciatus, 1-22 d	Y	CF	94	nw	6.4-7.2	35	17 w	NOEC	0.06[a]	α	Macek *et al.*, 1976
dimethoate											
Daphnia magna, 24 h	N	S	-	-	-	-	16 d	NOEC	0.029[L, j]		Deneer *et al.*,1988
Daphnia magna, 24 h	N	R	tech	am	-	200	21 d	NOEC	0.032[a,j]		Slooff and Canton, 1983
Daphnia magna, 24 h	N	R	tech	am	-	200	21 d	NOEC	0.1[h, j]		Slooff and Canton, 1983
diuron											
Daphnia magna	-	-	-	-	-	-	-	NOEC	0.056		IRC, 1997
DNOC											
Daphnia magna, 24 h	Y	R	-	am	8.0	48	21 d	NOEC	1.3[a]		Kühn *et al.*,1989
Daphnia magna	N	R	≥ 99	-	-	-	14 d	NOEC	0.6[a]		RIVM/CSR archives, 1992
Daphnia pulex, 24 h	N	R	-	am	-	200	21 d	NOEC	1.0[a,h]		Slooff and Canton, 1983
Daphnia pulex, < 24 h	N	R	-	am	7.8-8.2	200	16 d	NOEC	0.21[i]		Deneer *et al.*, 1988

Chronic data (continued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
isoproturon										
Daphnia magna	-	-	-	-	-	-	21 d	NOEC	0.064[b]	IRC, 1997
Daphnia magna	-	-	-	-	-	-	21 d	NOEC	0.093[b]	IRC, 1997
Daphnia magna	-	-	-	-	-	-	21 d	NOEC	0.41[b]	IRC, 1997
Daphnia magna	-	-	-	-	-	-	21 d	NOEC	8.9[b]	IRC, 1997
lindane										
Daphnia magna	N	CF	-	nw	6.1-7.3	38	64 d	NOEC	0.01[a]	Janssen *et al.*, 1988
Gammarus fasciatus	N	CF	-	nw	6.4-7.2	35	120 d	NOEC	0.009[a]	Janssen *et al.*, 1988
linuron										
Daphnia magna	-	-	-	-	-	-	21 d	NOEC	0.32[a]	IRC, 1997
MCPA										
Daphnia magna, 16-24 h	N	R	85-95	am	-	-	21 d	NOEC	100[a]	RIVM/CSR-archives, 1991
mecoprop										
Daphnia magna, 16-24 h	N	R	90-96	am	-	-	21 d	NOEC	3.3[k]	RIVM/CSR-archives, 1992
parathion-ethyl										
Asellus aquaticus	N	R	99	am	-	95	21 d	NOEC	0.001[h]	Dortland, 1980
Daphnia magna, < 24 h	N	R	99	am	-	95	21 d	NOEC	0.0002[l]	Dortland, 1980
Daphnia pulex, < 24 h	N	R	99	am	-	95	21 d	NOEC	0.0003[m]	Dortland, 1980
Daphnia pulex, 1st instar	Y	CF	99	nw	-	-	21 d	NOEC	0.00008[a]	Spacie *et al.*,1981
Daphnia magna, < 24 h	Y	R	-	am	7.8-8.2	250	21 d	NOEC	0.000002[n]	Kühn *et al.*,1989
propachlor										
Daphnia magna	N	-	-	-	-	-	21 d	NOEC	0.097	IPCS, 1993
primicarb										
Daphnia magna	-	-	-	-	-	-	-	NOEC	0.0009[a,b]	IRC, 1997

Chronic data (continued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
trifluralin											
Daphnia magna, < 24h, P gen	Y	CF	99	nw	6.8	37	22 d	NOEC	0.0024[o]	α	Macek *et al.*, 1976
Daphnia magna, < 24h, P gen	Y	CF	99	nw	6.9	37	22 d	NOEC	0.0024[a]	α	Macek *et al.*, 1976
Daphnia magna, < 24h, F1 gen	Y	CF	99	nw	6.8	37	42 d	NOEC	0.014[p]	α	Macek *et al.*, 1976

a reproduction
b original reference not available
c reproduction, renewal 2 times a week
d reproduction as youg/animal, over 3 generations
e reproduction as young/animal, 9.6 % decrease at lowest concentration tested is considered as NOEC, renewal every other day
f growth as length of adults, renewal every other day
g growth as adult carbon content, renewal every other day
h mortality
i growth
j substance purity unknown
k reproduction; 26 % effect at 10 mg/l (lowest tested concentration); NOEC = LOEC/3
l immobility
m reproduction as young/parent
n mortality and reproduction; actual concentration deviated less than 20 % from nominal; result reported as nominal concentration
o mortality; 15 % mortality in control
p reproduction; no eggs produced at concentration 0.0256 mg/l

Acute data.

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure - time	Crite-rion	Result mg/l		Reference
aldicarb											
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	EC50	0.051[a]	α	Foran *et al.*, 1985
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	LC50	0.21	α	Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	EC50	0.065[a]	α	Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	LC50	0.07	α	Foran *et al.*, 1985
aldicarb-sulfone											
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	LC50	1.1		Foran *et al.*, 1985
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	EC50	0.37[a]		Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	LC50	0.91		Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	EC50	0.56[a]		Foran *et al.*, 1985
aldicarb-sulfoxide											
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	LC50	0.10		Foran *et al.*, 1985
Daphnia laevis, adult	Y	S	-	tw	6.9	58	48 h	EC50	0.043[a]		Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	LC50	0.084		Foran *et al.*, 1985
Daphnia laevis, 1-3 d	Y	S	-	tw	6.9	58	48 h	EC50	0.057[a]		Foran *et al.*, 1985
amitrole											
Daphnia magna	-	-	-	-	-	-	48 h	EC50	1.54		IPCS, 1994
AMPA											
Daphnia magna	-	CF	-	-	-	-	48 h	LC50	690[b]		Goure, 1996
bentazone											
Daphnia laevis, 1st instar	N	S	> 99	am	7.6	38	48 h	LC50	64[c]		RIVM/CSR archives, 1990
dichlobenil											
Daphnia magna	-	-	-	-	-	-	48 h	EC50	10		Sanders, 1970
Cypridopsis vidua	-	-	-	-	-	-	48 h	EC50	7.8		Sanders, 1970
Gammarus fasciatus	-	-	-	-	-	-	48 h	EC50	18		Sanders, 1970
Asellus brevicaudus	-	-	-	-	-	-	48 h	EC50	34		Sanders, 1970
Palaemonetes kadiakensis	-	-	-	-	-	-	48 h	EC50	9.0		Sanders, 1970

Acute data (contiued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure - time	Crite-rion	Result mg/l		Reference
chlorpropham											
Daphnia magna, < 24 h	N	S	99.3	am	7.7-8.1	262	48 h	EC50	4.0[f]		Jongbloed *et al.*, 1997
Daphnia magna, < 24 h	Y	S	98.1	am	8.0-8.5	148	48 h	EC50	3.7[g]		Jongbloed *et al.*, 1997
2,4-D											
Cyclops vernalis, nauplii	N	S	tech.	am	6.7	70	96 h	LC50	9.0		Bunting, 1975
Gammarus fasciatus	N	S	tech.	nw	7.4	272	48 h	EC50	3.2[d]		Sanders, 1970
1,2-dichloropropane											
Daphnia magna, < 24 h	N	-	-	nw	8.0	173	48 h	LC50	52		Le Blanc, 1980
Daphnia magna, < 2 d	Y	-	-	am	-	-	48 h	EC50	45[e]	α	Hermens *et al.*, 1984
1,3-dichloropropene											
Daphnia magna, < 24 h	N	-	-	nw	8.0	173	48 h	LC50	6.2		Le Blanc, 1980
dimethoate											
Daphnia magna	N	S	98	-	-	-	48 h	LC50	6.4		RIVM/CSR archives, 1991
Daphnia magna	N	S	98	-	-	-	48 h	EC50	2.9[e]		RIVM/CSR archives, 1991
Daphnia magna, < 24 h	Y	S	> 99	-	-	-	48 h	LC50	1.7		Beusen and Neven, 1989
Daphnia magna, < 24 h	Y	S	> 99	-	-	-	48 h	EC50	1.5[e]		Beusen and Neven, 1989
dinoseb											
Gammarus fasciatus	N	S	-	nw	7.4	-	48 h	LC50	2.5		RIVM/CSR archives, 1990
Gammarus fasciatus	N	S	-	nw	7.4	-	96 h	LC50	1.8		RIVM/CSR archives, 1990
Daphnia magna, ≤ 24 h	N	S	> 99	nw	7.6-8.2	77	48 h	LC50	0.24[f]		Gersich and Mayes, 1986
dinoterb											
Daphnia magna	N	S	≥ 99	-	-	-	48 h	LC50	0.47		RIVM/CSR archives, 1989
DNOC											
Daphnia magna	Y	S	-	-	-	-	48 h	LC50	3.3	α	Hermens *et al.*, 1984
Daphnia pulex, 1st instar	N	S	100	-	7.1	44	48 h	EC50	0.15		Mayer and Ellersieck, 1986
Gammarus fasciatus, mature	N	S	100	-	7.1	44	96 h	LC50	1.1		Mayer and Ellersieck, 1986

Acute data (continued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure - time	Crite-rion	Result mg/l	Reference
diuron										
Asellus brevicaudus, mature	N	S	95	-	7.1	44	96 h	LC50	16	Mayer and Ellersieck, 1986
Daphnia magna	N	S	-	-	7.9	-	48 h	EC50	1.4	RIVM/CSR-archives, 1992
Daphnia pulex, 1st instar, 18 h	N	S	95	rw	7.1	44	48 h	EC50	1.4[a]	Sanders and Cope, 1969
Gammarus fasciatus, early instar	N	S	tech	nw	7.4	272	96 h	LC50	0.7[b]	Sanders, 1970
Gammarus fasciatus, mature	N	S	95	-	7.1	44	96 h	LC50	0.16	Mayer and Ellersieck, 1986
Gammarus lacustris, immature	N	S	tech	am	7.1	31	96 h	LC50	0.16[a]	Sanders and Cope, 1969
Simocephalus serrulatus, 1st instar, < 18 h	N	S	95	rw	7.1	44	48 h	EC50	2.0[b]	Sanders and Cope, 1966
ethoprofos										
Daphnia magna	N	S	-	nw	7.7	46	48 h	LC50	0.05	RIVM/CSR archives, 1989
ETU										
Daphnia magna	N	R	99	-	-	-	48 h	LC50	26	Van Leeuwen *et al.*, 1985
fluazifop										
Daphnia magna, < 24 h	N	S	-	-	-	-	48 h	EC50	436[g]	RIVM/CSR archives, 1988
Daphnia magna, < 24 h	N	S	-	-	-	-	48 h	EC50	240[g]	RIVM/CSR archives, 1988
fluazifop-butyl										
Daphnia magna, < 24 h	N	S	88.8	-	-	-	48 h	EC50	> 1.0[f]	RIVM/CSR archives, 1988
Daphnia magna, < 24 h	N	S	94.8	-	-	-	48 h	EC50	> 10[f]	RIVM/CSR archives, 1988
glyphosate										
Daphnia magna, ≤ 24h	N	S	≥ 98	rw	8.2-8.3	175	48 h	LC50	5.3	RIVM/CSR archives, 1990
Procambarus clarkii, 25-40 mm	N	S	-	tw	-	100	96 h	LC50	47	Holck and Meek, 1987
isoproturon										
Daphnia magna, 1.2-1.4 mm	N	S	95	am	-	-	48 h	EC50	510[h]	RIVM/CSR archives, 1992
lindane										
Daphnia magna	N	S	-	nw	8.2	138	48 h	EC50	0.52	Janssen *et al.*, 1988
Gammarus fasciatus	N	S	-	am	-	-	48 h	LC50	0.04	Janssen *et al.*, 1988
Gammarus pulex	N	S	-	tw	7.2	187	96 h	LC50	0.03	Janssen *et al.*, 1988
Gammarus pulex	N	R	-	tw	8.3	250	48 h	LC50	0.02[i]	Janssen *et al.*, 1988
Gammarus pulex	N	R	-	tw	8.3	250	96 h	LC50	0.01[i]	Janssen *et al.*, 1988

Acute data (contiued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure - time	Crite-rion	Result mg/l	Reference
linuron										
Daphnia magna	N	S	-	-	-	44	48 h	EC50	0.75[j]	RIVM/CSR archives, 1993
Daphnia magna, 1st instar	N	S	95.1	-	7.0	43	48 h	EC50	0.27	Mayer and Ellersieck, 1986
Daphnia magna	-	-	-	-	-	-	48 h	EC50	0.31[b]	IRC, 1997
Daphnia magna	-	-	-	-	-	-	48 h	LC50	0.75[b]	IRC, 1997
MCPA										
Daphnia magna, 16-24 h	N	-	85-95	am	-	-	48 h	LC50	1100	RIVM/CSR archives, 1991
Daphnia magna, 16-24 h	N	S	-	am	6.7	-	48 h	LC50	172	Fargasova, 1994
mecoprop										
Daphnia magna, 16-24 h	N	R	90-96	am	-	-	48 h	LC50	420	RIVM/CSR archives, 1992
metamitron										
Daphnia magna	N	S	≥ 97	am	-	-	48 h	EC50	100[e]	RIVM/CSR archives, 1993
metham-sodium										
Cypridopsis vidua, mature	N	S	100	-	7.4	44	48 h	LC50	0.035	Mayer and Ellersieck, 1986
metribuzin										
Copepod sp.	N	S	-	nw	7.0-7.4	-	24 h	LC50	206[k]	Naqvi *et al.*, 1981
Copepod sp	N	S	-	nw	7.0-7.4	-	48 h	LC50	150[k]	Naqvi *et al.*, 1981
parathion-ethyl										
Gammarus fasciatus, mature	N	S	tech.	rw	7.1	31	96 h	LC50	0.0013[l]	Sanders, 1972
Gammarus fasciatus, mature	N	S	tech.	nw	7.4	260	48 h	LC50	0.004[l]	Sanders, 1972
Gammarus fasciatus, mature	N	S	tech.	nw	7.4	260	96 h	LC50	0.0021[l]	Sanders, 1972
Orconectes nais, 3-5 w	N	S	tech.	nw	7.4	260	96 h	LC50	0.000036[l]	Sanders, 1972
Orconectes nais, mature	N	S	tech.	nw	7.4	260	96 h	LC50	0.015[l]	Sanders, 1972
Asellus brevicaudus, mature	N	S	tech.	rw	7.1	31	96 h	LC50	0.60[l]	Sanders, 1972
primicarb										
Gammarus pulex	-	-	-	-	-	-	-	LC50	0.9[b]	IRC, 1997

Acute data (contiued)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure - time	Crite-rion	Result mg/l	Reference
propachlor										
Daphnia magna, <24 h	N	S	96.6	nw	-	-	48 h	LC50	7.8	RIVM/CSR-archives, 1992
Daphnia magna, 1st instar	N	S	94.5	-	7.3	45	48 h	EC50	6.9	Mayer and Ellersieck, 1986
simazine										
Cypridopsis vidua, mature	N	S	98	-	7.4	272	48 h	LC50	3.7[n]	Mayer and Ellersieck, 1986
Cypridopsis vidua, early instar	N	S	> 95	nw	7.4	272	48 h	EC50	3.2[n]	Sanders, 1970
Daphnia magna, early instar	N	S	> 95	nw	7.4	272	48 h	EC50	1.0[n]	Sanders, 1970
Gammarus lacustris, 2 m	N	S	80	rw	7.1	31	96 h	LC50	13[o]	Sanders, 1969

a immobility; 1 ml acetone in 500 ml water; acetone control performed
b original reference not available
c substance is Na-bentazone salt
d immobility; cat 2 study; 1 ml/l ethanol
e immobility
f solvent is acetone (0.5 %)
g immobility; substance purity unknown; solvent is acetone (0.5%)
h immobility; above water solubility which is 72 mg/l (20°C)
i solvent is acetone, amount unknown
j parameter behavior (irritation and uncontrolled movements); incipient EC50 probably not reached
k 2 copepod species (*Eucyclops agilis* and *Diaptomus mississipiensis*) included in one test vessel; number of animals per concentration not clear; substance purity unknown
l LC50 reported as the median tolerance limit (TL50); solvent is ethanol, concentration ≤ 1 ml/l; no solvent control reported
m above water solubility, which is 3.5 mg/l (20°C)
n immobility; solvent is ethanol (1 ml/l)
o simazine 80% wetable powder

Freshwater toxicity: other organisms

Chronic data.

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
chlorpropham											
algae											
Chlorophyta											
Chlorococcum hypnosporum	N	-	-	am	-	-	2 w	NOEC	0.8[a]		Virmani *et el.*, 1975
Chlorella pyrenoidosa	N	-	-	am	-	-	2 w	NOEC	0.8[a]		Virmani *et el.*, 1975
Secenedesmus capricornutum	N	S	99.3	-	8.0-8.8	-	96 h	NOEC	0.1[b]		Jongbloed *et al.*, 1997
Cyanophyta											
Anacystis nidulans	N	S	99	-	-	-	13 d	NOEC	11[c]		Maule and Wright, 1984
2,6-dichlorobenzamide											
algae											
chlorophyta											
Scenedesmus pannonicus	N	S	97	am	8.7	90	96 h	NOEC	32[b]		Van Leeuwen and Maas, 1985
pisces											
Salmo gairdneri, eggs	N	S	97	rw	7.6	52	60 d	NOEC	10[d]		Van Leeuwen and Maas, 1985
Salmo gairdneri, larvae	N	S	97	rw	7.6	52	60 d	NOEC	10[d]		Van Leeuwen and Maas, 1985
fluazifop-butyl											
algae											
Chlorophyta											
Selenastrum capricornutum	Y	S	81.3	-	6.9-7.8	-	96 h	NOEC	0.88[e]	α	RIVM/CSR-archives, 1988
metham-sodium											
protists											
Euglena gracilis	N	S	-	am	5.5	-	5 d	NOEC	0.1[b]		Moore, 1970

a growth; LOEC/3=NOEC
b growth
c growth; concentration showing less than 10% effcet is considered the NOEC
d mortality and growth
e growth; reduction of 15% at the highest concentration; solvent is aecetone (0.1ml/l)

Acute data.

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
aldicarb-sulfone										
insecta										
Culex pipiens, 4th instar	N	S	99	-	--	-	24 h	LC50	1.35	Bayoumi *et al.*, 1988
amitrole										
algae										
Scenedesmus subspicatus	N	S	-	-	-	-	-	EC50	2.3	IPCS, 1994
pisces										
Oncorhynchus kisutch	-		-	-	-	-	96 h	LC50	70	IPCS, 1994
AMPA										
algae										
Selenastrum capricornutum	-	S	-	-	-	-	72	EC50	150[a]	Goure, 1996
pisces										
Salmo gairdneri	-	CF	-	-	-	-	96 h	LC50	> 520[a]	Goure, 1996
bromacil										
pisces										
Pimephales promelas, 30 d	Y	CF	95	nw	7.4	47	96 h	LC50	180	Call *et al.*, 1987
Pimephales promelas	-	-	-	-	-	-	96 h	LC50	182	RIVM/CSR-archives, 1988
chlorpropham										
macrophyta										
Lemna paucicostata	N	S	-	am	5.5	588	10 d	EC50	0.75[b]	Retzlaff, 1993
pisces										
Brachydanio rerio	N	-	pure	-	-	-	96 h	LC50	14	RIVM/CSR-archives, 1992
Brachydanio rerio, 0.13 g, 2.5 cm	N	S	99.3	-	7.5-8.2	262	96 h	LC50	13	Jongbloed *et al.*, 1997
Oncorhynchus mykiss, 1.4 g, 4,7 cm	N	S	99.3	-	7.9-8.9	230	96 h	LC50	7.5	Jongbloed *et al.*, 1997
2,6-dichlorobenzamide										
algae										
Chlorophyta										
Chlorella pyrenoidosa	N	S	97	am	8.7	90	96 h	EC50	100[c]	Van Leeuwen and Maas, 1985
pisces										
Salmo gairdnerii	N	S	97	rw	7.6	52	96 h	LC50	235	Van Leeuwen and Maas, 1985
Poecilia reticulata	N	S	97	nw	8.1	260	48 h	LC50	275	Van Leeuwen and Maas, 1985

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
fluazifop-butyl											
algae											
Chlorophyta											
Scenedesmus quadricauda	Y	S	≥ 97	-	7.2-7.4	-	96 h	EC50	1.9[d]	α	RIVM/CSR-archives, 1988
pisces											
Cyprinus carpio, 0.74 g, 29.6 mm	N	CF	≥ 97	-	7.2-8.0	-	96 h	LC50	1.3		RIVM/CSR-archives, 1988
Salmo gairdnerii, 2.6 g, 57 mm	Y	CF	≥ 97	-	7.4-8.2	-	96 h	LC50	1.4		RIVM/CSR-archives, 1988
fluazifop											
pisces											
Salmo gairdnerii, 6.2 g, 71 mm	Y	S	98	-	5.1-7.9	-	96 h	LC50	120	α	RIVM/CSR-archives, 1988
glyphosate											
cyanophyta											
Anabaena variabilis	N	-	-	am	-	-	48 h	EC50	2.0[d]		Hutber *et al.*, 1979
Nostoc	N	-	-	am	-	-	48 h	EC50	2.0[d]		Hutber *et al.*, 1979
macrophyta											
Lemna paucicostata	N	S	-	am	5.5	588	10 d	EC50	3.9[b]		Retzlaff, 1993
metribuzin											
macrophyta											
Lemna paucicostata	N	S	-	am	5.5	588	10 d	EC50	0.05[b]		Retzlaff, 1993
insecta											
Chironomus riparius, larvae	N	S	93	rw	7.6-7.8	42-44	48 h	EC50	44[e]		Buhl and Faerber, 1989
pisces											
Rasbora heteromorpha, 1-3 cm	N	CF	70	-	8.1	20	96 h	LC50	140		Tooby *et al.*, 1975

a original reference not available
b growth inhibition; unformulated compounds used
c chlorophyll-a content
d growth
e immobility

Freshwater toxicity: deviating tests

Crustaceans

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
2,6-dichlorobenzamide										
Daphnia magna, ≤ 24 h	N	S	97	nw	8.1	260	96 h	LC50	> 320[a]	Van Leeuwen and Maas, 1985
Daphnia magna, ≤ 24 h	N	S	97	nw	8.1	260	21 d	NOEC	> 320[b]	Van Leeuwen and Maas, 1985
dimethoate										
Asellus aquaticus	N	S	-	-	7.1	160	48 h	LC50	3.0[c]	Thybaud *et al.*, 1987
ETU										
Daphnia magna	N	R	99	-	8.1	225	21 d	LC50	18	Van Leeuwen *et al.*, 1985
glyphosate										
Daphnia spinulata, < 24 h	N	S	-	am	7.8	96	48 h	EC50	66[d]	Alberdi *et al.*, 1996
Daphnia magna, < 24 h	N	S	-	am	7.8	96	48 h	EC50	62[d]	Alberdi *et al.*, 1996
isoproturon										
Daphnia magna, < 24 h	N	-	-	-	-	-	48 h	EC50	>1.0[e]	Traunspurger *et al.*, 1996
lindane										
Daphnia magna, ≤ 24 h	N	S	-	-	-	-	24 h	EC50	1.6[e]	Calleja *et al.*, 1994
Daphnia magna, < 24 h	N	S	-	rw	7.6	-	24 h	EC50	15[e]	Lilius *et al.*, 1995
Asellus aquaticus	N	S	-	-	7.1	160	48 h	LC50	0.005[c]	Thybaud *et al.*, 1987
linuron										
Daphnia magna	-	-	-	-	-	-	24 h	EC50	0.31	Stephenson and Kane, 1984

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
primicarb										
Daphnia magna, 12 h, 0.8 mm	N	S	> 99	am	8.5	hard	48 h	EC50	0.000019[f]	RIVM/CSR archives, 1989

a no effect found at highest concentration
b reproduction
c substance purity unknown; four concentrations tested
d immobility; formulation is *RON-DO*® with 48% a.i. as isopropylamine salt
e immobility
f immobility; solvent is acetone, amount unknown; other organisms included in the test vessel: *Lymnea, Brassica,* Chlorococcales

Freshwater toxicity: deviating tests

Other organisms.

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
aldicarb-sulfone										
pisces										
Clarius lazera, 100-125 g	N	S	99	-	--	-	24 h	LC50	> 40	Bayoumi and El Basyouni, 1987
aldicarb-sulfoxide										
insecta										
Culex pipiens, 4th instar	N	S	99	-	--	-	24 h	LC50	> 5.0	Bayoumi *et al.*, 1988
pisces										
Clarius lazera, 100-125 g	N	S	98	-	--	-	24 h	LC50	> 40	Bayoumi and El Basyouni, 1987
bromacil										
pisces										
Pimephales promelas, 30 d	Y	CF	95	nw	7.4	47	60 d	NOEC	< 1.0[a]	Call *et al.*, 1987
Lepomis macrochirus	-	-	-	-	-	-	48 h	LC50	71	RIVM/CSR-archives, 1988
Cyprinus carpio	-	-	-	-	-	-	48 h	LC50	164	RIVM/CSR-archives, 1988
Salmo gairdnerii	-	-	-	-	-	-	72 h	LC50	28	RIVM/CSR-archives, 1988
glyphosate										
insecta										
Chironomus riparius	N	S	93	rw	7.6-7.8	42-44	48 h	EC50	5600[e]	Buhl and Faerber, 1989
pisces										
Cirrhinia mrigala, 4-5 cm	N	-	-	tw	-	-	96 h	LC50	5.5[c]	Singh and Yadav, 1978
Ctenopharyngodon idella, 9.5 cm, 15.8 g	N	CF	-	tw	8.1	270	96 h	LC50	15[b]	Tooby *et al.*, 1980
Lepomis macrochirus	-	-	-	-	-	-	-	LC50	5.6[d]	Le Blanc, 1984

a growth
b formulation is Roundup with 36% a.i.
c formulation is Roundup with 48% a.i.; LC50 calculated with Spearman and Karber
d originel reference not available
e immobility; formulation is Rodeo® with 53.5% a.i.

Microtox® data

compound	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
1,3-dichloropropene										
Vibrio fisheri	N	S	-	-	-	-	-	EC50	110	Blum and Speece, 1991
atrazine										
Vibrio fisheri	N	S	-	-	-	-	5 min	EC10	13	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	5 min	EC20	25.8	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	15 min	EC10	14.4	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	15 min	EC20	22.6	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	30 min	EC10	17.5	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	30 min	EC20	24	Kross *et al.*, 1992
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	20	Gaggi *et al.*, 1995
bentazone										
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	29	Ruiz et al ., 1997
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	29	Ruiz et al ., 1997
2,4-D										
Vibrio fisheri	N	S	99%	-	-	-	5 min	EC50	101[a]	Toussaint *et al.*, 1995
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	41.2[b]	Kahru *et al.*, 1996
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	13	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	10 min	EC50	23	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	31	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	-	EC50	101	Somasundaram *et al.*, 1990
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	10	Willemsen *et al.*, 1995
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	28	Willemsen *et al.*, 1995
Vibrio fisheri	N	S	-	-	-	-	30 min	EC50	8	Willemsen *et al.*, 1995
DNOC										
Vibrio fisheri	N	S	-	am	-	-	5 min	EC50	6.6	Curtis *et al.*, 1982
ETU										
Vibrio fisheri	N	S	99%	-	-	-	15 min	EC50	2,100	Van Leeuwen *et al.*, 1985
glyphosate										
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	7.7[b]	Kahru *et al.*, 1996; Willemsen *et al.*, 1995

compound	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Crite-rion	Result mg/l	Reference
lindane										
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	6,360[b]	Kahru *et al.*, 1996
Vibrio fisheri	N	S	-	-	-	-	10 min	EC50	5.7	Bazin *et al.*, 1987
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	38	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	10 min	EC50	50	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	56	Gosh *et al.*, 1997
Vibrio fisheri	N	S	-	-	-	-	5 min	EC50	316	Willemsen *et al.*, 1995
Vibrio fisheri	N	S	-	-	-	-	15 min	EC50	190	Willemsen *et al.*, 1995
MCPA										
Vibrio fisheri	N	S	99.9%	-	-	-	15 min	EC50	248	Vismara *et al.*, 1996 ; Vismara and Garavaglia (1997)
Vibrio fisheri	N	S	96%	-	-	-	15 min	EC50	121	Vismara *et al.*, 1996 ; Vismara and Garavaglia (1997)

a The median result of three test results was reported ; results were in a range of 61.6-112 mg/l; search for the original articles is initiated
b No original data ; search for the original article is initiated