BTO 2017.071 | December 2017

BTO report

Occurence of pesticides in drinking water sources in The Netherlands and Flanders

KWR Watercycle Research Institute

BTO

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BTO 2017.071 | December 2017

Project number
400554.125

Project manager
dr Stefan Kools, dr Klaasjan Raat

Client
BTO themagroepen *Duurzame bronnen en watersystemen* en *Nieuwe stoffen*

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Sent to
This report is distributed amongst BTO-participants

Year of publishing
2017

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Keywords
Nieuwe bestrijdingsmiddelen, signaleren, prioriteren, stoffen

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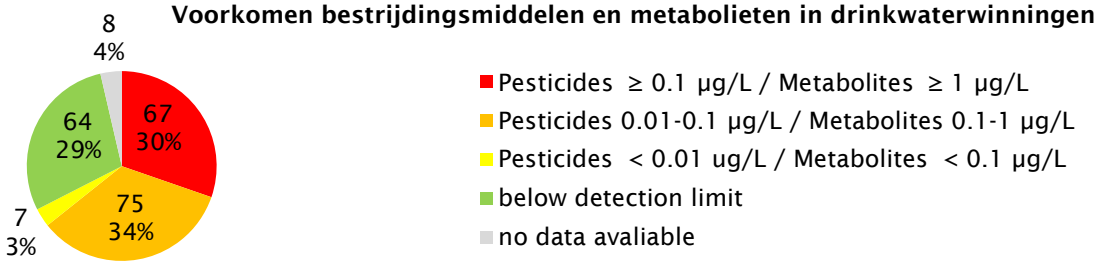
BTO *Managementsamenvatting*

Signaleren en prioriteren van bestrijdingsmiddelen in drinkwaterbronnen

Auteur(s) Rosa Sjerps, MSc, prof dr Pieter Stuyfzand, Pascal Kooij, dr Annemieke Kolkman, Beatriz de la Loma-Gonzalez, MSc, en drs Leo Puijker

Bestrijdingsmiddelen vormen een relevante groep stoffen met een drinkwaternorm die intensief worden gemonitord bij de drinkwaterbedrijven. Deze studie inventariseerde meetgegevens over het vóórkomen van bestrijdingsmiddelen, nieuw op de markt verschenen middelen inbegrepen, op nationale schaal. In grond- en oppervlaktewater van 149 van de 221 Nederlandse drinkwaterwinningen (67%) zijn tussen 2010 en 2014 op één of meerdere momenten sporen van pesticiden of afbraakproducten aangetroffen. Op basis van de huidige landsdekkende meetgegevens voor actieve stoffen die al langer op de markt zijn, zijn 65 bestrijdingsmiddelen en 6 metabolieten geprioriteerd voor monitoring. 15 van de 24 nieuw op de markt verschenen stoffen waarvoor een nieuwe analysemethode is geïmplementeerd, werden aangetroffen in Nederland en België, met name in oppervlaktewater. Om het gedrag van bestrijdingsmiddelen in de ondergrond (aquifers) te modelleren is in deze studie het model TRANSATOMIC.xlsx verder doorontwikkeld.



Drinkwaterwinningen met op één of meerdere momenten aangetroffen bestrijdingsmiddelen en/of afbraakproducten in de grondstof (innamepunt, gemengd ruwwater, pompputten en waarnemingsputten) over een periode van 5 jaar (2010-2014).

Belang: inventarisatie oude en nieuwe bestrijdingsmiddelen voor bescherming bronnen

De waterkwaliteitsnorm voor bestrijdingsmiddelen is 0,1 µg/L voor drinkwater (drinkwaterbesluit), oppervlaktewater bestemd voor de bereiding van drinkwater (drinkwaterregeling, Bkmw) en voor grondwater (grondwaterrichtlijn). De drinkwaterbedrijven monitoren op bestrijdingsmiddelen om de kwaliteit van drinkwater te waarborgen. Periodiek worden monitoringsmethoden aangepast n.a.v. nieuw toegelaten actieve stoffen. Deze studie inventariseerde meetgegevens over het voorkomen van oude en nieuwe bestrijdingsmiddelen op nationale schaal. We laten zien welke bestrijdingsmiddelen prioriteit verdienen aan de hand van vóórkomen en overschrijding van waterkwaliteitsnormen en welke stoffen nauwelijks worden aangetroffen. De exercitie laat zien hoe het ervoor staat met de bescherming van drinkwaterbronnen.

Aanpak: evaluatie bestaande monitoringsgegevens en uitgebreide meetcampagne naar nieuwe stoffen

Monitoringsgegevens van de drinkwaterbedrijven over een tijdsperiode van 5 jaar (2010-2014) werden geëvalueerd op het vóórkomen van bestrijdingsmiddelen in drinkwater en in bronnen van drinkwater. Onderzoek naar het gedrag van de stoffen in grondwaterlichamen, afhankelijk van redox condities en organisch stof gehalten, verschafte informatie over of de stoffen drinkwaterbronnen kunnen bereiken. Van de middelen die nieuw op de markt zijn geïntroduceerd, werden mobiele en persistente stoffen (PMOC) geselecteerd (50) voor de

implementatie in een analysemethode. Voor 24 van deze 50 stoffen zonder een beschikbare analysemethode, kon de analysemethode worden geïmplementeerd en toegepast tijdens een uitgebreide meetcampagne in Nederland en België in juni en augustus 2016.

Resultaten: evaluatie prioriteert 65 bestrijdingsmiddelen en zes metabolieten

In 149 van de 221 Nederlandse winningen (67%) zijn op één of meerdere momenten pesticiden of metabolieten aangetroffen in innamewater, ruwwater, pompputten of waarnemingsputten over de periode 2010-2014, zie de figuur. In 67 winningen (30%) was de 90 percentiel concentratie van de waarnemingen in de grondstof (in zowel waarnemingsputten, individueel ruw als gemengd ruwwater) voor één of meerdere pesticiden of metabolieten boven de drinkwaternorm. Drinkwaterbedrijven stellen hoge eisen aan de zuiveringsprocessen op deze locaties. Desondanks zijn over een periode van 5 jaar op ongeveer de helft van de 187 productielocaties op enig moment sporen van bestrijdingsmiddelen en/of metabolieten aangetroffen in het drinkwater. Incidenteel betrof dit normoverschrijdingen.
Van de 467 gemeten stoffen werden 65 bestrijdingsmiddelen en 6 metabolieten geprioriteerd vanwege het voorkomen in drinkwater (26 bestrijdingsmiddelen en 6 metabolieten) of in bronnen van drinkwater boven de drinkwaternorm (39 bestrijdingsmiddelen). Het merendeel van de gemonitorde bestrijdingsmiddelen is niet of nauwelijks aangetroffen.

Bestrijdingsmiddelen zijn meer uniform aanwezig en minder verwijderd in kunstmatig geïnfiltreerd oppervlaktewater en oeverfiltraat dan in grondwatersystemen. De gegevens impliceren dat AMPA, BAM, bromacil, diuron, glyfosaat en DMS behouden blijven in een (sub)oxisch milieu, en dat 2-chlooraniline en chloridazon behouden blijven in een anoxisch milieu. Daarnaast werden voor de top 20 stoffen significante lineaire relaties de componenten NH_4, PO_4, redox index, NO_3, DOC en Cl/Br. In deze studie is het model TRANSATOMIC.xlsx ontwikkeld om het gedrag van bestrijdingsmiddelen in de ondergrond (aquifers) te modelleren met een getrapte aanpak voor een heel puttenveld, uitgaande van (i) directe en lineaire sorptie en (ii) eerste orde (bio)degradatie als functie van drie redox klassen ((sub)oxisch, anoxisch en diep anoxisch).

15 van de 24 nieuw op de markt verschenen stoffen waarvoor een nieuwe analysemethode werd geïmplementeerd, zijn aangetroffen in een screeningsronde in zowel Nederland als België, met name in oppervlaktewater. Zes bestrijdingsmiddelen zijn in één of meerdere monsters aangetroffen boven de drinkwaternorm in oppervlaktewater: het herbicide fluxapyroxad, de insecticiden clothianidine, thiamethoxam en acetamiprid en de fungiciden fluopyram, fluxastrobin en mandipropamid. In slechts 2 van de 90 grondwatermonsters van zowel waarnemingsputten, individueel ruw als gemengd ruwwater zijn nieuwe bestrijdingsmiddelen aangetroffen, waarvan clothianidine boven de drinkwaternorm.

Implementatie: bescherming drinkwaterbronnen onvoldoende

Bestrijdingsmiddelen en hun metabolieten komen in grote mate voor in oppervlakte- en grondwater gebruikt voor de productie van drinkwater. Daaronder bevinden zich ook nieuw op de markt verschenen middelen. Deze informatie is relevant voor drinkwaterbedrijven (monitoring, kwaliteitsbewaking en belangenbehartiging) en beleidsmakers in Nederland en Vlaanderen. Omdat de bestrijdingsmiddelenmarkt continue in beweging is, adviseren wij om periodiek de monitoringsdata en meetprogramma's te evalueren.

Rapport

Dit onderzoek is beschreven in rapport *Occurrence of pesticides in drinking water sources in The Netherlands and Flanders* (BTO 2017.071) en *Gewasbeschermingsmiddelen en hun afbraakproducten in Nederlandse drinkwaterbronnen* (BTO 2017.079).

Year of publishing
2017

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Contents

1 Introduction

1.1 Introduction

Pesticides are used in agriculture to protect crops from fungi (fungicides), insects (insecticides) or weeds (herbicides). Pesticide products contain one or multiple active substances. Emissions of these biological active substances may form a risk for ecosystem or human health. Pesticides could enter surface water by drift or agriculture runoff, or leach into groundwater sources during or after use (González-Rodríguez et al., 2011; Heuvelink et al., 2010; van Eerdt et al., 2014).

Micropollutants, including pesticides, are commonly present in water at trace concentrations, ranging from ng/L to µg/L (Luo et al., 2014). In the Netherlands pesticides are regularly detected in surface- and groundwater (Hopman et al., 1990; Peters, 1985; RIWA, 2016a; RIWA, 2016b; Schreiner et al., 2016; Stuyfzand and Lüers, 1996; Vijver et al., 2011). The recent study of Swartjes et al. (2016 inventoried that in 25% of the 200 water abstraction areas pesticides were detected in groundwater near the abstraction wells. This includes 50 compounds, two thirds of which are still authorized. Most of the compounds are herbicides or metabolites of herbicides. BAM, bentazon and mecoprop were often detected.

1.2 Guidelines

According to the Drinking Water Directive, the drinking water quality standard for active substances of pesticide products and human toxicological relevant metabolites in drinking water is 0.1 µg/L (Drinkwaterbesluit, 2011; European Commission, 1998). Relevant metabolites include compounds with properties as targeted toxicity or genotoxicity. An exception are the pesticides aldrin, dieldrin, heptachloor and heptachloorepoxide, which have a standard of 0.03 µg/L (Drinkwaterbesluit, 2011). The drinking water quality standard for human toxicological non-relevant metabolites, such as AMPA and BAM, is 1 µg/L, equal to the signalling value for 'other anthropogenic substances'. The standard for the summed concentration of all active substances and metabolites present in drinking water is 0.5 µg/L.

The Water Framework Directive contains water quality standards for a good chemical condition of ground- and surface water (European Commision, 2000). During the production of drinking water from groundwater, treatment is limited. Therefore groundwater quality is evaluated using the drinking water guideline values (European Commission, 1998) according to the 'protocol voor monitoring en toetsing drinkwaterbronnen KRW'. The Groundwater Protection Directive has thus quality standards in groundwater as 0.1 µg/L per active substance or relevant metabolite of pesticides and biocides and 0.5 µg/L for the summed concentration of active substances (bkmw, 2009). For surface water used for the production of drinking water, a general water quality standard of 0.1 µg/L is set in the Drinkwaterregeling (Bijlage 5). In addition, individual pesticides on the Priority Substances list have ecotoxicological water quality standards (Environmental Quality Standards).

To monitor the exceedance of the water quality standards for pesticides, the drinking water companies monitor drinking-, surface- and groundwater quality for the presence of pesticides at the intake or abstraction points and during drinking water production.

1.3 Authorization of pesticides

In the European context pesticides are regulated in Regulation (EG) 1107/2009, for a harmonized authorization between member states. The European commission decides whether or not to allow an active substance on the European market, which is possible if a safe application of this substance is possible. All authorized and prohibited active substances are listed on the European Commission website (European Commission, 2016).

The authorization of pesticides takes place per climate zone. Applications for new permits, changes to existing authorizations, extensions and renewals of authorization are submitted in accordance with the zonal procedure. When a product already has been authorized in another EU member state, the authorization is carried out via mutual recognition. In the case of applications for new permits, the authorization will be applied directly to a European zone. The application will be reviewed by a single Member State, the zonal rapporteur. It assesses the applications in all Member States for which the application is intended (so-called. 'Concerned Member States', CMS). These CMS comment on the draft authorization and underlying dossiers. All member states have authorities to carry out risk assessments and authorization. Member state specific issues can be included in the risk assessment.

In The Netherlands this is performed by the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb, College voor de toelating van gewasbeschermingsmiddelen en biociden). The Ctgb evaluates the safety of pesticides and biocides for humans and the environment. The risk assessment is based on toxicity data and modelling studies. Monitoring data are incorporated in the assessment when available. Proactive monitoring of these compounds can be helpful to signal potential risks (Dolan et al., 2013; Dolan et al., 2014). The risk for drinking water is a member-state specific aspect of the Dutch authorization. This will be further illustrated in section 3.1.1.

Various governmental organizations monitor and maintain the use of pesticides:

- The Dutch Food and Safety Authority (NVWA, Nederlandse Voedsel en Warenautoriteit) controls the trade in pesticides, the use in agriculture and horticulture, and pesticide residues on products.
- Water boards control the use of pesticides in agriculture and horticulture with regard to their aqueous emissions.

The Ministry of Social Affairs (Inspectie SZW) controls the safety of pesticide use in companies.

1.4 PMOCs

Persistent Mobile Organic Compounds (PMOC) are a recently introduced class of compounds which are highly polar (mobile in water) and can pass through wastewater treatment plants, subsurface environments and potentially also drinking water treatment processes (Reemtsma et al., 2016). Reemtsma et al. (2016 addresses that few such compounds are known and gaps appear to exist in terms of analysis, monitoring, water treatment and regulation. Several pesticides could be classified as PMOCs as they are mobile and persistent in ground- and surface water systems and could end up in drinking water.

1.5 Goal of this study

The production, use and application of pesticides continuously changes, therefore the most relevant compounds nowadays may be different from those ten years ago. We assess the Occurrence of pesticides in drinking water sources from routine monitoring data in The Netherlands and with newly implemented analytical methods in The Netherlands and Flanders. Available monitoring data from groundwater abstraction areas, surface water intake points and drinking water in The Netherlands were used (Chapter 2). As these do not

consider recently authorised pesticides, in addition all authorised active substances were evaluated using environmental fate properties and suspect screening approaches (Chapter 3). An analytical method for recently authorized pesticides was implemented and applied in a Dutch and Flanders wide monitoring campaign (Chapter 4 and 5). The fate of pesticides in groundwater systems is studied in Chapter 6. As a result we provide a list of drinking water relevant active substances. The results of this study can be used by the drinking water companies, RIWA (Vereniging Rivierwaterbedrijven) and VEWIN (Vereniging van Waterbedrijven in Nederland) and to provide relevant data for new authorisations and re-assessments.

2 Prioritizing pesticides from monitoring data 2010-2014

2.1 Introduction

To prevent exceedance of the guideline values by pesticides, the drinking water companies monitor the presence of pesticides at drinking water sources in order to signal and manage water quality problems. The data collected in The Netherlands holds valuable information on the occurrence of pesticides in different water types, the relation with their sources and environment properties, and their behaviour in water systems. We use all data collected over the years 2010-2014 to prioritize relevant pesticides for a drinking water perspective, including the non-prioritization of rarely occurring compounds.

2.2 Method

We collected available monitoring data from the four waterlaboratoria of pesticides in the Netherlands over the years 2010-2014. All ten water companies in the Netherlands permitted the use of their monitoring data. The composite dataset includes 29,766 records, including samples of drinking water, ground water, river bank filtrate, dune filtrate and surface water of pesticide data. The data was not validated by KWR. The dataset covers 4,176 sampling locations from 221 different drinking water extraction locations, including surface water intake points (2875 samples, 8 locations), pre-treated surface water (6 locations), observation wells (1,760 filters from 107 locations) and pumping wells (1,944 filters from 177 locations) in groundwater, collected raw water (240 raw waters from 163 locations) and drinking water (187 locations).

The collected data provides information on a national scale about the extent of drinking water treatment plants that deal with water quality issues concerning pesticides and which pesticides are of largest concern. First, an overview was made of the amount of locations where drinking water sources and the produced drinking water contain pesticides above the threshold of 0.1 µg/L, above 1/10 of the threshold and above the detection limit. Second, pesticides were prioritized according to their presence in drinking water and their concentrations in groundwater and surface water.

Pesticides and metabolites detected in drinking water during the studied time frame were classified as high priority substances. The pesticides and metbaolites that were not present in drinking water but present in sources of drinking water were prioritised according to their 90 percentile concentration in sources water. Compunds with 10 or less detections, priority was assessed according to their maximum concentration. Pesticides with a 90 percentile concentration in source water above the threshold of 0.1 µg/L were classified as priority substances; for non-relevant metabolites we used the threshold of 1 µg/L. If the 90 percentile concentration of a pesticide exceeded the threshold of 0.01 µg/L in drinking water sources without exceeding the threshold of 0.1 µg/L it was classified as a potential priority compound; for non-relevant metabolites we used the threshold of 1 µg/L. These thresholds were chosen because concentrations could raise in the future by accumulation, increased use in agriculture or low river flows according to climate change (Sjerps et al., 2016a; Sjerps et al., 2016b). If the 90 percentile concentration of a pesticide or a metabolite has not exceeded respectively the threshold of 0.01 µg/L or 0.1 µg/L in drinking water

sources, the compound was classified as low priority. Pesticides and metabolites never detected above the detection limit in recent years were classified as low priority as well.

In de prioritization, we did not distuingish the presencence of the pesticides in different types of source water, such as observation wells, pumping wells and mixed raw water. A detailed study on the presencence of pesticides in the different source water types was carried out by van Loon et al. (2017).

2.3 Drinking water and source water

In half of the 187 drinking water production stations, traces of pesticides and/or metabolites have been detected in one or more samples of drinking water during the period 2010-2014, see Figure 2-1. In 23 drinking water production stations one or more pesticides and/or metabolites were incidently detected in concentrations above respectively 0.1 µg/L (pesticides) and 1 µg/L (metabolites) in drinking water. In 58 drinking water production stations pesticides were detected in concentrations between 0.01 µg/L and 0.1 µg/L (pesticides) and/or 0.1 µg/L and 1 µg/L (metabolites).

All standard-exceeding concentrations within routine monitoring of the produced drinking water were reported to inspection. However, measurements carried out within a research context are not obliged to be reported. The database contains the results of both routine and research monitoring campaigns.

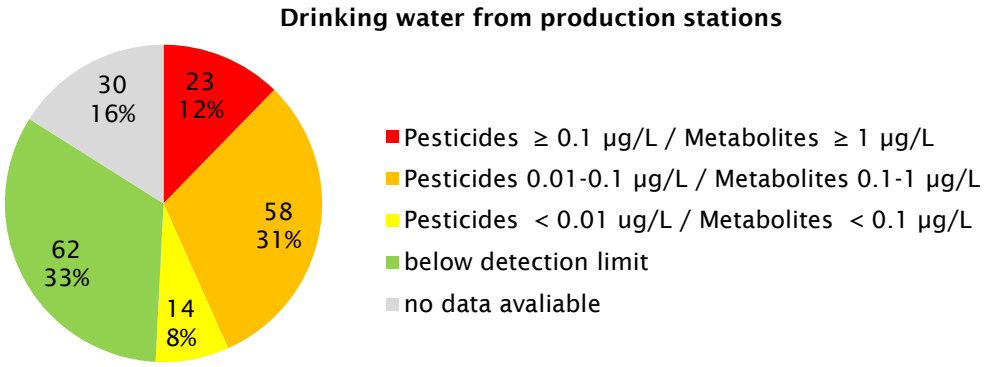


Figure 2-1 Drinking water production locations in The Netherlands where pesticides and/or metabolites were detected in one or more samples ofdrinking water (2010-2014).

In 149 of the 221 abstraction areas of ground- and surface water (67%) traces of pesticides and/or metabolites have been detected in one or more samples during the period 2010-2014, see

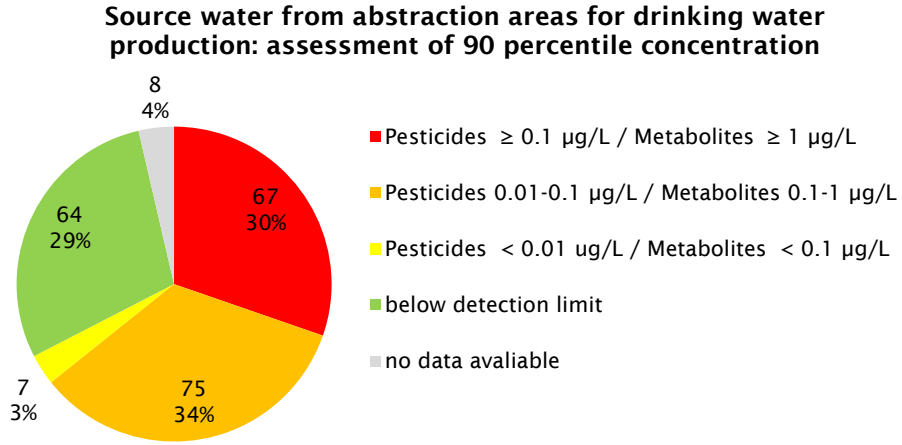


Figure 2-2. This figure includes concentrations found in surface intake water, observation wells, individual pumping wells and raw water. In 67 abstraction areas (30%) the 90 percentile concentration of the positive detections of one or more pesticides exceeded the threshold of 0.1 µg/L (pesticides) and/or 1 µg/L (metabolites). In 75 abstraction areas (34%), the 90 percentile concentration of the positive detections of one or more pesticides was between 0.01 µg/L and 0.1 µg/L (pesticides) and/or 0.1 µg/L and 1 µg/L (metabolites).

Pesticides were present in abstraction areas all over The Netherlands (Figure 2-3).

A detailed study on the presencence of pesticides in the different source water types, such as observation wells, pumping wells and mixed raw water, was carried out by van Loon et al. (2017).

The chance to detect a pesticide or a metabolite is dependent on the specific monitoring program at each location.These numbers thus represent the current status of the presencence of pesticides and metabolites at drinking water sources derived from the availbale monitoring programs.

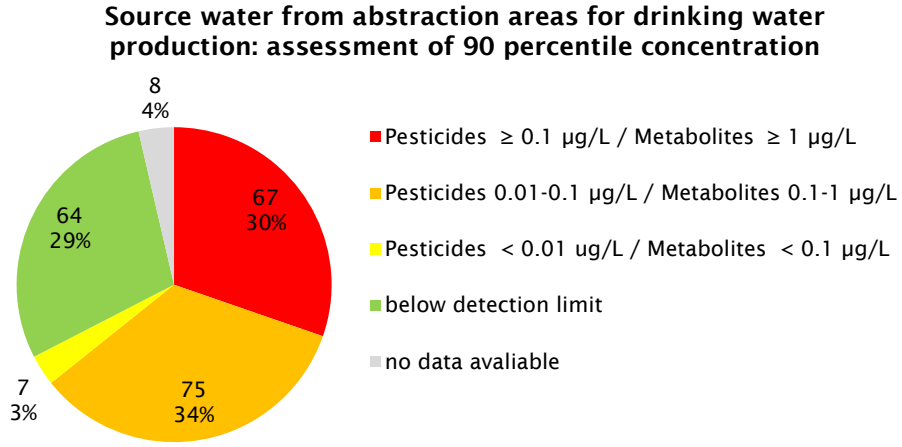


Figure 2-2 Abstraction areas in The Netherlands where pesticides and/or metabolites were detected in one or more samples of surface - and groundwater. The 90 percentile concentration was based on the positive detections above 0.1 µg/L, between 0.1-0.1 µg/L, below 0.01 µg/L, below the detection limit and with no available data (2010-2014). For metabolites the 90 percentile concentrations were assessed using 1 µg/L and 0.1 µg/L.

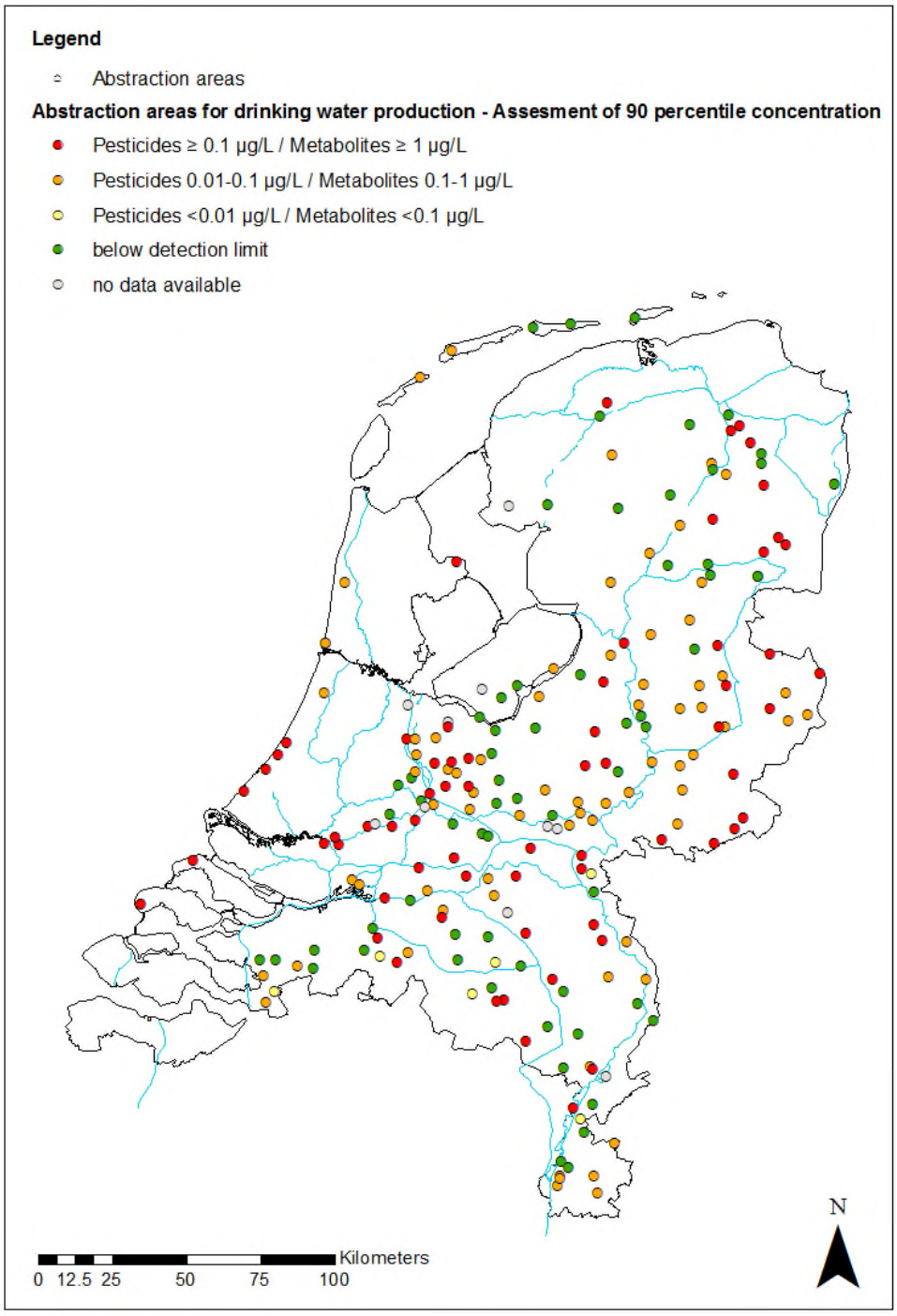


Figure 2-3 Abstraction areas in The Netherlands showing the presence of one or more pesticides and/or metabolites in surface water intakes and groundwater well fields (one or more samples, between 2010-

2014) with a 90 percentile concentration above 0.1 µg/L (conform figure 2-2), between 0.01-0.1 µg/L, below 0.01 µg/L, below the detection limit or with no available data. For metabolites the concentrations were assessed using 1 µg/L and 0.1 µg/L.

2.4 Prioritization of compounds

In total we collected data of 467 pesticides and their metabolites. Over the period of 2010-2014, 296 of these were permanently detected below the detection limit in the samples (see Attachment I). The other 158 pesticides and 13 metabolites were at least once detected above the detection limit and were prioritized according to the presence in drinking water or the 90 percentile concentration exceeded target values in sources of drinking water: 0.1 µg/L and 0.01 µg/L (Table 2-1), see Attachment I. When optimizing monitoring programs all local characteristics should be taken into account.

Table 2-1 Prioritization of pesticides according to their monitoring data. See list of compounds in Attachment I.

Class	Description	Number of pesticides
High priority	Pesticides detected in drinking water	26
Priority	Pesticides detected in source water P90>0.1 µg/L (not in dw)	39
Potential priority	Pesticides detected in source water P90 0.01-0.1 µg/L (not in dw)	91
Low priority	Pesticides detected in source water P90<0.01 µg/L (not in dw)	2
-	Not detected (below detection limit)	287
Class	**Description**	**Number of metabolites**
High priority	Metabolites detected in drinking water	6
Priority	Metabolites detected in source water >1 µg/L (not in dw)	0
Potential priority	Metabolites detected in source water 0.1-1 µg/L (not in dw)	5
Low priority	Metabolites detected in source water <0.1 µg/L (not in dw)	2
	Not detected (below detection limit)	9

The highest priority was given to 26 pesticides and 6 metabolites that have been detected in drinking water. Pesticides and metabolites not detected in drinking water, but in drinking water sources were classified as priority substances and potential priority substances. These priority substances had at least once been detected above the standard for drinking water quality, 0.1 µg/L (39 pesticides). The potential priority stubstances have been detected between 0.01-0.1 µg/L (91 pesticides) or between 0.1-1 µg/L (5 metabolites). Two remaining pesticides and two metabolites were never detected above the thresholds of respectively 0.01 µg/L or 0.1 µg/L in the available dataset and classified as low priority. 287 pesticides and 9 metabolites were never detected over the period 2010-2014.

It is recommended to include pesticides that are classified as priority and potential priority compounds in water quality screening. It is recommended to monitor the low priority pesticides with low frequency (once in five years).

Pesticides that were present in drinking water above the drinking water standard were the growth regulator dikegulac, the herbides glyphosate, bentazone, glufosinate-ammonium, bromacil, the fungicide dimethomorf and the insecticide oxamyl (Figure 2-4, Attachment II).

Dikegulac exceeded in 5% of the all measurements and 50% of the positive detections in drinking water the threshold of 0.1 µg/L (127x), while the other pesticides exceeded the

limit one to three times. Dikegulac has a high solubility in water, and is detected most in drinking water originating from river bank filtrate related to the high use of this compound in the years 1990-1994 (Brinkmann et al., 1995).

Metabolites found in drinking water are: AMPA, BAM, DMS, desphenylchloridazon, methyl-desphenylchloridazon and metolachloor-S-metabolite. These metabolites are however not known to be human toxicological relevant and have a water quality standard of 1 µg/L. It is known that the compound DMS can form NDMA during ozonation treatment. Since the compound NDMA is carcinogenic and toxic, its drinking water quality standard is 12 ng/L.

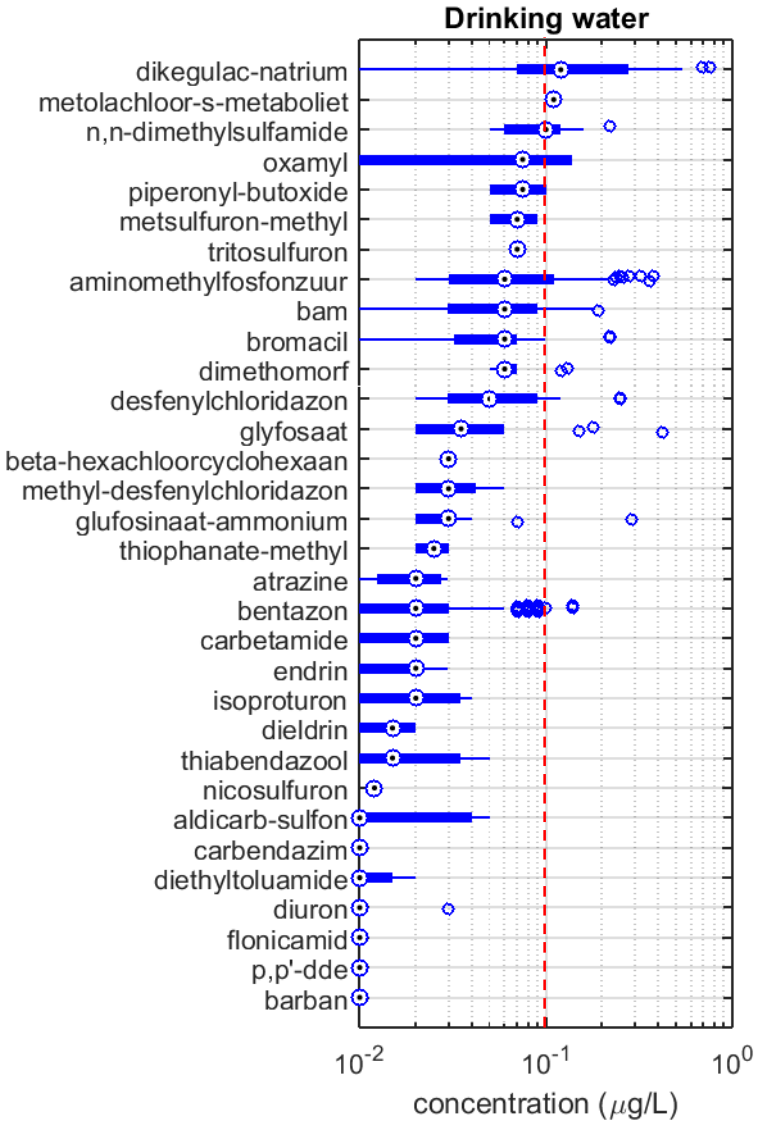


Figure 2-4 Pesticides and metabolites detected in drinking water (above the detection limit) (n=32). Pestides and relevant metabolites, such as n,n-dimethylsulfamide, have a drinking water guideline of 0.1 µg/L. Non-relevant metabolites have a drinking water guideline value of 1 µg/L and include metolachloor-s-metaboliet, aminomethylfosfonzuur (AMPA), BAM and (methyl-)desfenylchloridazon. Central mark is the median, the box represents the 25th and 75th percentiles, the whiskers extend to the extreme data points not considered outliers. Outliers are plotted individually.

Examples of pesticides that have exceeded the threshold of 0.1 µg/L in drinking water sources, that were not detected in drinking water, are the herbicides MCPA, MCPP, terbutylazine, isoproturon and the fungicides etridiazole and tolclofos-methyl. All these compounds are recommended for water quality screening; dependent on the local contamination and water system characteristics these compounds are relevant for uptake in monitoring programs.

In Figure 2.5 and Attachment II a selection is shown of 30 pesticides and metabolites occurring in groundwater at least once above the threshold of 0.1 µg/L, including data from pumping wells, observation wells and collected raw groundwater (see details in Attachment I). The metabolites BAM and desfenylchloridazon show the highest concentrations in groundwater with maximum concentration of 13 µg/L and 21 µg/L respectively.

Focussing solely on the collected raw water before drinking water treatment, four pesticides were detected in concentrations above 0.1 µg/L: bentazon, bromacil, dikegulac and glyphosate. Five metabolites were detected in collected raw water: BAM, DMS, desfenylchloridazon, AMPA, metolachloor-s-metabolite. Mecoprop was found >0.1 µg/L in individual pumping wells, however not in collected raw water. The drinking water company Brabant Water uses interception wells to discharge mecoprop contaminated to protect the remaining well field. More details on the presence of pestices in the different source water types, such as observation wells, pumping wells and mixed raw water, can be found in BTO 2017.079 (van Loon et al., 2017).

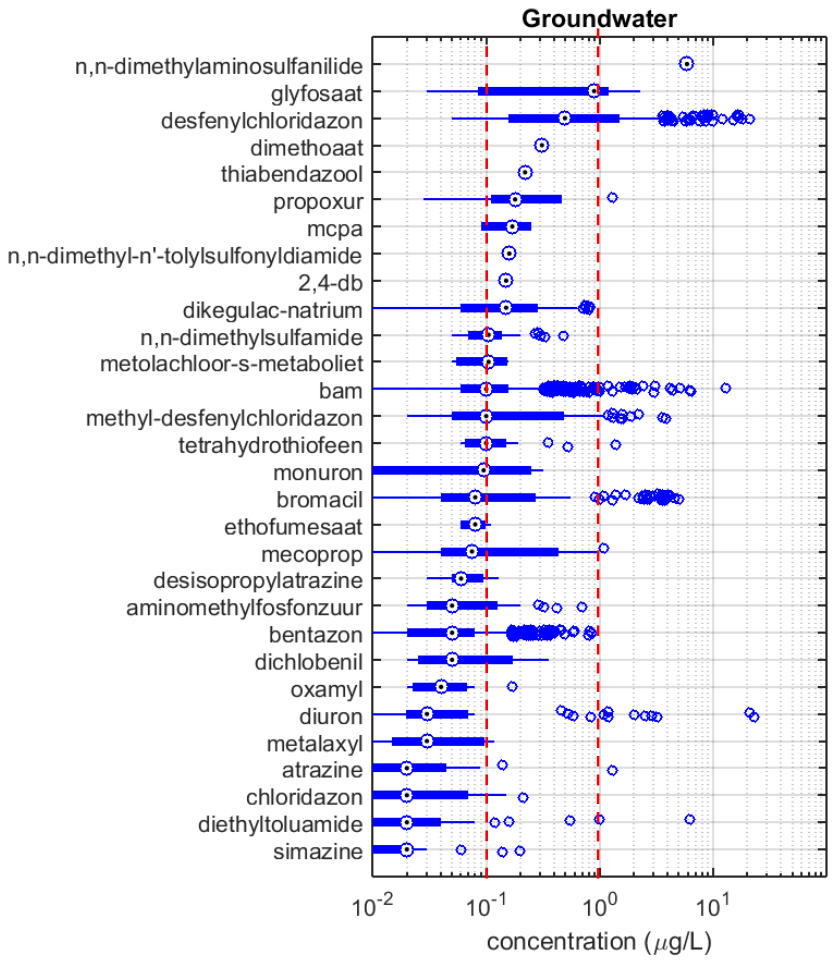


Figure 2-5 Pesticides and metabolites detected in groundwater above a concentration of 0.1 µg/L, the drinking water guideline value for pesticides and relevant metabolites such as n,n-dimethylsulfamide. Non-relevant metabolites have a drinking water guideline value of 1µg/L and include n,n-dimethylaminosulfanilide, (methyl-) desfenylchloridazon, n,n-dimethyl-n'-tolylsolfonyldiamide, metolachloor-s-metaboliet, BAM, desisopropylatrazine and aminomethylfosfonzuur (AMPA). Central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually.

In Figure 2-6 and Attachment II a selection is shown of 46 pesticides and metabolites occurring in surface water at least once above the threshold of 0.1 µg/L or 1 µg/L (see details in Attachment II). The maximum concentration of dimethomorf was 52 µg/L, detected at the pumping station Brakel in the Meuse (Dunea). This high concentration is the result of an incident concerning high amounts of dimethomorf discharged in the Meuse in the period februari to april 2012. In addition to routine moniting, extra samples have been taken due to this incident, to monitor the development of dimethomorf concentrations in the Meuse at Brakel. Three metabolites have been detected above the standard of 1 µg/L for human toxicological non-relevant metabolites in sources of drinking water over the years 2010-2014. Glyphosate and its metabolite AMPA had maximum concentrations of 1.1 and 4.2 µg/L.

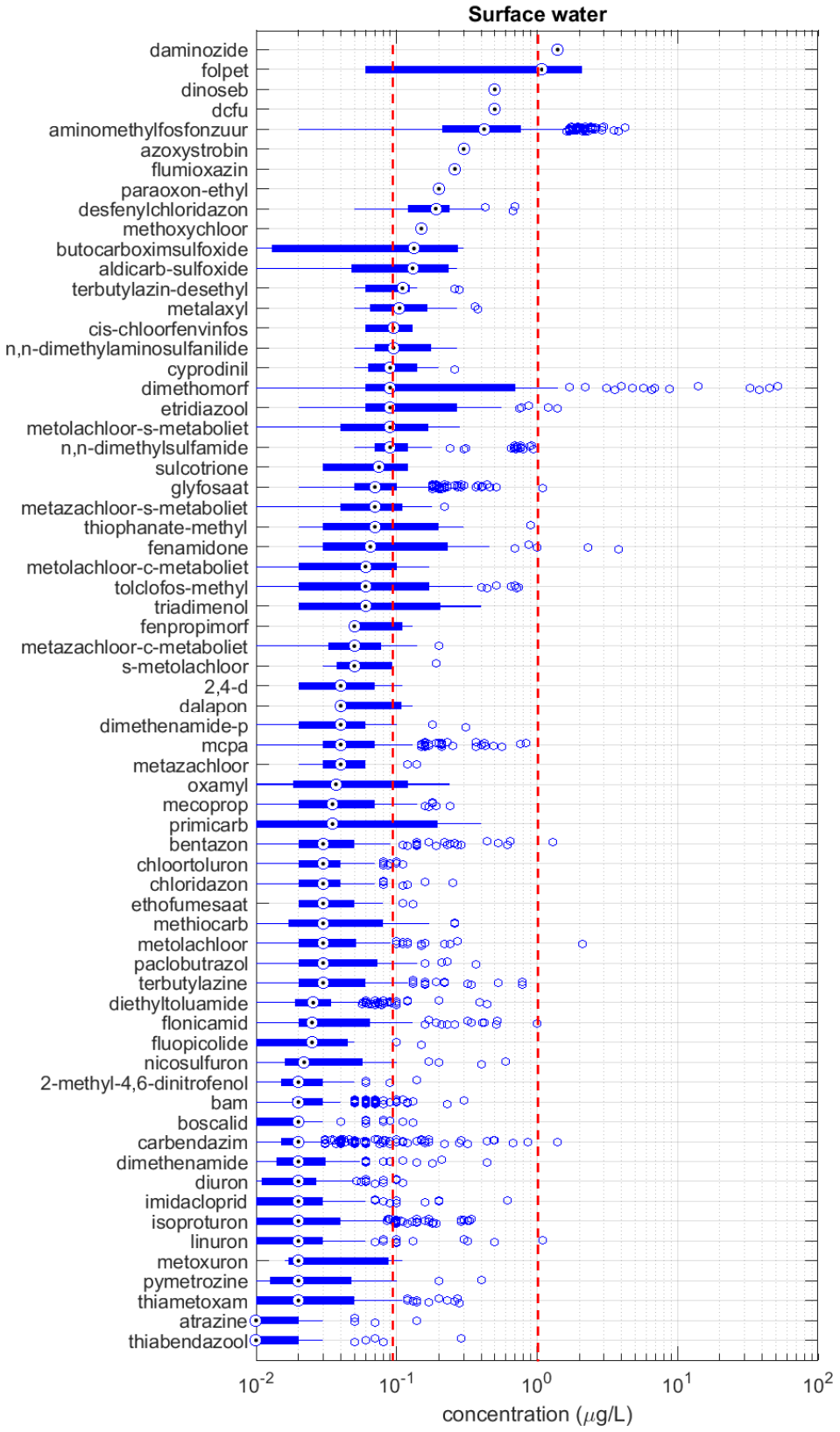


Figure 2-6 Pesticides and metabolites detected in surface water above a concentration of 0.1 µg/L, the drinking water guideline value for pesticides and relevant metabolites, such as n,n-dimethylsulfamide. Non-relevant metabolites have a drinking water guideline value of 1 µg/L and include

aminomethylfosfonzuur (AMPA), desfenylchloridazon, terbutylazine-desethyl, n,n-dimethylaminosulfanilide, metolachloor-s-metaboliet, metazachlor-s-metaboliet, metolachloor-c-metaboliet, metazachloor-c-metaboliet en BAM. Central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually.

In Figure 2-7 and Attachment II a selection is shown of 21 pesticides and metabolites occurring in river bank filtrate at least once above the threshold of 0.1 µg/L or 1 µg/L. Examples are the pesticides bentazon, dikegulac, dimethomorf and glyphosate. AMPA was detected in highest concentrations.

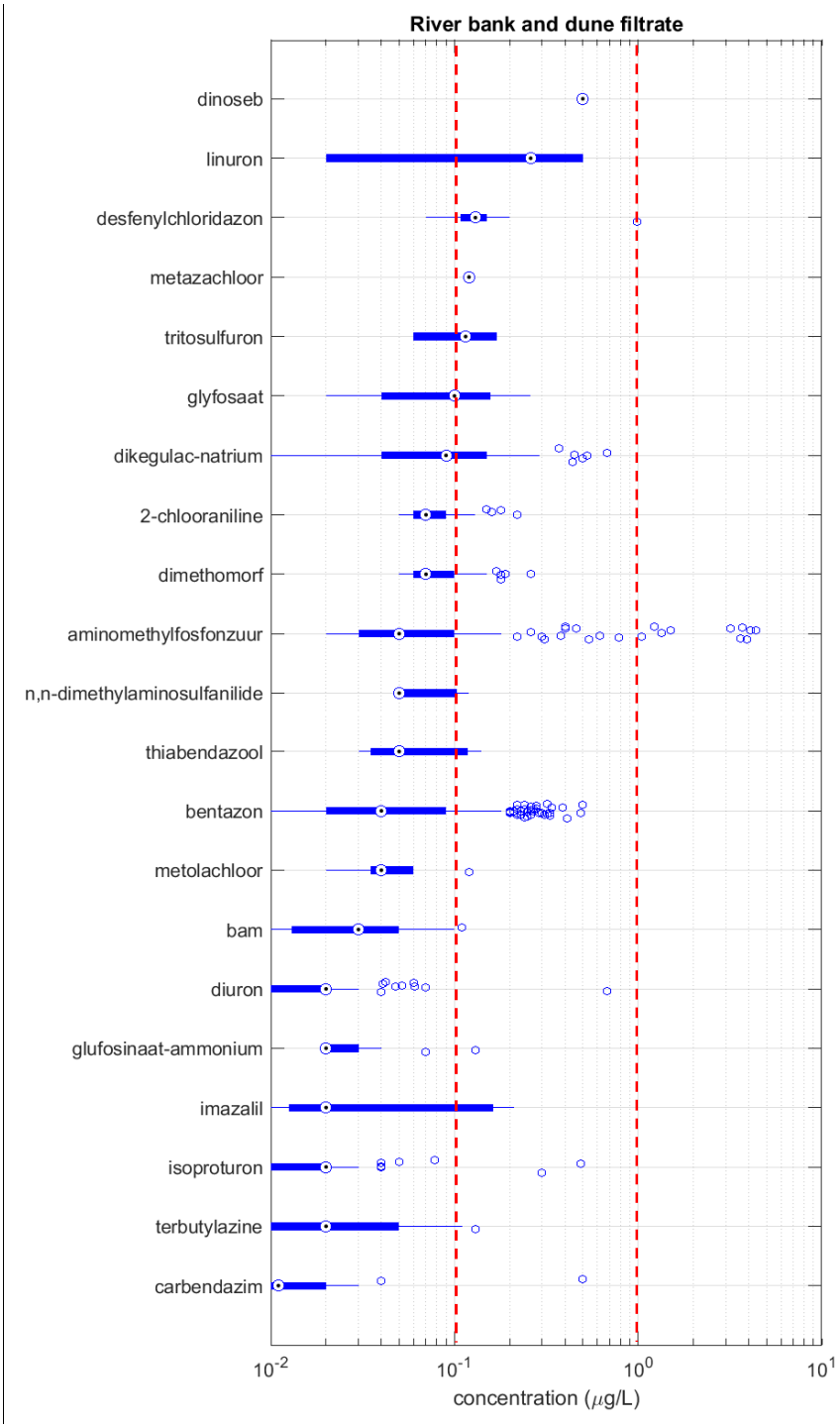


Figure 2-6 Pesticides and metabolites detected in river bank and dune filtrate above a concentrations of 0.1 µg/L, the drinking water guideline value for pesticides and relevant metabolites. Non-relevant metabolites have a drinking water guideline value of 1 µg/L and include desfenylchloridazon, aminomethylfosfonzuur (AMPA) and n,n-dimethylaminosulfanilide. Central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers and outliers are plotted individually.

The figures show that pesticides are generally more frequently detected in surface water in concentrations above the drinking water standard. The number of pesticides with

concentrations during 2010-2014 above 0.1 µg/L was 46 for surface water, 21 for riverbank/dune filtrate and 30 for groundwater. In groundwater BAM, bentazon and desfenylchloridazon are most frequently detected >0.1 µg/L. For surface water these are AMPA, glyphosate, desphenylchloridazon; for river bank and dune filtrate these are bentazon, dikegulac and AMPA.

Table 2-2 Detected persticides in the different water types.

Pesticides	**drinking water**	**groundwater**	**surface water**	**rivier bank and dune filtrate**
Detected pestcides	26	59	117	50
including > 0.1 µg/L	7	21	35	18
metabolites				
Detected metabolites	6	10	14	6
including > 0.1 µg/L	0	4	1	1
n detected total	32	69	131	56
most frequently detected >0.1 µg/L	Dikegulac, AMPA, BAM	BAM, bentazon and desfenyl-chloridazon	AMPA, glyphosate and desphenyl-chloridazon	bentazon, dikegulac and AMPA

2.5 Conclusion

In 67% of the 221 abstraction areas covering groundwater and surface water bodies in the Netherlands, pesticides have been detected. In 51% of the 193 drinking water production stations pesticides and/or metabolites have been detected in drinking water. Around 65 pesticides and 6 metabolites have been prioritized according to the extensive dataset in The Netherlands over 2010-2014. 26 pesticides and 6 metabolites were classified as high priority substances according their occurrence in drinking water and 39 pesticides were classified as priority substances according to their 90 percentile concentration in drinking water sources above the drinking water quality standard of 0.1 µg/L. 91 pesticides and 5 metabolites were classified as potential priority substances which exceeded 1/10th of the drinking water standard. These compounds are recommended for water quality screening; dependent on the local contamination and water system characteristics these compounds are relevant for uptake in monitoring programs. More details on the presence of pestices in the different source water types, such as observation wells, pumping wells and mixed raw water, can be found in BTO report 2017.070 (van Loon et al., 2017).

Examples of pesticides that were present in drinking water are: growth regulator dikegulac, the herbides glyphosate, bentazone, glufosinate-ammonium, bromacil, the fungicide dimethomorf and the insecticide oxamyl. Examples of pesticides that have exceeded the threshold of 0.1 µg/L in drinking water sources are the herbicides MCPA, MCPP, terbutylazine, isoproturon and the fungicides etridiazole and tolclofos-methyl.

300 compounds were not prioritized; these compounds were detected below the detection limit (296) or below 0.01 µg/L (4) and have recently no priority for uptake in intensive monitoring programs. It is recommended to monitor these compounds with low frequency (once in five years).

3 Recently authorized pesticides

3.1 Introduction

Pesticides that are available on the Dutch market might end up in drinking water sources, especially if the pesticide is mobile in water and not readily degradable. In this chapter recently authorized pesticides on the market are prioritized according to these properties. The prioritized pesticides are candidates for the implementation of a monitoring method (see Chapter 4), which will be applied in a large monitoring campaign in The Netherlands and Belgium (Chapter 5). In addition, pesticides prioritized in the BTO project "Data-driven prioritization of chemicals for various water types using suspect screening LC-HRMS" are included in section 3.4.

3.1.1 Drinking water assessment in authorization

In section 1.3 the authorization framework is outlined. Within Europe, the Dutch Authorization Board for pesticides (Ctgb) solely assesses the risk for drinking water production. In the drinking water assessment, the Ctgb uses water quality standards for groundwater equal to the standards set in the Drinking Water Directive (Drinkwaterbesluit, 2011; European Commission, 1998). In groundwater protection areas used for drinking water production the Ctgb applies in the first two tiers a safety factor of 10, so the assessment criteria in groundwater becomes 0.01 µg/L instead of 0.1 µg/L. In addition to monitoring data, for both surface water and groundwater concentrations are modelled. In addition for new substances, predicted concentrations in drinking water sources are modelled.

The leaching of pesticides to the groundwater is modeled by software programs FOCUS, PEARL and GeoPEARL (Tiktak et al., 2006). Authorization of the pesticides is based on a two tier approach, estimating the predicted environmental concentration (PEC) in groundwater. In the first tier the software FOCUS models the PEC in the Kremsmunster scenario. The compound is authorized if the PEC is below 0.01 µg/L (the standard of 0.1 µg/L with the additional safety factor of 10 for vulnerable groundwater protection areas in the Dutch-specific situation). A PEC exceeding the threshold of 0.01 µg/L will lead to a detailed exposure study using the software GeoPEARL. This spatial distribution model includes the leaching in the potential area of use. If the concentration is between 0.01 and 0.1 µg/L the use of the pesticide is restricted for groundwater protection areas.

The risks of pesticides for drinking water abstraction from surface water is described by Adriaanse (2008. The methodology exists of 2 tiers: pre-registration modelling and post-registration monitoring (initially, in-between tiers would be developed, but only the first and highest tier are currently available). The pre-registration modelling tier (first tier) is based on the model DROPLET (Van Leerdam and Adriaanse, 2009) that starts scenarios from FOCUS (FOCUS, 2001; Linders et al., 2010), but with Dutch drift values. From the edge-of-field concentration from FOCUS the concentration at the abstraction point is calculated by multiplying with certain factors, such as the relative crop area, difference in timing of applications within the area of use, degradation, volatilisation and dilution (Ctgb, 2014). The post-registration monitoring tier (highest tier) for the relevant substances (indicated by VEWIN), consists of an analysis of monitoring data on all abstraction points. A 90th percentile value is calculated for each individual abstraction point.

3.1.2 Active substances

Active substances are those compounds in the pesticides that are biologically active, and are responsible for the biological control with the function as herbicide, fungicide or insecticide. As these compounds are biological active they may form a risk for the ecological environment or for human health. The authorization as well as the environmental guidelines are well set for these active substances.

3.1.3 Adjuvants

Adjuvants are added to the pesticide product to enhance the pesticides performance, eg. increase the ability of the pesticide to penetrate, target or protect the target organism. At this moment, the regulation for adjuvants still has to be established in European procedures, member states may apply national provisions for authorization of adjuvants until the adoption of detailed rules. The Dutch authorization board Ctgb does generally not perform risk assessments for adjuvants, except when adjuvants with a prohibited formulant included in Annex III of Regulation (EG) 1107/2009 are present. In water quality guidelines, adjuvant will have a signaling value of 1 µg/L for all “other anthropogenic substances”.

Typical adjuvants are surfactants (extenders, wetting agents), oils, thickeners, sticking agents and anti-foaming agents. The function of these adjuvant types will be discussed below.

Surfactants

Surfactants (surface acting agents), also called wetting agents or spreaders, change the surface tension of a spray droplet allowing the pesticide to disperse more evenly on a surface in order to reach its target. Most surfactants have a polar or hydrophilic head and non-polar tail. Surfactants can be classified into anionic surfactants, cationic surfactants, nonionic surfactants and organo-silicone surfactants.

Oils

Oils are being used to break down the plants waxile layer to improve the penetration of a pesticide spray into the leaf or through an insect’s shell. Oils have the function of activator or carrier. The three types of oil-based adjuvants include crop oils, crop oil concentrates, and vegetable oil concentrates.

Thickeners

Thickeners are used to reduce drift of sprays. They increase the viscosity of spray mixtures to control drift, or slow evaporation after the spray has been deposited on the target area. They may contain polyacrylamide, polyethylene polymers, polysaccharides (long-chain sugars), or vegetable oils. It reduces drift, odor, and waste.

Sticking agents

Sticking agents are adjuvants that increase the adhesion of the pesticide to the plant leaf and improve the drying period of products. The stickers have also properties which reduce evaporation of the pesticide or to provide a waterproof casing. The adhesion properties are assigned to latex (rubber), polyethylene (plastic), resins (rosin), polymenthenes (rosin-like), or other waterproofing agents.

Anti-foaming agents

Some formulations create foam as a result of both the surfactants used and the type of spray tank agitation. Foam is an emulsion of air in water and forms when the surfactant has a preferential air/water interface and good tensile strength. This foam can be reduced or eliminated by adding a surfactant which destabilizes these air/water emulsions. The most

commonly used one is a silicone/carbon polymer known as polydimethylsiloxane (pds) (sileconenkit).

3.2 Materials and methods

According to the Ctgb, a list is composed of recently authorized pesticides on the market from 2004 to 2015. Several factors influence the potential (future) risk for drinking water production of a pesticide. An important factor is the scale of use, coupled to the potential to enter the environment. Large scale of use is often coupled to crops that are cultivated on large areas such as potatoes, flower bulbs, beets, wheat, barley, spelled wheat and corn.

These recently authorized active substances are prioritized based on their persistence and mobility. The criteria for half-life in soil (DT_{50}) and mobility expressed by the octanol-water partition coefficient (log K_{ow}) are DT50 > 7 days and Log Kow < 4. These values are adopted from publicly available authorization reports by the Ctgb. We obtained information on the PEC in groundwater and in surface water from the first authorization document of the newly introduced product ('nieuwe toelating'). We included the information of the restrictions in that specific use, the presence of metabolites and the ADI-value (advisable daily intake).

The variation of DT_{50} values is large for different types of studies (lab studies, field studies) and conditions (aerobic, anaerobic). Therefore we adopted the normalized geometric mean of the DT_{50} under aerobic conditions in soil used in the calculations with the software PEARL and FOCUS by the Ctgb. Compounds with half-life less than a week are not concerned priority substances, however their metabolites could be relevant (not studied). Compounds having a log K_{ow} larger than 4 are more eager to sorb to soil and sediment or in treatment processes, and therefore considered less mobile in water and less relevant for drinking water.

Less well known are the adjuvants applied, therefore all available information on ingredients in adjuvant products is collected.

3.3 Results and discussion

3.3.1 Recently authorized pesticides

In general, at February 2015, the Ctgb authorized:

- 855 pesticide products containing:
  - 249 active organic substances
  - 7 active inorganic substances
  - 3 bacteria
- 78 adjuvant products

Since 2005, 66 active substances were introduced on the market. Eleven compounds were considered as not relevant for the implementation of a monitoring method by the following causes:

- Three of these compounds were previously studied by Emke et al. (2007) and have been implemented monitoring method: prosulfuron (not detected), triflumizool (not detected) and sulcotrion (detected in ground- and surface water in concentrations >0.1 µg/L).
- Compounds applied in closed systems with no possibilities for emission to groundwater and surface water.

- Four of these compounds are considered non-relevant because of their non-toxicological properties: laminarin (polysaccharide), dodecan-1-ol and tetradecane-1-ol (fatty alcohols) and the pheromone (Z)-tetradec-9enylacetaat.

The remaining 55 recently authorized pesticides on the market, shown in Table 3-1, were prioritized in a drinking water perspective. These pesticides consist of 18 fungicides, 19 herbicides, 13 insecticides, 3 acaracides and 2 growth regulators.

Table 3-1 Recently authorized pesticides (Source: Ctgb).

Fungicide	**Herbicide**	**Insecticide**
ametoctradin	aminopyralid	acetamiprid
amisulbrom	benfluralin	chlorantraniliprole
ddssa	bromoxynil butyraat	clothianidine
benthiavalicarb-isopropyl	clethodim	emamectin benzoaat
bixafen	flumioxazin	flonicamid
cyflufenamide	imazomox	flubendiamide
fenamidone	ioxynil octanoaat	lufenuron
fenpyrazamine	jodosulfuron-methyl-sodium	methoxyfenozide
fluopicolide	mesosulfuron-methyl	pyridalyl
fluopyram	napropamide	spiromesifen
fluoxastrobin	pinoxaden	spirotetramat
fluxapyroxad	pyraflufen-ethyl	tefluthrin
isopyrazam	pyroxsulam	thiamethoxam
mandipropamid	quinoclamine	**Acaracide**
metconazole	tembotrione	acequinocyl
metrafenon	thifensulfuron-methyl	cyflumetofen
prothioconazool	topramezone	etoxazool
silthiofam	tribenuron-methyl	**Growth regulator**
	tritosulfuron	mepiquatchloride
		triclopyr

3.3.2 Prioritization of recently authorized pesticides

The 55 active substances are prioritized according to their properties for their possible drinking water relevance, see properties in Attachment III. The predicted environmental concentration (PEC) in surface water for 42 pesticides exceeded 0.1 µg/L at drinking abstraction points, see Figure 3-1 (source: Ctgb authorisation documents). Two of the prioritized active substances had a PEC in groundwater that exceeded the threshold of 0.1 µg/L in groundwater (Figure 3-1). The metabolites of 16 active substances exceed this threshold as well. These modelling studies only cope with individual authorizations and do not include cumulation from the use in multiple uses in several crops or by the use of multiple pesticides with the same active substance.

The results of the prioritization based on the chemical properties are shown in Table 3-2. 26 active substances have the highest priority, 24 substances have a potential priority (Table 3-3) and 6 substances have a low priority (Table 3-4). These high priority and potential priority active substances are candidates for the implementation of a measurement method. This will be illustrated in Chapter 4.

Table 3-2 Priority, potential priority and no priority active substances.

	Log Kow < 4	**Log Kow > 4**
DT50 > 7 days	26 (high priority)	12 (potential priority)
DT50 < 7 days	12 (potential priority)	6 (low priority)

Table 3-3 Priority and potential priority actives substances.

Priority		**Potential Priority**	
aminopyralid	mandipropamid	amisulbrom	acetamiprid
benalaxyl-M	mepiquatchloride	benfluralin	fenamidone
benthiavalicarb-isopropyl	mesosulfuron-methyl	cyflufenamide	flonicamid
bixafen	metconazole	emamectin benzoaat	imazomox
bromoxynil butyraat	methoxyfenozide	etoxazool	jodosulfuron-methyl-sodium
chlorantraniliprole	napropamide	flubendiamide	pinoxaden
clothianidine	tembotrione	isopyrazam	prothioconazool
fenpyrazamine	thiamethoxam	lufenuron	pyraflufen-ethyl
flumioxazin	topramezone	metrafenon	pyroxsulam
fluopicolide	tribenuron-methyl	pyridalyl	quinoclamine
fluopyram	triclopyr	silthiofam	spirotetramat
fluoxastrobin	tritosulfuron	tefluthrin	thifensulfuron-methyl
fluxapyroxad	spiromesifen		

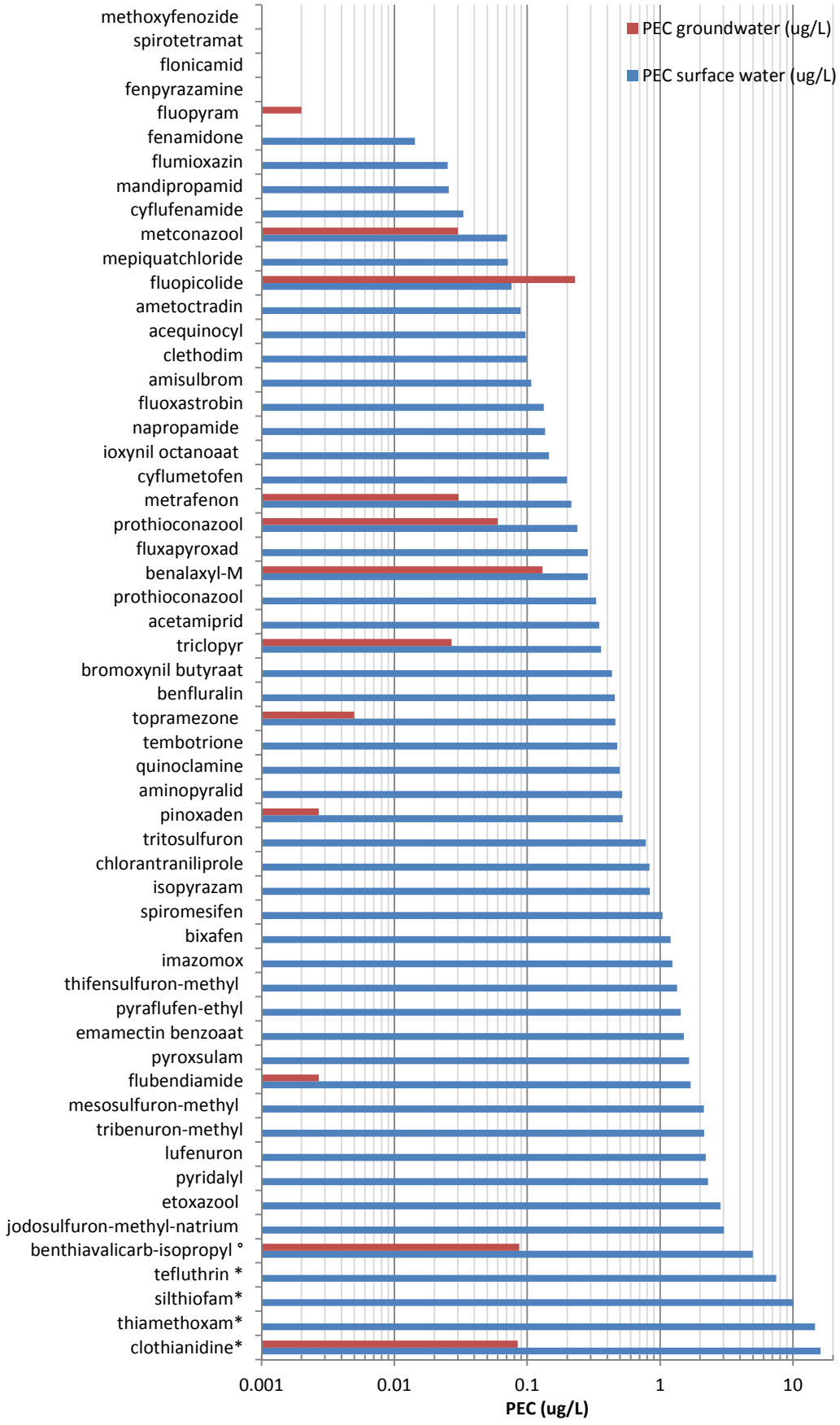

PEC groundwater (ug/L)
PEC surface water (ug/L)
methoxyfenozide
spirotetramat
flonicamid
fenpyrazamine
fluopyram
fenamidone
flumioxazin
mandipropamid
cyflufenamide
metconazool
mepiquatchloride
fluopicolide
ametoctradin
acequinocyl
clethodim
amisulbrom
fluoxastrobin
napropamide
ioxynil octanoaat
cyflumetofen
metrafenon
prothioconazool
fluxapyroxad
benalaxyl-M
prothioconazool
acetamiprid
triclopyr
bromoxynil butyraat
benfluralin
topramezone
tembotrione
quinoclamine
aminopyralid
pinoxaden
tritosulfuron
chlorantraniliprole
isopyrazam
spiromesifen
bixafen
imazomox
thifensulfuron-methyl
pyraflufen-ethyl
emamectin benzoaat
pyroxsulam
flubendiamide
mesosulfuron-methyl
tribenuron-methyl
lufenuron
pyridalyl
etoxazool
jodosulfuron-methyl-natrium
benthiavalicarb-isopropyl °
tefluthrin *
silthiofam*
thiamethoxam*
clothianidine*
0.001
0.01
0.1
1
10
PEC (ug/L)

*Figure 3-1 The predicted environmental concentration (PEC) in surface water for the selected active compounds in recently authorized pesticides. Maximal concentrations are shown for one of the modelled applications. °Data not available * Drift not expected from application (seed treatment).*

Table 3-4 Low priority actives substances.

Low priority
acequinocyl
ametoctradin
clethodim
cyflumetofen
ioxynil octanoaat

3.3.3 Adjuvants

The Ctgb has public accessible information on the authorization of 76 adjuvant products for crop cultivation since June 2012. The Ctgb does not assess the risk of the use of adjuvants for the environment. The Ctgb exclusively wants to assess the presence of a prohibited adjuvant (Regulation (EG) 1107/2009 Annex III) but this list of prohibited adjuvants has not yet been established by the EU. The applicant therefore does not need to provide information on the composition, properties and application of adjuvants. Occasionally, the composition of adjuvants has been submitted to the Ctgb. In some cases, the information was retrieved at the website of the authorization holder.

More than half of the adjuvants are surfactants (44/76) with or without extra functions such as a sticking agent or a thickener. Other adjuvants are antifoams, conditioners, oils and a marker.

Table 3-5 Types of adjuvants in the authorized adjuvants by the Ctgb.

Adjuvants	Nr of adjuvants in authorized products
Surfactant (with or without other functions such as sticking agent or thickener)	45
Antifoam	20
Sticking agent	5
Thickener	3
Conditioner	2
Oil	2
Marker	1

The composition of the adjuvants was found for half of these products. The adjuvant composition was submitted to the Ctgb (+/- 5 products) or could be found at authorization holder website (+/- 30). For several products the ingredients were only roughly described, such as synthetic latex, organo-silicone surfactant, or non-ionic surfactant. Eventually, 44 identities of ingredients for adjuvants are established (Table 3-6). Of these, 19 surfactants, 15 polymers, 2 inorganic compounds and 8 other compounds are present in adjuvants.

Surfactants are added to the pesticide because of their properties to break surface tension in water. The surfactants consist of glycols, alcohols, ethers and trisiloxanes. Most surfactants are non-ionic. Besides the surfactants, adjuvants contain several polymers, molecules with

repeating units, for thickening purposes. Oil compounds, such as solvent-nafta, rapeseed oil and plantoil increase uptake by plants. Rapeseed oil is present in minimum 12 adjuvants on the market. However its relevance for drinking water, such as natural compounds sojalectin and l-(+)-lactic acid is minimal by its hydrophobic properties. The adjuvants are not prioritised.

Table 3-6 Compounds present in adjuvant products.

Nonionic surfactants	**Polymers**
Alcohols and ethers	*Polyethers*
2,2'-oxydiethanol (di-etheenglycol)	alpha-i-tridecyl omega hydroxypolyglycolether
2-ethylhexan-1-ol	alpha-octadecyl omega hydroxypolyglycolether
2-methoxymethylethoxy propanol	oxirane, 2-methyl-, polymer with oxirane, ether with 2,2'-[(9Z)-9-octadecen-1-ylimino]bis[ethanol]
alkoxylated alcohol	polyethylene oxide monoisodecyl ether
C12-15-branched and linear ethoxylated alcohols	polyoxyethyleen(7)tridecyl ether
C9-11-iso-, C10-rich, ethoxylated alcohols	propylheptanol ethoxylate
ethoxy (7) tridecanol	copolymer of glycerol/coconut oil fatty acid/phthalic anhydride
glycerol	copolymer of vinylacetate + ethylene
terpineol	
	Polysiloxanes
Others	polyalkaleneoxide modified heptamethyl trisiloxane
1,2-benzisothiazolin-3-one	polydimethylsiloxane
1-octyl-2-pyrrolidon	polyether modified trisiloxane
alcoholethoxylate	
alkylethersulphate	*Others*
butanedioic acid, sulfo-1,4 (2-ethylhexyl) ester	polyacrylamide
ethoxylated rapeseedoil	terpene polymer
2-[Hydroxy(polyethyleneoxy)-propyl]heptamethyltrisiloxane (8EO)	alkyl polyglucoside
sojalecithin	fatty alcohol polyalkoxylate phosphate
trisiloxane	
	Other compounds
Anionic surfactants	azorubin (pigment)
Calcium dodecylbenzenesulphonate	l-(+)-lactic acid
	Propionic acid (=propanoic acid)
Anorganic compounds	sulfosuccinic acid di-(isooctyl)ester
sodium salt	heavy aromatic solvent-nafta (petroleum)
ammonium-sulphate	Heavy aromatic solvent naphtha (petroleum), naphthalene depleted
	rapeseed oil
	plantoil

3.4 Prioritized pesticides in suspect screening

In a suspect screening study we identified priority pesticides present in waste-, surface-, ground- and drinking water (Sjerps et al., 2016). The prioritization thresholds of 1, 0.1, 0.01 and 0.01 µg/L internal standard equivalents for respectively waste-, surface-, ground- and drinking water selected 21 pesticides (Table 3-7). Seven compounds are detected at surface water abstraction points for the production of drinking water: metolachloor, DEET, terbutylazine (all three confirmed), dimethomorf, fenamidone, fludioxonil and imazamethabenz-methyl (probable suspects, not yet confirmed).

Table 3-7 Prioritized pesticides detected in suspects screening using prioritization thresholds of 1, 0.1, 0.01 and 0.01 µg/L. for respectively waste water (WW), surface water (SW), groundwater (GW) and drinking water (DW). SW indicates the presence of a compound above the threshold of 0.1 µg/L. at an abstraction point of surface water for the production of drinking water. Compounds with identification level 1 are confirmed substances and compounds with level 4 are probable suspects.*

CAS	Compound	Identification level (Schymanski et al., 2014)	WW	SW	SW*	GW	DW
002634-33-5	1,2-benzisothiazol-3(2H)-on	1	✔				
1698-60-8	chloridazon	1				✔	
163515-14-8	dimethanamide-p	1		✔			
51218-45-2	metolachloor	1		✔	✔	✔	✔
134-62-3	N,N-Diethyltoluamide (DEET)	1		✔	✔	✔	
122-34-9	simazin	1				✔	
5915-41-3	terbuthylazine	1		✔	✔	✔	✔
25057-89-0	bentazone	4		✔		✔	✔
1563-66-2	carbufuran	4	✔	✔			
110488-70-5	dimethomorf	4		✔	✔		
1593-77-7	dodemorf	4		✔		✔	✔
161326-34-7	fenamidone	4		✔	✔		
120068-37-3	firponil	4		✔			
131341-86-1	fludioxonil	4		✔	✔		
81405-85-8	Imazamethabenz-methyl	4	✔	✔	✔	✔	
28159-98-0	Irgarol	4		✔			
143390-89-0	Kresoxim-methyl	4	✔				
94-74-6	MCPA	4		✔			
7085-19-0	mecoprop (MCPP)	4		✔		✔	✔
12750-92-4	piperonylbutoxide	4				✔	
107534-96-3	tebuconazool	4		✔			

3.5 Conclusion

Based on their properties for persistence and mobility we prioritized 50 recently authorized substances for persistence and mobility in the environment. The first teir PEC in surface water for 42 pesticides exceeded 0.1 µg/L at drinking abstraction points (Ctgb). Besides, the active products, 78 adjuvants products are authorized on the market. Whilst the composition of these adjuvants has hardly been submitted to the authorization board, the identity of 44 ingredients in adjuvants was established. Of these, 19 surfactants, 15 polymers, 2 inorganic

compounds and 8 other compounds are present in adjuvants which are not considered relevant for drinking water. Suspects screening in waste-, surface-, ground- and drinking water samples, followed by prioritization, selected 21 pesticides, including fenamidone, fludioxonil and imazamethabenz-methyl at abstraction points.

4 Implementation LC-MS/MS method

4.1 Introduction

This chapter describes the development and validation of a novel LC-MS/MS method for the simultaneous detection and sensitive quantification for the prioritized recently authorized pesticides.

4.2 Materials and methods

4.2.1 Selection of pesticides

For the prioritised compounds, a LC-MS/MS was developed and validated for the substances in Table 4-1 and Table 4-2 (selection KWR). For several pesticides a LC-MS/MS, GC-MS or GC-MS/MS method was already available at one or more drinking water laboratories (see Table 4-1 and Table 4-2).

Table 4-1 Priority active substances of recently authorized pesticides, with an available analytical method at the drinking water laboratories.

Priority	Method available at drinking water laboratories	Selection KWR
aminopyralid		x
benalaxyl-M		x
benthiavalicarb-isopropyl	x	x
bixafen		x
bromoxynil butyraat	x	
chlorantraniliprole		x
clothianidine		x
fenpyrazamine		x
flumioxazin	x	x
fluopicolide	x	
fluopyram	x	x
fluoxastrobin	x	x
fluxapyroxad	x	x
mandipropamid	x	x
mepiquatchloride		x
mesosulfuron-methyl	x	
metconazole	x	x
methoxyfenozide	x	
napropamide		x
spiromesifen	x	x
tembotrione	x	
thiamethoxam	x	x
topramezone	x	

tribenuron-methyl	x	
triclopyr	x	x
tritosulfuron	x	x
N=26	18	19

Table 4-2 Potential priority active substances of recently authorized pesticides, with an available analytical method at the drinking water laboratories.

Potential Priority	Method available at drinking water laboratories	Selection KWR
acetamiprid	x	x
amisulbrom		x
benfluralin		x
cyflufenamide		x
emamectin benzoaat		x
etoxazool		x
fenamidone	x	
flonicamid	x	
flubendiamide		x
imazomox		x
isopyrazam		
jodosulfuron-methyl-sodium	x	
lufenuron	x	x
metrafenon	x	
pinoxaden	x	
prothioconazool	x	
pyraflufen-ethyl	x	
pyridalyl		x
pyroxsulam	x	
quinoclamine	x	
silthiofam		x
spirotetramat		x
tefluthrin		x
thifensulfuron-methyl	x	
24	12	13

4.2.2 Standards

All solvents used were of analytical grade with minimual purity of 96%. Acetonitrile (ultra gradient HPLC grade) was obtained from Avantor Performance Materials B.V. (Deventer, the Netherlands). Acetic acid (HPLC quality) was purchased from Sigma Aldrich (Steinheim, Germany). The pesticides were purchased from Sigma Aldrich (Zwijndrecht, the Netherlands) and Toronto Research Chemicals (Toronto, Canada). Individual standards from all the pesticide were prepared in acetonitrile at a concentration of 100 mg/L. The isotope labeled internal standard atrazine-d_5 was purchased from CDN Isotopes (Nieuwegein, the

Netherlands) and bentazone-d_6 from Sigma Aldrich (Zwijndrecht, the Netherlands). Ultrapure water was obtained from a Veolia ELGA PURELAB Chorus system (Ede, the Netherlands)

4.2.3 Sample treatment

Approximately 45 mL of water sample was transferred into a 50 mL flask. 50 µL of an internal standard solution of a concentration of 0.50 mg/L was added, resulting in a final concentration of 0.50 µg/L internal standards in the flask. The flask was then filled up to the mark and homogenized. The samples were filtered with a 0.20 µm filter and transferred into an auto sampler vial for the analysis with the LC-MS/MS.

4.2.4 LC-MS/MS analysis

A Thermo Fischer Accela UHPLC system equipped with a Hypersil GOLD C18 (100 mm x 2.1 mm, 1.9 µm) column was used for the chromatographic separations of the pesticides. Mobile phase A was composed of 0.05% (v/v) acetic acid in water and mobile phase B was composed of 0.05% (v/v) acetic acid in acetonitrile. The column temperature was kept at 25 ˚C and the flow rate was 300 µL/min. The gradient conditions were as follows: initial time 5% B; 1.0 min 5% B; 15 min 100% B; 17 min 100% B; 17.5 min 5% B and re-equilibration at 5% B till 20 min. The auto sampler temperature was kept at 15 ˚C and 100 µL was injected into the LC-MS/MS system.

The pesticides were identified and quantified with a Thermo Fisher TSQ Vantage mass spectrometer. Each pesticide was identified and quantified using two transitions in selected reaction monitoring mode. Calibration standards in drinking water were used to obtain external calibration curves for the pesticides ranging from 0.01 µg/L to 10.0 µg/L. All pesticides, except flubendiamide, were detected in positive heated electrospray ionization mode (HESI+). The capillary and vaporizer temperature were 275 ˚C and 350 ˚C, respectively. The pressure for the sheath gas was 30 psi and for the ion sweep 5 psi. The auxiliary gas flow was set to 10 L/min.

The selected reaction monitoring settings are shown in Attachment IV.

4.3 Method development

The individual standards from the pesticides in acetonitrile were infused in the Thermo Fisher TSQ Vantage to determine the S-lens voltage and the collision energy needed to obtain products ions from the precursor ion. During the infusing of benfluralin there were no useable products ions visible. For this reason benfluralin was not included in the method.

After optimization of the S-lens and the collision energy, the individual standards were injected to determine the retention time and peak shape. During these injections the polar compounds aminopyralid, mepiquatchloride and tefluthrin showed no retention on the C18 column, and they were therefore omitted from the method.

For the validation, the remaining pesticides were spiked at three concentration levels to drinking- and surface water to determine relative standard deviation and recovery. Eventually the limit of quantification was calculated from the standard deviation. During the validation emamectin benzoaat, lufenuron, pyridalyl and spiromesifen showed a decrease in response of the standards up to 75%. For this reason the mentioned pesticides also were not included in the method. The decrease in response of pyridalyl was so quickly that eventually no peaks were detected anymore. For this reason no data for pyridalyl is given in table 4-3 and 4-4.

4.4 Method validation

For the validation of the LC-MS/MS method the pesticides were spiked to drinking- and surface water at three concentration levels, i.e. 0.01, 0.10 and 1.0 µg/L at. From these data the recovery and relative standard deviation were calculated. The results are shown in Table 4-3 and Table 4-4 for drinking – and surface water, respectively.

Table 4-3 Relative standard deviation and recoveries in drinking water.

Compound	Level 0.01 µg/L		Level 0.10 µg/L		Level 1.0 µg/L	
	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)
Acetamiprid	1.5	79.5	1.7	100.9	0.3	101.1
Amisulbrom	n.c.	n.c.	11.0	98.4	3.6	108.5
Benalaxyl-M	5.5	101.2	4.2	102.6	1.8	101.1
Benthiavalicarb-isopropyl	3.2	94.9	2.3	103.4	0.7	102.2
Bixafen	11.5	103.9	5.8	96.3	0.8	100.4
Chlorantraniliprole	10.4	81.1	0.8	102.8	0.6	104.2
Clothianidine	7.1	80.9	2.0	104.8	0.6	102.1
Cyflufenamide	7.9	117.1	6.1	105.5	2.4	104.3
Emamectin benzoaat	n.c.	n.c.	n.c.	n.c.	30.6	77.3
Etoxazool	8.4 #	128.1 #	7.0	133.2	11.4	122.9
Fenpyrazamine	4.7	70.5	2.1	107.2	1.1	105.2
Flubendiamide	n.c.	n.c.	n.c.	n.c.	9.8	94.8
Flumioxazin	n.c.	n.c.	n.c.	n.c.	5.9	109.8
Fluopyram	4.3	98.6	2.7	99.7	0.8	99.9
Fluoxastrobin	5.7	104.4	2.7	101.5	2.5	101.9
Fluxapyroxad	4.8	90.8	2.4	103.3	0.8	103.4
Imazamox	6.2	89.8	2.8	106.0	0.5	102.8
Lufenuron	n.c.	n.c.	n.c.	n.c.	36.1	112.5
Mandipropamid	4.7	95.3	3.4	100.7	1.1	100.5
Metconazole	5.2	118.9	3.6	89.4	2.4	91.4
Napropamide	5.1	79.8	1.9	112.1	1.2	105.7
Pyridalyl	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Silthiofam	6.9	83.8	2.4	108.9	1.1	104.4
Spiromesifen	n.c.	n.c.	n.c.	n.c.	18.4	122.1
Spirotetramat	5.7	101.1	4.2	110.8	2.3	106.3
Thiamethoxam	7.5	81.3	2.3	109.9	0.9	103.3
Triclopyr	3.7 #	101.5 #	6.5	99.1	2.3	99.3
Tritosulfuron	5.5	79.5	1.5	101.1	1.0	100.9

n.c. = not calculated.
 # = spike level is 0.05 µg/L.

Table 4-4 Relative standard deviation and recoveries in surface water.

Compound	Level 0.01 µg/L		Level 0.10 µg/L		Level 1.0 µg/L	
	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)
Acetamiprid	1.7	103.7	1.1	111.1	1.2	104.1
Amisulbrom	n.c.	n.c.	6.7	91.8	5.6	102.8
Benalaxyl-M	6.7	114.4	3.1	101.2	1.6	99.5
Benthiavalicarb-isopropyl	2.7	110.7	2.7	101.5	0.6	97.9
Bixafen	5.1	119.0	4.3	98.7	0.7	96.4
Chlorantraniliprole	6.5	97.2	2.8	98.7	0.7	97.8
Clothianidine	5.0	98.2	2.2	101.3	1.1	95.9
Cyflufenamide	5.2	95.7	3.4	100.2	2.7	100.2
Emamectin benzoaat	n.c.	n.c.	n.c.	n.c.	55.9	17.7
Etoxazool	8.1 #	100.0 #	10.8	118.3	12.0	124.9
Fenpyrazamine	3.2	93.0	1.8	108.1	0.8	104.9
Flubendiamide	n.c.	n.c.	n.c.	n.c.	9.8	82.4
Flumioxazin	n.c.	n.c.	n.c.	n.c.	6.0	98.5
Fluopyram	3.7	99.0	2.3	107.7	1.0	99.3
Fluoxastrobin	5.8	122.2	3.3	102.5	1.5	98.7
Fluxapyroxad	1.8	87.5	1.9	104.2	1.1	99.8
Imazamox	3.0	95.4	0.8	123.7	2.5	122.0
Lufenuron	n.c.	n.c.	n.c.	n.c.	77.0	48.3
Mandipropamid	6.3	110.2	3.6	98.7	1.3	97.8
Metconazole	3.2	90.5	1.9	109.5	1.6	108.4
Napropamide	3.7	95.5	1.4	110.7	1.2	102.9
Pyridalyl	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Silthiofam	6.1	90.2	2.8	105.7	0.8	98.5
Spiromesifen	n.c.	n.c.	n.c.	n.c.	34.5	58.2
Spirotetramat	7.2	106.7	3.9	94.4	3.1	87.7
Thiamethoxam	8.3	105.5	1.7	116.1	0.8	106.0
Triclopyr	4.7 #	101.5 #	7.4	102.0	1.9	99.0
Tritosulfuron	3.1	106.8	2.3	101.9	1.6	97.0

n.c. = not calculated.
 # = spike level is 0.05 µg/L.

From the calculated standard deviation the limit of detection and the limit of quantification were calculated for 24 pesticides. These results are shown in Table 4-5.

Table 4-5 CAS number, application, limit of detection (LOD) and limit of quantification (LOQ) (in µg/L) of the pesticides in drinking- and surface water.

Compound	CAS number	Application	Drinking water		Surface water	
			LOD	LOQ	LOD	LOQ
Acetamiprid	135410-20-7	insecticide	0.001	0.01	0.001	0.01
Amisulbrom	348635-87-0	fungicide	0.034	0.10	0.019	0.10
Benalaxyl-M	98243-83-5	fungicide	0.002	0.01	0.003	0.01
Benthiavalicarb-isopropyl	177406-68-7	fungicide	0.001	0.01	0.001	0.01
Bixafen	581809-46-3	fungicide	0.004	0.01	0.002	0.01
Chlorantraniliprole	500008-45-7	insecticide	0.003	0.01	0.002	0.01
Clothianidine	210880-92-5	insecticide	0.002	0.01	0.002	0.01
Cyflufenamide	180409-60-3	fungicide	0.003	0.01	0.002	0.01
Etoxazool	153233-91-1	acaracide	0.017	0.05	0.013	0.05
Fenpyrazamine	473798-59-3	fungicide	0.001	0.01	0.001	0.01
Flubendiamide	272451-65-7	insecticide	0.293	1.0	0.255	1.0
Flumioxazin	103361-09-7	herbicide	0.196	0.50	0.179	0.50
Fluopyram	658066-35-4	fungicide	0.001	0.01	0.002	0.01
Fluoxastrobin	361377-29-9	fungicide	0.002	0.01	0.002	0.01
Fluxapyroxad	907204-31-3	fungicide	0.001	0.01	0.001	0.01
Imazamox	114311-32-9	herbicide	0.002	0.01	0.001	0.01
Mandipropamid	374726-62-2	fungicide	0.001	0.01	0.002	0.01
Metconazole	125116-23-6	fungicide	0.002	0.01	0.002	0.01
Napropamide	15299-99-7	herbicide	0.001	0.01	0.001	0.01
Silthiofam	175217-20-6	fungicide	0.002	0.01	0.002	0.01
Spirotetramat	203313-25-1	insecticide	0.002	0.01	0.002	0.01
Thiamethoxam	153719-23-4	insecticide	0.002	0.01	0.003	0.01
Triclopyr	55335-06-3	Growth regulator	0.006	0.03	0.007	0.03
Tritosulfuron	142469-14-5	herbicide	0.001	0.01	0.001	0.01

Satisfactory LOD and LOQ results were obtained for the developed LC-MS/MS method for drinking- and surface water. The LOQ for most of the pesticides is in the range of 0.01 – 0.05 µg/L. For flubendiamide and flumioxazin higher LOQs of respectively 1.0 and 0.50 µg/L were obtained. The recoveries in drinking- and surface water are between the acceptable range of 87.7 and 124.9%. The repeatability for all pesticides are below 12%.

4.5 Conclusion

A novel LC-MS/MS method for the simultaneous detection and sensitive quantification for 24 recently authorized pesticides on the market was developed and validated in drinking- and surface water (see table 4-5). Several compounds were dropped out of the method:

- Benfluralin could not be analysed as this compound did not show any visible products ions.
- The polar compounds aminopyralid, mepiquatchloride and tefluthrin showed no retention on the C18 column, and they were therefore omitted from the method.

- The pesticides emamectin benzoaat, lufenuron, pyridalyl and spiromesifen showed a large decrease in response of the standards and could not be included in the method.

5 Monitoring campaign recently authorized pesticides in The Netherlands and Belgium

5.1 Introduction

Of the 50 recently authorized pesticides in the Netherlands classified as priority or potential priority (see Chapter 3), 24 compounds could be implemented in the LC-MS/MS method (see Chapter 4). This Chapter describes the results of the analyses with the currently implemented analytical method and with the analytical method developed in 2007 (Emke, 2007) in an extensive monitoring campaign in the Netherlands and Belgium in june and august 2016.

5.2 Materials and methods

The samples were analysed with the implemented LC- MS/MS analytical method for 24 recently authorized pesticides (see Chapter 4). This method is referred to as 'analytical method 2016'. In addition, the samples were screened for 26 other pesticides with a LC-MS/MS analytical method developed in 2007 (Emke, 2007). This method is referred to as 'analytical method 2007'. The pesticides that have been authorized over a longer period have had over 10 years' time to reach groundwater aquifers and drinking water sources and could therefore have a higher change to be detected in groundwater sources compared to recently authorized pesticides. Therefore we included these compounds in the screening for recently authorized pesticides. The compounds analysed with both methods can be found in Attachment VI.

The analysed recently authorized pesticides detected in the water samples in concentrations above the drinking water quality guideline of 0.1 µg/L, were assessed for human health effects using the value for the acceptable daily intake (ADI).

5.2.1 Sampling

128 water samples were taken at from groundwater and surface water in The Netherlands and a part of Belgium (The Watergroep), see Attachment VI. 24 samples originate from surface water used for the production of drinking water. The 24 samples correspond to 23 locations, since one location, the Meuse at Brakel, was accidentally sampled twice. All surface water locations were sampled a second time in august. Other samples include 4 locations with dune filtrate (i.e. surface water infiltration in the dunes), 10 samples from river bank filtrate, and in groundwater water abstraction areas 90 samples had been taken. The sampling was carried out in two campaigns; at the end of May/beginning of June all surface water and groundwater locations were sampled (results are shown in section 5.3); at the end of August the surface water were sampled in a second round (results are shown in section 5.4).

Table 5-1 Number of samples per water company.

Water Company	Number of samples	Remarks
BW	17	
De Watergroep	40	
Dunea	7	7 samples originate from 6 locations, since location Brakel was sampled twice
Evides	6	
Oasen	5	
PWN	1	
Vitens	22	
Waternet	4	
WBG	1	
WMD	12	
WML	13	
Totaal	**128**	

5.3 Results monitoring campaign May/June 2016

The results of the analysis with both methods are discussed separately as the analytical methods had different detection limits: 0.01 µg/L (2016) versus 0.03 µg/L (2007). The results of the analyses with the analytical method from 2016 are discussed in section 5.3.1 and the results of the analyses with analytical method from 2007 in section 5.3.1.

Each analytical method (2016 and 2007) resulted in the detection of almost half of the total number of compounds analysed (Table 5-1).

Most compounds have been detected in surface water; in 23 out of 24 surface water samples one or more pesticides were detected (not in the Drentse Aa). In 3 out of 4 samples from abstracted dune filtrate one pesticide was detected. The analysed recently authorized pesticides were not detected in the 10 samples from river bank filtrate. In only four out of 90 groundwater samples the recently authorized pesticides were detected, from both The Netherlands and Belgium. In four surface water samples, ten or more pesticides were detected (Figure 5-1). The groundwater samples contained up to 3 pesticides per sample (Figure 5-1).

Table 5-2 Number of compounds analysed with the two analytical methods, number of compounds detected above the detection limit, with threshold values of 0.1 µg/L and 0.05 µg/L.

	Compounds in screening (n)	Detected compounds (n)	Compounds above threshold n > 0.1 µg/L	Compounds above threshold n > 0.05 µg/L
Analytical method 2016[1]	24	12	3	8
Analytical method 2007[2]	26	10	4	9

[1]The detection limit is 0.01 µg/L for most pesticides, except for flubendiamide (1 µg/L), flumioxazin (0.5 µg/L), amisulbrom (0.1 µg/L) and etoxazool (0.05 µg/L).
[2]The detection limit is 0.03 µg/L.

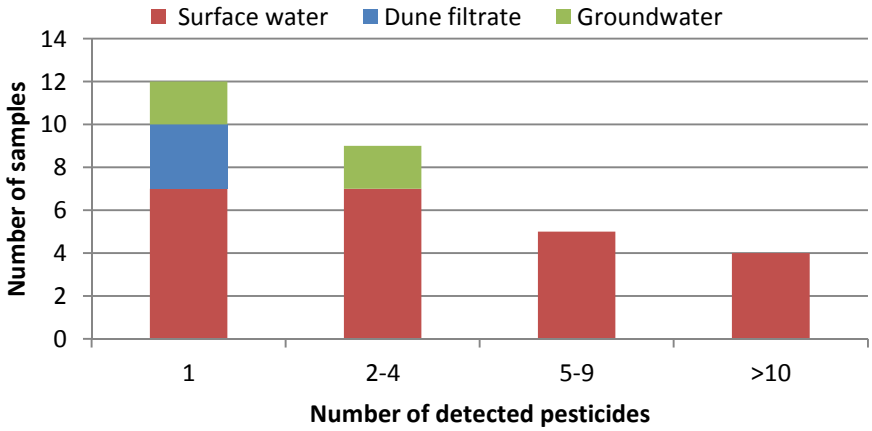


Figure 5-1 The amount of samples from the monitoring campaign in June 2016 with one or more pesticides detected in the analysis with both analytical methods.

5.3.1 Analytical method 2016

The results of analyses with the analytical method 2016 are presented in Figure 5-2 and Attachment VII. The method detected 12 out of 24 pesticides in the samples. The detected pesticides are 7 fungicides, 4 insecticides and 1 herbicide.

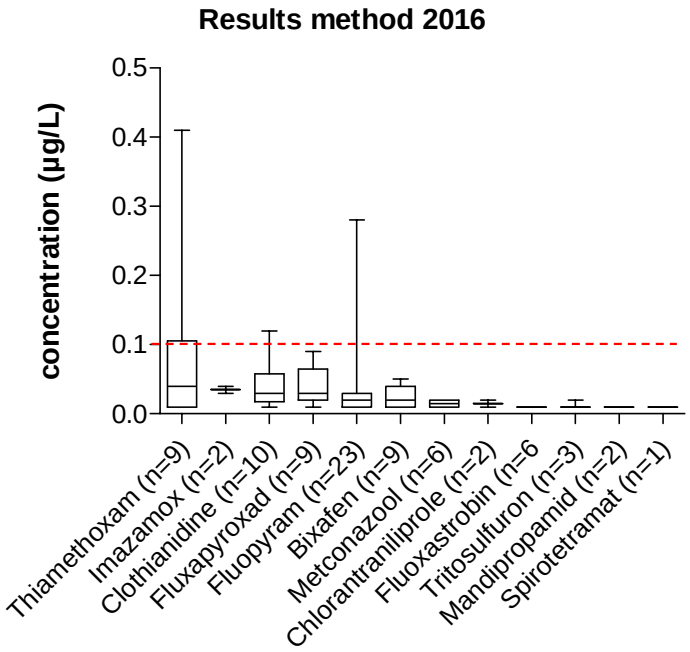


Figure 5-2 Concentration range of the 12 pesticides detected in the samples from june 2016 with the analytical method 2016. The box represents the 25th, 50th and 75th percentiles and the edges the min-max boundaries. The detection limit of the compounds is 0.01 µg/L. Data can be found in Attachment VII.

All of the pesticides were detected in surface water from The Netherlands and Belgium (see results in Attachment VII). Only two compounds were detected in groundwater: the insecticides clothianidine and thiamethoxam. The insecticide clothianidine was detected in a shallow monitoring well in Brabant. The concentrations of the detected pesticides in Belgian surface waters were on average higher than the concentrations detected in Dutch surface waters. However, the highest concentrations of individual pesticides were detected in samples from the Dutch part of the river Meuse (Brakel): the insecticide thiamethoxam and the fungicide fluopyram exceeded the drinking water standard of 0.1 µg/L. The concentrations in Belgian surface water were below 0.1 µg/L, except for fluopyram.

Thiamethoxam, fluopyram and clothianidine: authorization

Thiamethoxam is present in six products on the market since 2005, functioning as an insecticide and as a biocide. The anti-aphid should be applied as a seed treatment agent for floriculture (greenhouse), nurseries, potatoes, lettuce and endive. Thiamethoxam belongs as to the group of neonicotinoid insecticides. During the authorization was modelled that the proposed application of thiamethoxam does not result in an exposure of surface water, so also no exposure to surface water at drinking water abstraction points. However, the compound is detected in 9 samples, including surface water of the river Meuse (0.41 µg/L), infiltration pond Berkheide and the river IJzer in Belgium.

Fluopyram is used as a fungicide authorized since 2014. The product is used for application on fruits, leaf vegetables, flower bulbs and floriculture. The maximum predicted environmental concentration (PEC_{max}) in the authorization of Fluopyram is 0.05 µg/L at drinking water abstraction point Nieuwegein. However the compound is detected in 23 samples, including samples of the river Meuse (maximum 0.28 µg/L), the Rhine, infiltrated ponds and abstracted dune filtrate.

Clothianidine is used as in insecticide and authorized since 2008. The product is used for seed treatment to prevent damage from insects for beetroot seads. The compound belongs to the group of neonicotinoids. In the authorization document was included that the model PEARL estimated for clothiamidine a PEC in groundwater of 4.14 µg/L during springtime. In the second tier, detailed modelling with the model GeoPEARL estimated a 90 percentile PEC of 0.001 µg/L in groundwater. The concentration found in this study was 0.11 µg/L in groundwater.

Surface water

As stated before, two of the 12 detected pesticides occur in concentrations above the drinking water standard of 0.1 µg/L in surface water: the insecticide thiamethoxam and the fungicide fluopyram were detected in concentrations of respectively 0.41 µg/L and 0.28 µg/L in surface water of the river Meuse (Brakel). Fluopyram was also detected in a concentration of 0.1 µg/L in raw water from the IJzer at treatment station Blankaart. Furthermore, both the herbicide fluxapyroxad and the fungicide bixafen were detected in concentrations between 0.05 and 0.1 µg/L in Belgian surface waters. The seven other pesticides, the herbicides imazamox and tritosulfuron, the insecticides chlorantraniliprole and spirotetramat, and the fungicides metconazole, fluxatrobin and mandipropamid were detected in concentrations below 0.05 µg/L (see also Attachment VII).

To compare the total presence of pesticides in rivers and reservoirs, the sum concentrations per sample in surface water from rivers and reservoirs originating from water from the Meuse, the river Rhine, the River IJzer, the river Scheldt and the Ieperse ponds are shown in

Figure 5-3. In the small Belgian river IJzer 9 pesticides were detected in concentrations just below the drinking water standard of 0.1 µg/L. In the Belgian river Scheldt respectively 5 pesticides were detected in concentrations below 0.05 µg/L. Only one pesticide was detected in the river Rhine, fluopyram, in concentrations of 0.01-0.02 µg/L.

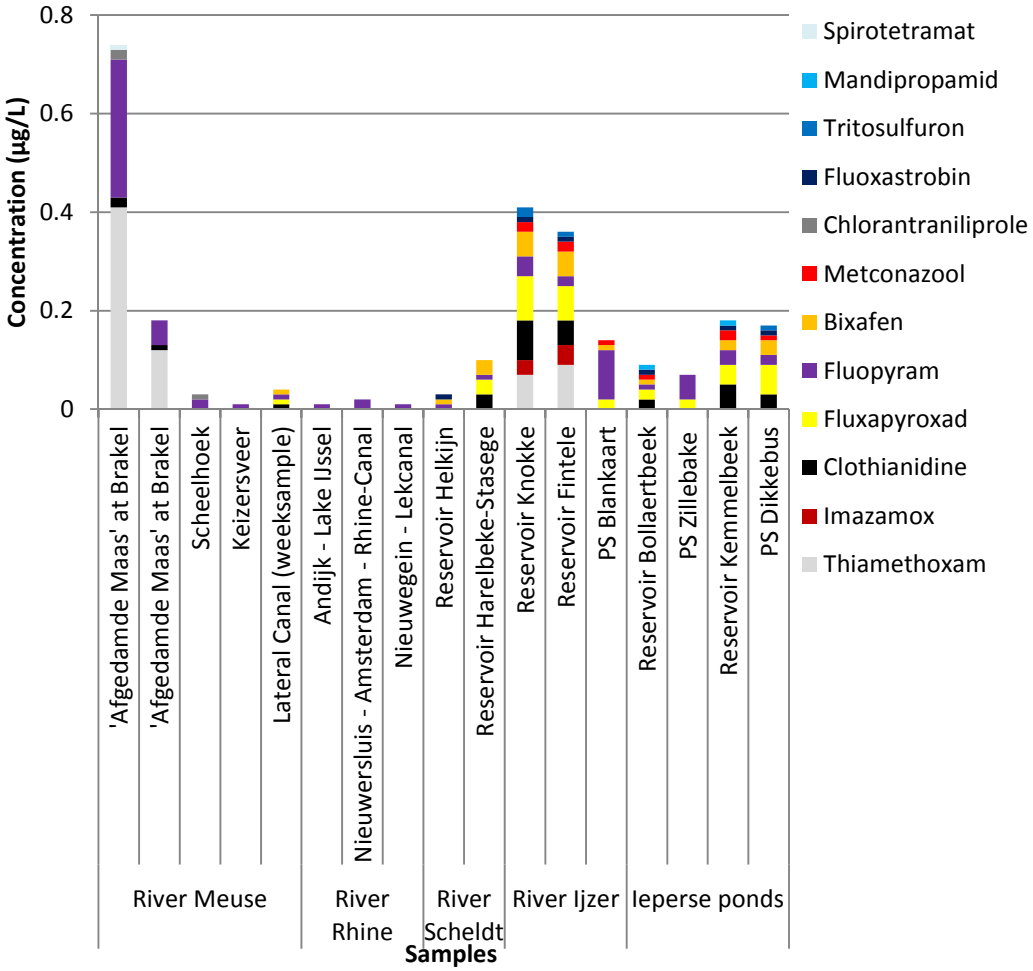


Figure 5-3 Sum concentration per sample in surface water from rivers and reservoirs (june 2016). Data can be found in Attachment VII.

Surface water and dune filtrate

Samples were taken from surface water, infiltration ponds and abstracted dune filtrate. Figure 5-4 shows the development of the detected concentrations of thiamethoxam and fluopyram downstream the Meuse, the infiltrated and abstracted dune filtrate. Other pesticides were not detected in dune filtrate with the analytical method 2016. Bixafen, chlorantraniliprole, fluxapyroxad and spiratetramat were only detected in surface water (up to a concentration of 0.02 µg/L).

Figure 5-4 shows that the concentrations of thiamethoxam and fluopyram have increased in the Meuse at location Brakel (Afgedamde or Andelse Maas). Upstream, at the intake point Lateral canal and downstream at the intake point of Scheelhoek concentrations are below 0.02 µg/L.

The intake point Brakel is located in the Meuse at the 'Afgedamde Maas' or 'Andelse Maas'. The residence time of the water in the Andelse Maas is 60 days. During this time the water is pre-treated with coagulation (Fe-dosing). The water at the 'Andelse Maas' is fed by two sources: the Meuse itself and drained polder water from the 'Bommelerwaard'. The water from the polder enters the Meuse through four pumping stations, including 'Gemaal Brakel'. Compounds discharged in the ditches in the polder could thus reach the surface water intake point.

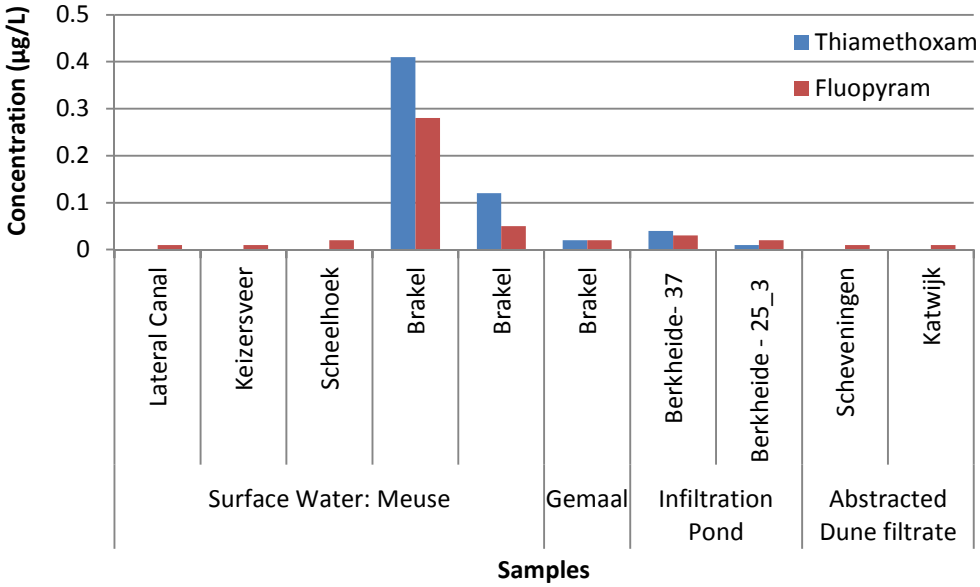


Figure 5-4 Concentrations of the pesticides thiamethoxam and fluopyram in the Meuse, infiltration ponds and abstracted dune filtrate originating from the Meuse (june 2016). Data can be found in Attachment VII.

The surface water of the Meuse at Brakel was sampled at two dates: May 23 and May 25 2016. The highest concentrations were detected at May 25. The pesticides could be discharged to the Meuse at Brakel through one of the four pumping stations (gemalen).

The pesticides were detected below 0.05 µg/L in the infiltration ponds of Berkheide, as well as the abstracted dune water at Katwijk and Scheveningen.

In the river Rhine only the compound fluopyram was detected. The concentrations of the samples taken at Nieuwegein, Nieuwersluis and Andijk were below 0.02 µg/L. In the abstracted water at Leiduin this compound was detected in a concentration of 0.01 µg/L.

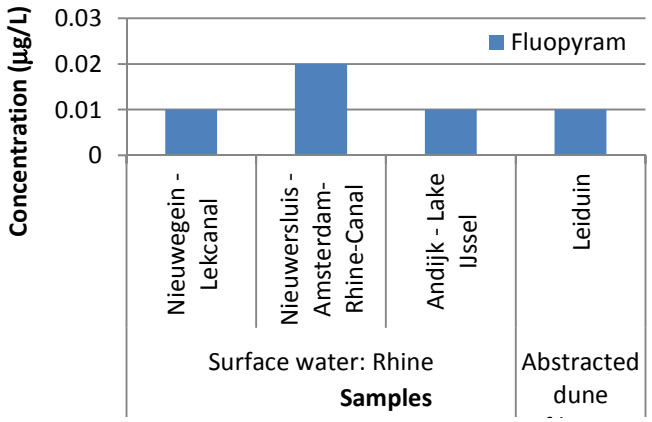


Figure 5-5 Concentration of the pesticide fluopyram in the river Rhine and abstracted dune filtrate originating from the Rhine (june 2016). Data can be found in Attachment VII.

Groundwater

In groundwater, two pesticides were detected in observation wells: the insecticide clothianidine was detected with a concentration of 0.12 µg/L in a shallow monitoring well in Brabant as well in a concentration of 0.01 µg/L at Well Field Heumensoord (Vitens); the insecticide thiamethoxam was detected in a concentration of 0.01 µg/L at Well Field Heumensoord (Vitens), see Figure 5-6. Clothianidine had a concentration above the drinking water standard of 0.1 µg/L in a shallow monitoring well in Brabant; this observation well (B50E-0366) is located in agricultural land with corn crops; the filter is located 3.5m below surface level. In surface water this compound was detected below 0.08 µg/L.

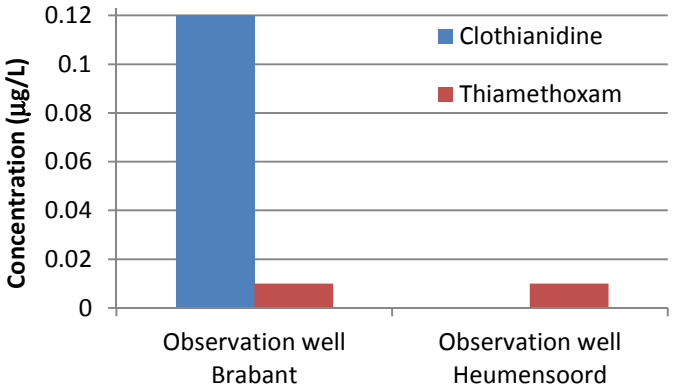


Figure 5-6 Concentration of pesticides detected in groundwater (june 2016). Data can be found in Attachment VII.

Clothiadine and thiamethoxam are classified as neonicotinoids, equal to imadacloprid, and are used in the treatment of beetroot seads. Clothiadine and thiamethoxam were both classified as priority substances in this report with a log K_{ow} of 0.9 / -0.13 and a DT_{50} of 100 days / 133 days (Chapter 3, section 3.3.2).

5.3.2 Analytical method 2007

The results of analyses with the analytical method 2007 are presented in

Figure 5-7. The method detected 10 out of 26 pesticides in the samples. These compounds have been authorized over 10 years. The detected pesticides are: 6 herbicides, 3 insecticides, 1 fungicide and 1 nematicide (pesticide against worms).

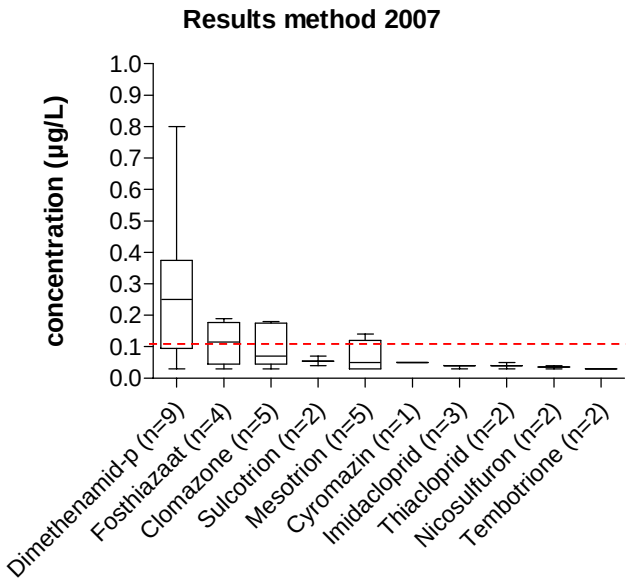


Figure 5-7 Concentration range of the 10 pesticides detected in the samples from june 2016 with the analytical method 2007. The box represents the 25th, 50th and 75th percentiles and the edges the min-max boundaries. The detection limit of the compounds is 0.03 µg/L. Data can be found in Attachment VII.

These compounds were often detected in samples from Belgian waters (9 samples); only two samples taken in the Dutch part of the river Meuse contained the studied pesticides. Four pesticides exceeded the drinking water standard of 0.1 µg/L in surface water: dimethenamid-p, fosthiazate, clomazone and mesotrion. Dimethenamid-p was besides being detected in surface water samples, also detected in two groundwater samples in concentrations larger than 0.1 µg/L.

Surface water

Nine pesticides were detected in surface water (cyromazin was only detected in groundwater). Four detected pesticides had concentrations above the drinking water standard of 0.1 µg/L: the herbicides clomazone, dimethamid-p and mesotrion and the nematicide fosthiazaat. All of these compounds were detected in concentrations of 0.1-0.5 µg/L in the two samples from the river IJzer. Dimethamid-p was found in the highest concentration of 0.8 µg/L in surface water at drinking water treatment station Dikkebus (De Watergroep). The herbicide sulcotrion and the insecticide thiacloprid are detected in concentrations between 0.05-0.1 µg/L. The insecticide imidacloprid, the herbicides nicosulfuron and tembotrione were detected below 0.05 µg/L.

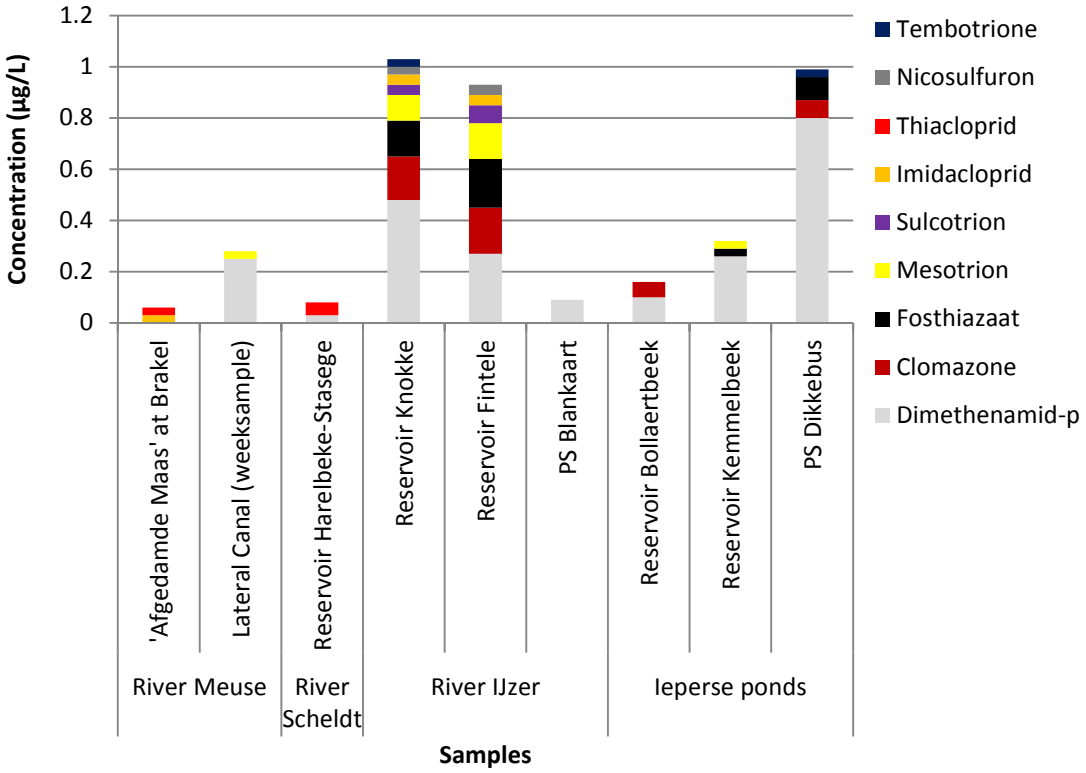


Figure 5-8 Sum concentration per sample in surface water from rivers and reservoirs (june 2016). Data can be found in Attachment VII.

Groundwater

Four compounds were detected in groundwater (see Figure 5-9). The concentrations range from 0.03 µg/L (the herbicide clomazone), to 0.05 µg/L (the herbicide mesotrion and the insecticide cyromazin) up to 0.18 µg/L (the herbicide dimethanamid-p). While three of the four where detected in surface water as well, cyromazin was only present in groundwater.

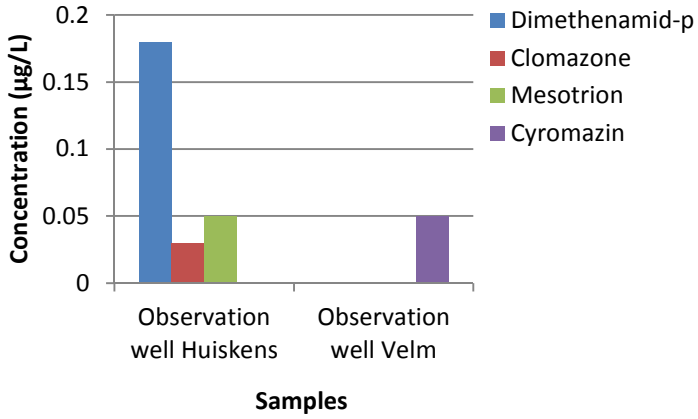


Figure 5-9 Concentration of the pesticides detected in groundwater (june 2016). Data can be found in Attachment VII.

Compared to monitoring campaign in 2007

In the monitoring campaign of 2007, 70 samples were screened for these similar compounds (Emke, 2007). In 2007 only four out of 26 pesticides were detected: nicosulfuron and sulcotrion in both surface- and groundwater and dimethenamid-p and mesotrione in surface water. Three out of four pesticides exceeded the drinking water standard of 0.1 µg/L. Nicosulfuron was detected in three well fields and three surface water intake points above 0.1 µg/L. Sulfuron was detected in one groundwater well field above 0.1 µg/L. Dimethenamid-p was detected at one surface water intake point above 0.1 µg/L. Mesotrione was detected at 6 water intake points in concentrations below 0.1 µg/L.

The detected concentrations of dimethenamid-p and mesotrione in the monitoring campaign of 2016 were above the detected concentrations in the monitoring campaign of 2007. Detected concentrations of nicosulfuron and sulcotrion in 2016 were below the detected concentrations in 2007.

5.4 Results monitoring campaign August 2016

In addition to the sampling campaign in May/June, the locations with surface water were sampled in a second campaign at the end of the summer period when application is highest (august). All 23 locations were sampled, except Boschmolenplas (WML).

5.4.1 Analytical method 2016

The method detected in the samples from august 14 out of 24 pesticides in the samples. The detected pesticides are 9 fungicides, 4 insecticides and 1 herbicide. Spirotetramat which was detected in one sample taken in June was not detected in the samples of August. Acetamiprid, benthiavalicarb-isopropyl and cyflufenamide were detected in the samples of August and were not detected in the samples of June.

Equal to the results of the sampling campaign in June, only two pesticides were detected above 0.1 µg/L in Dutch samples: the insecticide thiamethoxam and the fungicide fluopyram. In august, in the sample taken at the pumping station Brakel (Gemaal Brakel) they exceeded the concentration of 0.1 µg/L, while in june this was in the sample of the intake water. The concentrations of the detected pesticides in Belgian waters were increased compared to the sampling campaign in June. Six pesticides were detected above the drinking water standard of 0.1 µg/L in surface water: mandipropamid, fuxapyroxad, fluopyram, thiamethoxam, acetamiprid and fluxastrobin.

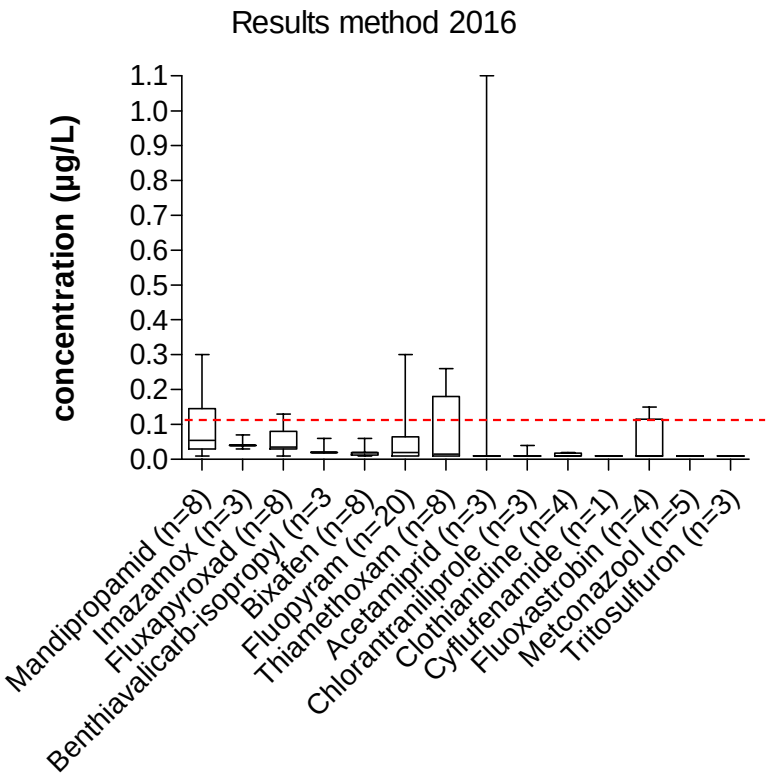


Figure 5-10 Concentration range of the 14 pesticides detected in the samples taken in august 2016 with the analytical method 2016 in august. The box represents the 25th, 50th and 75th percentiles and the edges the min-max boundaries. The detection limit of the compounds is 0.01 µg/L. Data can be found in Attachment VII.

5.4.2 Analytical method 2007

The method detected in the samples from august 10 out of 24 pesticides in the samples. The detected pesticides are: 6 herbicides, 3 insecticides, 1 fungicide and 1 nematicide (pesticide against worms). Fosthiazaat which was detected in one sample of June was not detected in the samples of August. Pymetrozine was detected in one sample of August and was not detected in the samples of June.

Equal to the samples of June, these compounds were often detected in samples from Belgian surface waters (8 samples); only three Dutch samples (taken in the Dutch part of the river Meuse and in the infiltration ponds) contained the studied pesticides. Two pesticides exceeded the drinking water standard of 0.1 µg/L in surface water: dimethenamid-p (similar to June) and tembotrione (not detected in June). The other compounds that exceeded the drinking water standard in June, were not detected (fosthiazaat) or detected below 0.1 µg/L (clomazone and mesotrion).

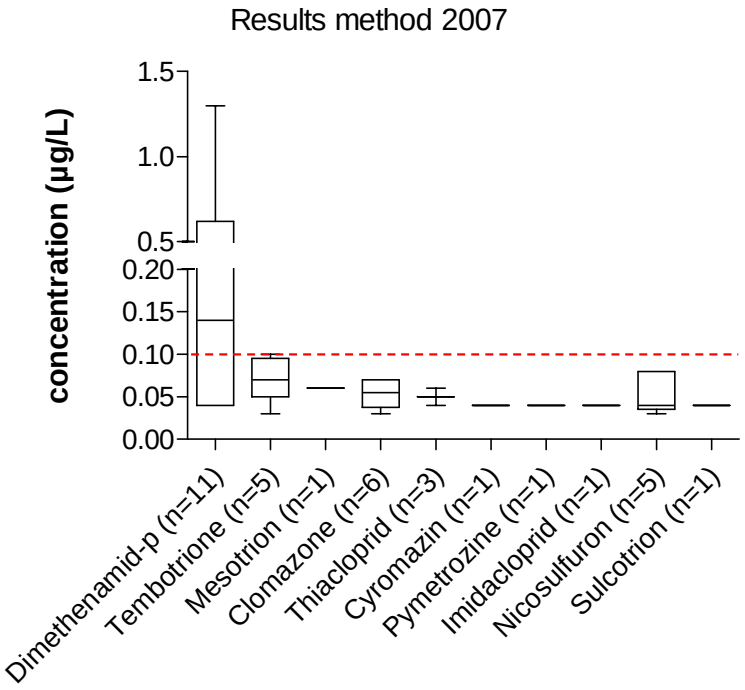


Figure 5-11 Concentration range of the 10 pesticides detected in the samples from august 2016 with the analytical method 2007 in august. The box represents the 25th, 50th and 75th percentiles and the edges the min-max boundaries. The detection limit of the compounds is 0.03 µg/L. Data can be found in Attachment VII.

5.5 Evaluation human health effects

In accordance to the European Drinking Water Directive, as implemented in the Dutch Drinking Water Guideline, the drinking water quality standard for pesticides is 0.1 µg/L (European Commission, 1998; Drinkwaterbesluit, 2011). Specific groups of pesticides may have other quality standards, such as organochlorine pesticides which have a drinking water quality standard of 0.03 µg/L (Drinkwaterbesluit, 2011). Standards for pesticide metabolites depend on their relevance for human toxicity, and differ between 0.1 µg/L and 1 µg/L for non-toxicological relevant metabolites.

The standard of 0.1 µg/L complies with drinking water guidelines, however the value is not risk based. Therefore, this study evaluates the recently authorized pesticides detected in the water samples in concentrations above the drinking water quality standard of 0.1 µg/L. Brief assessments of their relevance for human health effects and tentative target values in drinking water based on human chronic toxicological reference values (Acceptable daily intake) are included below.

Fluopyram [658066-35-4]

Fungicide fluopyram (from the class of pyridinyl ethylbenzamide fungicides) is approved for use in the Netherlands and has been discovered 41 times in water samples, including 6 times at concentrations >0.1 µg/L.

EFSA (2013) has defined the Acceptable Daily Intake of fluopyram to be 0.012 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 1.2 mg /kg body weight per day in a chronic (2-year) repeated exposure study with rats and the application of a safety factor of 100. At higher exposure levels bodyweight decreases, effects on the eyes, and effects in liver, thyroid and kidney were observed. At high exposure concentrations, liver cell adenoma and carcinoma were observed in female rats, for which a non-genotoxic threshold mechanism is considered likely. Exposure to fluopyram did not result in specific effects on fertility, reproduction, development or the nervous system (EFSA 2013).

Based on the Acceptable Daily Intake (0.012 mg/kg body weight per day) a tentative health based target value for of fluopyram in drinking water is estimated to be 0.084 mg/L.

Thiamethoxam [153719-23-4]

Insecticide thiamethoxam (from the class of neonicotinoid insecticides) is approved for use in the Netherlands and has been discovered 17 times in water samples, including 4 times at concentrations >0.1 µg/L.

EFSA (2014) has defined the Acceptable Daily Intake of thiamethoxam to be 0.026 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 2.6 mg /kg body weight per day in a chronic (18-month) repeated exposure study with mice and the application of a safety factor of 100. This study was performed with an unspecified E/Z isomer mixture of thiamethoxam.

Based on the Acceptable Daily Intake (0.026 mg/kg body weight per day) a tentative health based target value for of thiamethoxam in drinking water is estimated to be 0.182 mg/L.

EFSA (2014) proposed that a cumulative effect of thiamethoxam and clothianidin should be considered in view of the similarity in critical effects, i.e. on development.

Mandipropamid [374726-62-2]

Fungicide mandipropamid (from the class of carboxylic acid fungicides) is approved for use in the Netherlands and has been discovered 10 times in water samples, including 3 times at concentrations >0.1 µg/L.

After oral exposure, mandipropamid is readily absorbed resulting in the highest residue levels in liver and kidney. Mandipropamid does not appear to bioaccumulate and is extensively metabolized without cleavage of the molecule. EFSA (2012) has defined the Acceptable Daily Intake of mandipropamid to be 0.15 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 15.2 mg /kg body weight per day in a chronic (2-year) repeated exposure study with rats and the application of a safety factor of 100. There are no indications for genotoxic or carcinogenic potential of mandipropamid in humans. Exposure to mandipropamid did not result in specific effects on fertility, reproduction, development or the nervous system (EFSA 2012). It should be noted that mandipropamid is a racemic mixture of a pair of enantiomers. The relative toxicity of the different isomers is unclear. Moreover, a number of impurities are considered to be of toxicological relevance, and a limit of 0.1 g/kg is considered acceptable (EFSA 2012).

Based on the Acceptable Daily Intake (0.015 mg/kg body weight per day) a tentative health based target value for of mandipropamid in drinking water is estimated to be 1.05 mg/L.

Fluxapyroxad [907204-31-3]

Fungicide fluxapyroxad (from the class of pyrazole-carboxamide fungicides) is approved for use in the Netherlands and has been measured 17 times in water samples, including once at a concentration >0.1 µg/L.

EFSA (2012) has defined the Acceptable Daily Intake of fluxapyroxad to be 0.02 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 2.1 mg /kg body weight per day in a chronic (2-year) repeated exposure study with rats and the application of a safety factor of 100. The main target organs in rats were the liver and the thyroid. At higher exposure concentrations, liver tumours were observed, for which a non-genotoxic threshold mechanism is considered likely. Exposure to fluxapyroxad did not result in specific effects on fertility, reproduction, development or the nervous system (EFSA 2012). Low levels of impurities are present after storage but these are considered to be of minor toxicological concern. A number of environmental metabolites of fluxapyroxad were also tested, showing lower or similar potency in comparison with parent compound fluxapyroxad.

Based on the Acceptable Daily Intake (0.02 mg/kg body weight per day) a tentative health based target value for of fluxapyroxad in drinking water is estimated to be 0.14 mg/L.

Clothianidin [210880-92-5]

Insecticide clothianidine (from the class of neonicotinoid insecticides) is approved for use in the Netherlands and has been measured 14 times in water samples, including once at a concentration >0.1 µg/L.

EFSA (2014) has defined the Acceptable Daily Intake of clothianidin to be 0.097 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 9.7 mg /kg body weight per day in a chronic (2-year) repeated exposure study with rats and the application of a safety factor of 100. This toxicological study was performed with the E-isomer of clothianidin.

Based on the Acceptable Daily Intake (0.097 mg/kg body weight per day) a tentative health based target value for of clothianidine in drinking water is estimated to be 0.679 mg/L.

EFSA (2014) proposed that a cumulative effect of thiamethoxam and clothianidin should be considered in view of the similarity in critical effects, i.e. on development.

Fluoxastrobin [361377-29-9]

Fungicide fluoxastrobin (from the class of dihydro-dioxazine fungicides) is approved for use in the Netherlands and has been measured 10 times in a water samples, including once at a concentration >0.1 µg/L.

Fluoxastrobin is readility absorbed from the gastrointestinal tract and widely distributed within the body. Highest residue levels are detected in liver, kidneys and bladder as well as in the gastrointestinal tract. Fluoxastrobin does not appear to bioaccumulate and is readility excreted, in particular via bile and faeces (in rats). Many different metabolites are identified, but the most prominent are a small number of hydroxylated metabolites. Experimental studies indicate that the toxicity of the different (E/Z) isomers of fluoxastrobin is equivalent (EFSA 2012). EFSA (2007) has defined the Acceptable Daily Intake of fluxapyroxad to be 0.015 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of

1.5 mg /kg body weight per day in a semichronic (1-year) repeated exposure study with dogs and the application of a safety factor of 100. The critical endpoint in this study is the increase of serum alkaline phosphatase. A genotoxic or carcinogenic potential of fluoxastrobin in humans is unlikely. Exposure to fluxapyroxad did not result in specific effects on fertility, reproduction, development or the nervous system (EFSA 2007).

Based on the Acceptable Daily Intake (0.015 mg/kg body weight per day) a tentative health based target value for of fluoxastrobin in drinking water is estimated to be 0.105 mg/L.

Acetamiprid [135410-20-7]

Insecticide acetamiprid (from the class of neonicotinoid insecticides) is approved for use in the Netherlands and has been measured 3 times in water samples, including once at a concentration >0.1 µg/L.

Acetamiprid is rapidly absorbed after oral administration, resulting in highest residue levels in the adrenals, thyroid, liver and kidney, with no accumulation and main excretion via urine. EFSA (2016) has defined the Acceptable Daily Intake of acetamiprid to be 0.025 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 2.5 mg /kg body weight per day in a developmental neurotoxicity study with rats (EFSA PPR Panel, 2013) and the application of a safety factor of 100. Specific genotoxic, endocrine modulating, immunomodulating or neurotoxic potential of acetamiprid in humans is unlikely. Between EU member states disagreement exists on the carcinogenic potential of acetamiprid. No adverse effects on fertility or reproduction were observed. The toxicity of environmental metabolites is considered to be covered by the risk assessment of the parent compound acetamiprid.

Based on the Acceptable Daily Intake (0.025 mg/kg body weight per day) a tentative health based target value for of acetamiprid in drinking water is estimated to be 0.175 mg/L.

Bixafen [581809-46-3]

Fungicide bixafen (from the class of pyrazoles) is approved for use in the Netherlands and has been measured 17 times in water samples (all <0.1 µg/L).

Bixafen is rapidly and extensively absorbed after oral administration, does not bioaccumulate in the body and is rapidly eliminated via bile and urine. Metabolization of bixafen involves demethylation, hydroxylation and conjugations. EFSA (2012) has defined the Acceptable Daily Intake of bixafen to be 0.02 mg/kg body weight per day. This is based on the No-Observed Adverse Effect Level of 2 mg /kg body weight per day in a chronic (2-year) repeated exposure study with rats and the application of a safety factor of 100. Specific genotoxic or carcinogenic potential of bixafen in humans is unlikely. Exposure to bixafen did not result in specific effects on fertility, reproduction or development. Toxicity of the main metabolite (in rat) is considered to be covered by the risk assessment for the parent compound.

Based on the Acceptable Daily Intake (0.02 mg/kg body weight per day) a tentative health based target value for of bixafen in drinking water is estimated to be 0.14 mg/L.

Metconazole [125116-23-6]

Fungicide metconazole (from the class of triazole fungicides) is approved for use in the Netherlands has been measured 11 times in water samples (all <0.1 µg/L).

Metconazole is a mixture of cis/trans isomers, and the toxicity of the cis/trans mixture depends on the relative presence of the cis isomer. Metconazole is well absorbed and distributed widely in the body, resulting in highest residue levels in adrenals, liver and gastrointestinal tract. Metconazole is extensively metabolized and excreted mainly via bile. EFSA (2006) has defined the Acceptable Daily Intake of metconazole to be 0.01 mg/kg body weight per day. This is based on an overall No-Observed Adverse Effect Level of 4 mg /kg (taking into account long term and reproductive effects) and the application of a safety factor of 400. The applied safety factor is higher in comparison to the standard safety factor (100) due to the observed teratogenicity. The main target organs are adrenals, liver and spleen. Genotoxic or carcinogenic potential of metconazole in humans is considered unlikely.

Based on the Acceptable Daily Intake (0.01 mg/kg body weight per day) a tentative health based target value for of metconazole in drinking water is estimated to be 0.07 mg/L.

Resume

The derived tentative health based target values of fluopyram, thiamethoxam, mandipropamid, fluxapyroxad, clothianidine, fluoxastrobin, acetamiprid, bixafen and metconazole were in the range of 0.07-1.05 mg/L, see Table 5-3.

The tentative health based target vaues are several orders of magnitude above the drinking water standard 0.1 µg/L and detected concentration (<dl up to 1.1 µg/L), Therefore, if drinking water contained similar concentrations as detected in ground an surface water, health effects are not expected. However, without sufficient treatment concentrations in drinking water could exceed standards and mixture toxicity was not assessed.

Table 5-3 Summary of tentative health based target values for occurring recently authorized pesticides [1].

Pesticide	Acceptable Daily Intake (ADI)	Tentative target value
1. fluopyram	0.012 mg/kg body weight per day (EFSA 2013)	0.084 mg/L
2. thiamethoxam	0.026 mg/kg body weight per day (EFSA 2014)	0.182 mg/L
3. mandipropamid	0.15 mg/kg body weight per day (EFSA 2012)	1.05 mg/L
4. fluxapyroxad	0.02 mg/kg body weight per day (EFSA 2012)	0.14 mg/L
5. clothianidine	0.097 mg/kg body weight per day (EFSA 2014)	0.679 mg/L
6. fluoxastrobin	0.015 mg/kg body weight per day (EFSA 2007)	0.105 mg/L
7. acetamiprid	0.025 mg/kg body weight per day (EFSA 2016)	0.175 mg/L
8. bixafen	0.02 mg/kg body weight per day (EFSA 2012)	0.14 mg/L
9. metconazole	0.01 mg/kg body weight per day (EFSA 2006)	0.07 mg/L

[1] *This tentative target value is calculated assuming the intake of 2 L drinking water per day by an adult (body weight: 70 kg), with 20% of the ADI allocated to drinking water.*

5.6 Conclusion

15 out of 24 compounds were detected with the analytical method developed in 2016 and 10 out of 11 compounds were detected with the analytical method from 2007.

Most compounds have been detected in surface water; in 23 out of 24 surface water samples one or more pesticides were detected. In only four out of 90 groundwater samples pesticides were detected. Since the compounds recently have been introduced on the market, they

might haven't reached groundwater wells yet. In general, more pesticides were detected in samples from Belgian waters than samples taken from Dutch waters.

In Dutch surface water two pesticides exceeded the drinking water standard of 0.1 µg/L: the insecticide thiamethoxam (max. 0.41 µg/L) and the fungicide fluopyram (max. 0.28 µg/L). The compounds could originate from polder water from the 'Bommelerwaard', entering surface water through one of the pumping stations (gemalen). The compounds were also detected in infiltration ponds and dune filtrate.

In Belgian surface waters six pesticides were detected above the drinking water standard of 0.1 µg/L in water: thiamethoxam, fluopyram, fluxapyroxad, fluxastrobin, mandipropamid and acetamiprid. These samples originate from the river IJzer and the Ieperse ponds.

Only two compounds were detected in groundwater: the insecticides clothianidine and thiamethoxam, both neonicotinoid insecticides, similar to imidacloprid. The insecticide clothianidine was detected above the drinking water standard of 0.1 µg/L in a shallow monitoring well in Brabant.

The detection and concentration of pesticides, especially in surface water, can vary in space and time. It is recommended to repeat analyses seasonally.

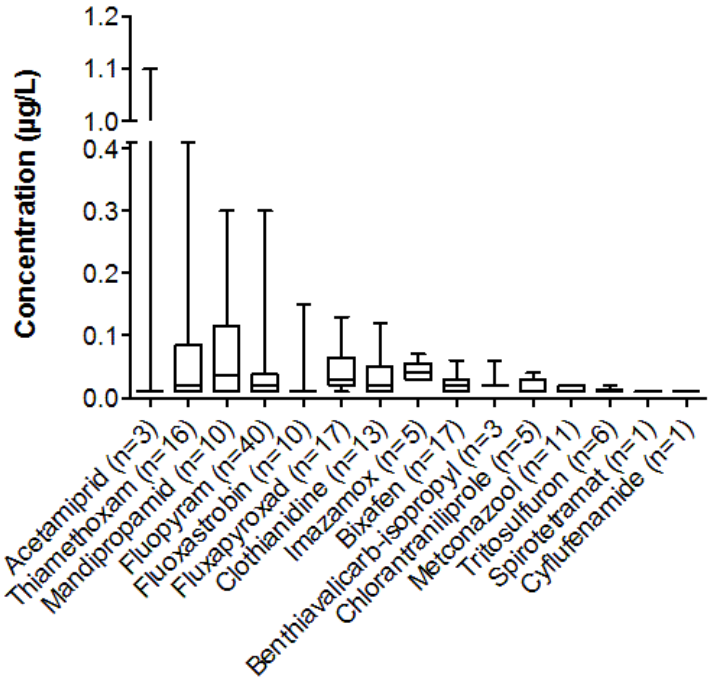


Figure 5-12 Concentration range of the 15 pesticides detected with the analytical method 2016 in both monitoring cmapaigns of june and august. The box represents the 25th, 50th and 75th percentiles and the edges the min-max boundaries. The detection limit of the compounds is 0.01 µg/L. Data can be found in Attachment VII.

Table 5-4 Detected pesticides in both sampling campaigns using the 'analytical method 2016'. Data can be found in Attachment VII.

method 2016 (15/24)	Type	Number of samples with detected pesticides	Number of samples with pesticide>0.1µg/L
Fluopyram	fungicide	41	6
Thiamethoxam	Insecticide	17 (including 2 GW samples)	4
Mandipropamid	Fungicide	10	3
Fluxapyroxad	Fungicide	17	1
Clothianidine	Insecticide	14 (including 1 GW sample)	1 (including 1 GW sample)
Fluoxastrobin	Fungicide	10	1
Acetamiprid	Insecticide	3	1
Bixafen	Fungicide	17	0
Metconazole	Fungicide	11	0
Tritosulfuron	Herbicide	6	0
Imazamox	Herbicide	5	0
Chlorantraniliprole	Insecticide	5	0
Benthiavalicarb-isopropyl	Fungicide	3	0
Spirotetramat	Insecticide	1	0
Cyflufenamide	fungicide	1	0

Table 5-5 Not detected pesticides in both sampling campaigns using the 'analytical method 2016'.

Not detected	Type
Amisulbrom	Growth regulator
Benalaxyl-M	Fungicide
Etoxazool	Acaricide
Fenpyrazamine	Fungicide
Flubendiamide	Insecticide
Flumioxazin	Herbicide
Napropamide	Herbicide
Silthiofam	Fungicide
Triclopyr	Growth regulator

The analysed recently authorized pesticides detected in the water samples in concentrations above the basic guideline value of 0.1 µg/L, were assessed for human health effects using the value for the acceptable daily intake (ADI). The derived tentative target values of fluopyram, thiamethoxam, mandipropamid, fluxapyroxad, clothianidine, fluoxastrobin, acetamiprid, bixafen and metconazole were in the range of 0.07-1.05 mg/L, a factor 1000 above the drinking water standard.

The screening using the analytical method of 2007 detected five pesticides above the drinking water standard of 0.1 µg/L in surface water: dimethenamid-p, fosthiazate, clomazone, mesotrion and tembotrione. The herbicide dimethenamid-p was mainly detected in Belgian surface water, up to 0.67 µg/L. Dimethenamid-p was besides being detected in surface water samples, also detected in two

groundwater samples in concentrations of 0.18 µg/L and 0.25 µg/L. These compounds were not assessed for human health effects. Data can be found in Attachment VII.

Table 5-6 Detected pesticides in both sampling campaigns using the 'analytical method 2007'.

Method 2007 (10/26)	Type	Number of samples with detected pesticides	Number of samples with pesticide>0.1µg/L
Dimethenamid-p	Herbicide	20 (including 1 in GW)	13 (including 1 in GW)
Clomazone	Herbicide	11 (including 1 in GW)	2
Mesotrion	Herbicide	6 (including 1 in GW)	2
Fosthiazaat	Nematicide	4	2
Tembotrione	Herbicide	7	1
Nicosulfuron	Herbicide	7	0
Thiacloprid	Insecticide	5	0
Imidacloprid	Insecticide	4	0
Sulcotrion	Herbicide	3	0
Cyromazin	Insecticide	2 (including 1 in GW)	0

Table 5-7 Not detected pesticides in both sampling campaigns using the 'analytical method 2007'.

Not detected	Type
Amidosulfuron	Herbicide
Azimsulfuron	Herbicide
Ethoxysulfuron	Herbicide
Florasulam	Herbicide
Foramsulfuron	Herbicide
Jodosulfuron-methyl	Herbicide
Mefenpyr-diethyl	Herbicide
Oxasulfuron	Herbicide
Prosulfuron	Herbicide
Pyrimethanil	Fungicide
Rimsulfuron	Herbicide
Sulfosulfuron	Herbicide
Thiodicarb	Molluscoide
Triflusulfuron-methyl	Herbicide

6 Behaviour of pesticides in groundwater; observations and predictions

6.1 Introduction

In this chapter, the data on groundwater collected in 2010-2014 are explored, and a new, tiered modelling approach of pesticide behaviour in groundwater catchment areas is presented and applied. The new modelling approach should fill up the gap between advanced 3D reactive transport codes such as PHT3D (Prommer and Post 2010; often data hungry and difficult to use) and analytical models that are too simpel either hydrologically or hydrogeochemically, or still difficult to apply rapidly for a multitude of pesticides.

National data inventories on pesticides in Dutch groundwater have been frequently made, e.g. by Van Beek ([ed] 1987), Hopman et al. (1990), Van der Linden et al. (2007), and Swartjes et al. (2016).
Modelling pesticide behaviour in the Dutch groundwater compartment started probably in the late 1970s. Peters (1985) presented a comprehensive study on the analytical modelling of pesticide behaviour in groundwater catchment areas and the consequences for groundwater protection zones. This still forms a highly recommended and largely up to date report. Kovar et al (1998) applied a 3D flow model to predict pesticide breakthrough in the raw water of various phreatic, public supply well fields under worst case conditions, i.e. without retardation and without (bio)degradation. Observed pesticide trends showed that conservative behaviour could not be assumed for the pesticides tested. Another approach was recently followed by Vink et al. (2012), applying the flow model Ibrahim and subsequently the non-reactive, partly empirical transport model RESPOND.

6.2 Data collection and elaboration

In this chapter, the data regarding groundwater from monitoring wells (GWO, all with a short well screen of 1-2 m), pumping wells (GWP, all with a longer well screen of 5-50 m), drains (DR; Ouddorp only) and public supply well fields (GWR) are explored. In the current hydrochemical data set as provided by the drinking water utilities, pesticides formed the core, but also data were supplied on main constituents, trace elements, depth and type of sampling points (MW, PW or PWSF), and origin of the water (local groundwater = G, river bank filtrate = RBF, artificially recharged water = AR).

We focus on the detected 155 pesticides and 16 metabolites. Data below LOQ or MDL were set 0, in order to prevent differences between laboratories to offset the results of comparison.
A summary of the available groundwater data is presented in Table 6-1. Important to notice, that the samples in the period 2010-2014 for each observation point have been used without averaging. This means that the patterns shown in this chapter, cannot be attributed to a specific number of observation points because they include a variable number of site specific observations over time.
Land use in the surroundings of the wells and well fields was not taken up in our inventory, so that the relation between land use and pesticide concentration has not been studied here.

Table 6-1. Overview of KWR's 2010-2014 water quality inventory regarding drinking water supply in the Netherlands.

Lab: Water Utility	Origin #	Sampling types ##	Data on well depth	No. samples	No. well fields
Brabant Water	GW	GWO, GWP, GWR, DW	yes	17420	38
Evides	GW, DUN, RIV, RES	GWO, GWP, GWR, DR, SW, SWT, DW	no	28325	6
HWL: Dunea	RIV, DUN	DW, GWR, SW, SWT, POL	no	3229	3
HWL: PWN	DW, GW, DUN	GWR, DW, SW, SWT	no	2162	4
HWL: Waternet	RES, DUN, GW, RIV	DW, GWR, SW, SWT	no	1854	1
Oasen	DW, GW	GWO, GWP, GWR, DW	no	7133	9
Vitens	DW, GW, SW	GWO, GWP, GWR, DW, SW	yes	62324	108
WLN: W.Gro, WMD	GW, RIV	GWO, GWP, SW	yes	6303	19
WML	GW, RES, RBF, AR	GWO, GWP, GWR, SW, DW	no	14743	21
			TOTAL =	*143493*	*209*

AR = Artificial Recharge outside dunes; DUN = dune infiltrate; DW = drinking water; GW = groundwater; RBF = River Bank Filtrate; RES = surface w. reservoir; RIV = river; SW = Surface water

GWO = groundwater observation well; GWP = groundwater pumping well; GWR = groundwater PSWF; POL = surface water polder; SW = Surface water; SWT = treated surface water

In total, the data for observation wells (GWO) and pumping wells (GWP) refer to ~206 PSWFs, which is ~100% of all PSWFs, with most PSWFs from Vitens. The sampling depth of the available GWO and GWP data is lacking in ~21% of the samples. The data for PSWFs refer to ~190 PSWFs, which covers ~91%.

6.3 The global picture

Some statistical parameters for the 20 most frequently detected pesticides in groundwater samples are listed in Table 6-2, with distinction between the 3 monitoring systems (GWO, GWP, GWR) and 3 origins (G, AR, RBF) of water.

It is concluded that BAM, bentazone, desphenyl chloridazone and DMS are the most frequently detected (in 32-53% of all samples), followed by AMPA, dikegulac, isoproturone and mecoprop (in 6-11% of all samples). There is a significant difference between autochthonous groundwater (G) and infiltrated surface waters (AR and RBF). Concentrations and frequency of detection in groundwater are higher than in infiltrated surface waters mainly for BAM, bromacil and mecoprop. On the other hand, concentrations and frequency of detection in infiltrated surface waters are higher than in groundwater, especially for 2-chloroaniline, AMPA, bentazone, carbendazim, chloridazone, desphenyl chloridazone, diethyltoluamide (DEET), dikegulac, dimethomorph, diurone, glyphosate, isoproturone and DMS.
Less retention can be explained by the lack of an unsaturated zone and shorter travel times in AR and RBF systems compared to G systems, all of which contribute to less (bio)degradation.

There are relatively small overall differences between the 3 monitoring systems, with the following average order of decreasing concentrations and detections: GWR > GWP > GWO. There are, however, significant deviations from this order for selected pesticides (Table 6-2).

TABLE 6-2. Overview of statistical parameters of the 20 most detected pesticides and metabolites in groundwater, with distinction based on monitoring system (GWO, GWP, GWR) and origin (G, AR, RBF) of water. sd = standard deviation. DL = Minimum Detection Limit; GWO= observation wells; GWP = pumping wells; GWR = Raw water from public supply well fields; G= groundwater from locally infiltrated rainwater; AR = artificially recharged surface water; RBF = River bank filtrate. Metabolites in red.

Origin / type	Statistics	2-chloro-aniline	AMPA	BAM	benta-zone	bromacil	carben-dazim	chloroto-lurone	chlorida-zone	desfenyl chlorida-zone	methyl-desfenyl chlorida-zone	diethylto-luamide (DEET)	dikegu-lac-sodium	dimetho-morf	dinoterb	diurone	glufosi-nate-ammo-nium	glyfosate	isopro-turone	meco-prop (MCPP)	DMS
Standard drinking water		1	1	1	0.1	0.1	0.1	0.1	0.1	1	1	1	0.1	0.1	0.1	0.1	1	0.1	0.1	0.1	1
GWR	average	0.011	0.007	0.042	0.015	0.003	0.002	0.000	0.001	0.149	0.000	0.001	0.004	0.022	0.000	0.002	0.001	0.001	0.001	0.000	0.049
	sd	0.030	0.026	0.061	0.033	0.024	0.006	0.001	0.008	0.149	0.003	0.003	0.024	0.042	0.004	0.005	0.006	0.009	0.005	0.000	0.072
	max	0.22	0.42	0.60	0.29	0.56	0.04	0.01	0.09	0.99	0.04	0.04	0.37	0.26	0.09	0.04	0.13	0.15	0.03	0.00	0.48
	no. samples	589	855	885	1700	1367	1062	1284	1075	55	695	880	1146	293	1021	726	884	961	947	539	172
	no. samples>DL	82	104	438	448	36	127	8	52	47	10	34	44	74	3	92	14	10	73	0	74
GWP	average	0	0.001	0.065	0.024	0.050	0.000	0.000	0.001	0.197	0.002	0.000	0.016	0.000	0.001	0.002	0.000	0.020	0.001	0.027	0.096
	sd	0	0.012	0.114	0.053	0.390	0.002	0.001	0.006	0.385	0.012	0.004	0.074	0.000	0.006	0.006	0.002	0.162	0.005	0.136	0.086
	max		0.29	1.00	0.60	4.60	0.05	0.02	0.11	2.70	0.18	0.08	0.82	0.00	0.10	0.04	0.05	2.30	0.04	1.10	0.31
	no. samples	1158	1611	1680	2721	1942	1512	1359	1795	260	1471	1467	2104	230	1656	648	1265	1560	1119	1163	32
	no. samples>DL	0	27	767	968	98	23	18	60	112	39	34	190	0	28	53	6	29	43	95	24
GWO	average	0	0.008	0.161	0.027	0.007	0.000	0.000	0.002	1.894	0.081	0.015	0.000488	0.000	0.000	0.106	0.000	0.005	0.001	0.011	
	sd	0	0.043	0.767	0.083	0.162	0.003	0.002	0.013	3.805	0.333	0.257	0.00937	0.000	0.004	1.306	0.003	0.059	0.006	0.042	
	max		0.70	13.00	0.86	5.00	0.04	0.02	0.21	21.00	3.80	6.30	0.18		0.07	23.00	0.04	1.20	0.05	0.44	
	no. samples	163	690	631	694	969	557	522	714	236	534	621	369	220	630	586	428	439	395	497	
	no. samples>DL	0	64	160	195	16	17	9	27	132	83	46	1	0	8	62	6	15	29	61	
G	average	0	0.002	0.087	0.019	0.029	0.000	1.23E-05	0.001	0.979	0.018	0.004	0.009	0.000	0.001	0.047	2.89E-05	0.014	4.54E-05	0.019	0.046
	sd	0	0.021	0.375	0.050	0.296	0.001384	0.000453	0.007	2.732	0.158	0.128	0.056	0.000	0.006	0.869	0.000982	0.132	0.00101	0.110	0.079
	max		0.70	13.00	0.86	5.00	0.05	0.02	0.21	21.00	3.80	6.30	0.82		0.10	23.00	0.04	2.30	0.03	1.10	0.48
	no. samples	1642	2592	2835	4238	3686	2659	2439	3105	511	2479	2507	3206	450	2875	1327	2073	2422	1761	1883	139
	no. samples>DL	0	47	1303	1245	149	4	2	37	254	122	72	138	0	39	58	2	44	4	156	50
AR	average		0.015	0.002	0.003	3.64E-05	0.010	3.39E-05	0.001	0.163		0.000		0.022	0	0.002	0.001	0.001	0.000	0.000	
	sd		0.029	0.005	0.008	0.000603	0.009	0.000582	0.003	0.177		0.000		0.042	0	0.004	0.008	0.011	0.002	0.000	
	max		0.16	0.02	0.05	0.01	0.04	0.01	0.03	0.99				0.26		0.02	0.07	0.15	0.02		
	no. samples		215	111	232	275	193	295	207	24		163		293	113	295	106	215	295	56	
	no. samples>DL		63	18	28	1	123	1	11	24		0		74	0	46	4	3	8	0	
RBF	average	0.024	0.123	0.005	0.043	0	0.003	0.001	0.008	0.108	0.001	0.003	0.029		0.000	0.009	0.001	0.010	0.009	0.000	0.031
	sd	0.040	0.570	0.017	0.075	0	0.028	0.003	0.016	0.076	0.004	0.007	0.077		0.000	0.038	0.008	0.038	0.030	0.000	0.035
	max	0.22	4.40	0.11	0.50		0.50	0.02	0.09	0.20	0.03	0.06	0.68			0.68	0.13	0.26	0.49		0.09
	no. samples	268	288	277	601	285	327	432	308	12	217	266	389		292	339	338	262	406	230	32
	no. samples>DL	82	69	32	337	0	42	32	91	9	10	45	97		0	109	14	24	136	0	15
ALL	% >DL	4	6	42	32	4	5	1	4	53	5	4	7	10	1	11	1	2	6	7	43
G	% >DL	0	2	46	29	4	0	0	1	50	5	3	4	0	1	4	0	2	0	8	36
AR+RBF	% >DL	31	26	13	44	0	32	5	20	92	5	10	25	25	0	24	4	6	21	0	47
GWR	% >DL	14	12	49	26	3	12	1	5	85	1	4	4	25	0	13	2	1	8	0	43
GWP	% >DL	0	2	46	36	5	2	1	3	43	3	2	9	0	2	8	0	2	4	8	75
GWO	% >DL	0	9	25	28	2	3	2	4	56	16	7	0	0	1	11	1	3	7	12	

6.4 Relations with main constituents and depth

Main constituents

There are two main reasons to investigate the relation of pesticides with macroparameters. Firstly, to find potential indicators of pesticides (and metabolites) to optimize the monitoring program. For instance, if the cheap macroparameter reaches a specific concentration range, then the expensive pesticide (group) should be analyzed. And secondly, to shed light on the behaviour of pesticides in the groundwater compartment, especially regarding the potential effects of redox environment, pH, temperature, EC, DOC etc.

A partial, linear Pearson correlation matrix was therefore constructed for the top 20 pesticides incl. metabolites with a selection of macroparameters, among which the main dissolved species, pH, EC and redox level, with distinction between autochthonous groundwater (G), artificially recharged surface water (AR) and river bank filtrate (RBF). The result is presented in Table 6-3. The redox level (1-7; 1 = oxic, 7 = methanogenic) was determined on the basis of the main redox sensitive constituents (→ § 6.4).

Table 6-3. Linear correlation coefficients (R) for the top 20 pesticides and metabolites with macroparameters, with distinction between autochthonous groundwater, artificially recharged surface water and river bank filtrate. R values >0.3 and <-0.3 are very significant thanks to the high number of samples.

Parameter	2-chloro-aniline	AMPA	BAM	benta-zone	bromacil	carben-dazim	chloroto-lurone	chlorida-zone	desfenyl chlorida-zone	methyl-desfenyl chlorida-zone	diethylto-luamide (DEET)	dikegu-lac-sodium	dimetho-morf	dinoterb	diurone	glufosi-nate-ammo-nium	glyfosate	isopro-turone	meco-prop (MCPP)	DMS
Groundwater (G)																				
redox level		-0.01	-0.09	-0.03	-0.04	0.03	0.00	0.03	-0.05	0.00	-0.04	0.00		-0.01	-0.06		-0.03	-0.02	0.04	
EC		0.00	0.01	0.19	0.06	0.00	0.02	0.01	0.00	-0.01	0.28	0.04		0.09	0.00	0.02	0.09	0.03	-0.03	0.52
pH		0.02	-0.18	0.02	0.02	-0.01	0.02	0.01	-0.30	-0.14	0.00	0.08		0.00	-0.02	0.00	0.00	0.03	0.04	0.13
T		0.00	0.06	-0.02	0.03	0.01	0.01	0.03	-0.08	-0.04	0.05	0.07		0.01	0.01	0.00	0.05	-0.02	-0.03	-0.11
O2		-0.04	-0.04	-0.14	-0.01	0.00		-0.02	-0.23	0.07	0.01	-0.03		-0.02	0.18	-0.03	-0.04		-0.03	
CH4		0.00	-0.02	-0.09	-0.01	-0.01	-0.01	-0.03	-0.06	-0.03	0.00	-0.05		0.07	0.24	-0.01	0.16	-0.02	-0.03	-0.39
Cl		-0.01	0.02	0.07	0.03	0.00	0.03	0.03	-0.02	0.00	0.02	0.05		0.06	-0.01	0.00	0.06	0.03	0.01	0.25
SO4		-0.03	0.10	0.20	0.06	0.02	0.01	0.01	0.16	0.02	0.11	-0.02		-0.05	0.00	-0.03	-0.06	0.01	-0.03	0.32
NO3		0.01	0.10	-0.13	0.11	-0.01	-0.01	-0.01	0.63	-0.01	0.02	-0.05		0.05	-0.01	-0.02	-0.02	-0.02	-0.02	0.56
Mn		0.04	0.03	0.27	0.00	-0.01	0.03	0.00	0.07	0.01	0.18	0.01		0.00	-0.02	-0.01	0.01	0.04	-0.02	-0.18
Fe		-0.03	-0.04	0.19	-0.05	-0.02	-0.01	-0.02	0.18	0.16	-0.02	-0.05		0.05	-0.01	-0.01	0.05	0.00	-0.01	-0.26
NH4		0.00	0.01	0.06	0.00	0.00	0.00	0.07	0.27	0.00	0.99	-0.01		0.14	0.04	0.00	0.00	0.01	0.00	0.16
PO4		-0.02	-0.02	0.06	-0.03	-0.02	0.21	0.07		-0.03	0.37	-0.02		-0.01	0.61		-0.03	0.24		
B		0.01	-0.02	0.01	0.12	0.01	0.03	0.05		-0.01	0.33	-0.01		-0.03	0.45		0.01	0.05		
F		-0.04	-0.19	-0.01	-0.13				-0.14	0.00	0.00			0.05		0.10	-0.12		-0.15	
DOC		0.01	-0.02	0.16	-0.05	0.04	-0.01	0.05	0.05	-0.01	0.58	-0.07		0.13	0.08	0.01	0.00	0.01	0.17	
SiO2																				
Cl/Br			0.73																	
nr samples	1642	2592	2835	4238	3686	2659	2439	3105	511	2479	2507	3206	450	2875	1327	2073	2422	1761	1883	139
nr samples>DL	0	47	1303	1245	149	4	2	37	254	122	72	138	0	39	58	2	44	4	156	50
Artificial Recharge (AR)																				
redox level		-0.44	0.37	0.18	0.10	-0.07	0.01	0.13	0.23				-0.30		0.22		-0.09	0.05		
EC		0.44	-0.29	-0.04	-0.02	-0.47	-0.03	-0.02	0.15				-0.15		-0.22	-0.13	0.06	-0.04		
pH		-0.39	-0.24	-0.06	0.04	-0.47	0.02	-0.10	0.00				-0.10		0.06	0.09		0.03		
T		-0.15	-0.03	0.14	-0.04	0.31		0.18	-0.04				-0.11		0.18	0.06		0.01		
O2		0.33	-0.20	-0.21		-0.72	0.02	-0.11	0.02				-0.04		-0.13	-0.06		0.03		
CH4																				
Cl		0.40	-0.36	-0.09	-0.04	-0.44	-0.04	0.02	0.11				-0.23		-0.25	-0.17	0.06	-0.07		
SO4		-0.43	-0.03	0.15	-0.02	0.43	0.06	0.09	-0.07				0.02		0.26	0.17		0.11		
NO3		-0.34	0.15	-0.13	0.04	-0.17	0.04	-0.19	0.07				0.15		-0.03	0.22		0.01		
Mn		0.05	0.03	0.03	0.09	-0.58	-0.03	-0.02	0.16				-0.26		-0.11	-0.08	-0.09	0.00		
Fe		0.02	0.07	-0.08	-0.01	-0.22	-0.02	-0.06	0.10				-0.09		-0.10	-0.02	-0.01	0.00		
NH4		-0.02	0.32	0.17	0.02	-0.47	-0.03	-0.03	0.02				-0.22		-0.12	-0.11	-0.10	-0.01		
PO4		0.53	-0.05	0.31		-0.01	-0.03	-0.02	0.21				-0.13		-0.14			-0.06		
B			-0.19	0.19		0.19	0.07	0.08	0.26				0.16		0.36			0.12		
F																				
DOC		0.00	-0.01	0.17	-0.07	0.41	0.10	0.02	-0.24				0.46		0.06			0.03		
SiO2		0.00	-0.06	-0.05		-0.17		-0.04					-0.29		-0.22			-0.26		
Cl/Br		0.98	-0.06	-0.11		-0.01		-0.09	0.17				0.54		-0.43			-0.18		
nr samples	0	215	111	232	275	193	295	207	24	0	163	0	293	113	295	106	215	295	56	0
nr samples>DL	0	63	18	28	1	123	1	11	24	0	0	0	74	0	46	4	3	8	0	0
River Bank Filtrate (RBF)																				
redox level	0.14	-0.56	-0.16	0.34		-0.06	0.20	0.42	0.23	0.20	0.08	-0.04			-0.07	0.25	-0.66	-0.01		
EC	0.25	0.06	0.15	0.19		-0.02	0.04	0.15		0.00	0.15	0.01			0.23	-0.15	0.03	0.26		0.36
pH	0.07	0.27	0.14	0.09		0.36	0.26	0.16		0.17	0.27	0.02			0.47	-0.15	0.47	0.54		0.29
T	-0.07	-0.02	-0.09	-0.12		-0.08	0.01	-0.03		0.14	-0.09	0.04			0.02		-0.04	-0.05		
O2	-0.14		0.04	-0.11		0.01	-0.07	-0.16		-0.10	-0.11	-0.09			0.31		0.12	0.16		
CH4	0.12	-0.01	-0.08	-0.02		-0.09	-0.03	-0.06			0.02	-0.06			0.02		-0.02	-0.09		
Cl	0.31	0.03	0.11	0.18		0.06	0.09	0.23		0.07	0.20	0.01			0.16	-0.11	0.00	0.30		0.32
SO4	0.21	0.01	0.09	-0.10		0.23	0.11	0.01		0.15	0.00	-0.15			0.13	-0.06	-0.07	0.28		0.32
NO3	-0.23	-0.11	-0.13	-0.07		0.08	-0.23	-0.29			-0.22	-0.36			-0.31	-0.14	-0.03	-0.38		0.11
Mn	0.13	-0.08	0.25	0.23		-0.06	0.04	0.19		-0.08	0.21	0.00			0.34	-0.10	0.02	0.31		-0.28
Fe	-0.03	-0.10	0.05	0.25		-0.21	-0.09	0.09		-0.12	0.07	0.18			0.13	-0.06	0.01	0.11		-0.30
NH4	0.63	-0.01	-0.11	0.31		-0.25	-0.09	0.48		-0.08	0.42	0.02			-0.28	-0.10	0.11	-0.18		
PO4	-0.07	0.33	0.44	0.02		-0.08	-0.07	0.08		-0.07	0.04	-0.09			0.15		0.11	-0.14		
B	0.02	-0.09	-0.15	-0.12		0.01	0.04	0.00		0.10	0.00	-0.17			-0.17		-0.02	-0.03		
F	-0.05	-0.07	0.20	0.02							0.05				0.12	-0.20	-0.02	0.13		0.42
DOC	-0.04	0.01	0.72	0.30		-0.14	-0.09	0.21		-0.05	0.40	-0.04			0.28		-0.02	-0.06		
SiO2	-0.17			-0.35							-0.06				-0.41			-0.68		
Cl/Br		-0.27		0.10												0.19				-0.33
nr samples	268	288	277	601	285	327	432	308	12	217	266	389	0	0	339	338	262	406	0	32
nr samples>DL	82	69	32	337	0	42	32	91	9	10	45	97	0	292	109	14	24	136	230	15

All available observation facilities (GWR< GWP, GWO) included. The total number of samples and number of samples above minimum detection limit (>DL) refer to the pesticides and metabolites. The macroparameters marked in blue are the main redox parameters.

Table 6-4. Number of pesticides displaying a significant linear correlation with main constituents, within the indicated correlation coefficient (R) class (0.3 = 0.3-0.4; 0.9 = 0.9-1.0). Number is sum for all sampling types (GWR, GWP and GWO) and all origins (G, AR, RBF), thus.

Parameter	0.9	0.8	0.7	0.6	0.5	0.4	0.3
redox level				1	1	2	5
EC					1	4	3
pH					1	3	3
T							3
O2			1	0	0	0	2
CH4			1	1	1	2	2
Cl					1	2	5
SO4						3	2
NO3				1	2	1	5
Mn					2	2	4
Fe							1
NH4	2	0	0	1	2	6	3
PO4				2	1	2	5
B			1	1	0	1	3
F			1	0	1	1	3
DOC	1	0	1	1	1	3	2
SiO2				1	0	1	2
Cl/Br	1	0	1	0	2	3	2

The interpretation of the results in Table 6-3 proved, however, very time-consuming due to serious complications. The a priori division into origins G, AR and RBF still is too coarse, because they contain various source waters (e.g. within AR we have Rhine, Meuse and Haringvliet waters), and various age spectra (e.g within RBF we have young and old river bank filtrate, together displaying a significant and nearly complete trend reversal for various parameters).

In Table 6-4, the number of the top 20 pesticides incl. metabolites is shown, displaying a significant linear correlation with main constituents, within each correlation coefficient (R) class. It is concluded from Table 6-4 that NH_4, PO_4, redox level, NO_3, DOC and Cl/Br show the highest number (9-14) of relatively significant correlations (≥0.3), and Fe, temperature, O_2 and SiO_2 the lowest (1-4). All correlation coefficients>0.7 should be further investigated. Correlations >0.3 are already statistically significant thanks to the high number of observations.

Depth

in Figure 6-1 and 6-2, depth plots are shown for 9 of the 20 more frequently occurring pesticides incl. metabolites, with distinction between observation wells (GWO), pumping wells (GWP) and well fields (GWR). The following conclusions are drawn:
First, there are distinct differences in depth reached by the pesticides, from deep to shallow: bentazone (125 m) > dinoterb (100 m) > dikegulac (90 m) > BAM, chloridazone, desphenyl chloridazone (80 m) > mecoprop (70 m) > glyphosate (65 m) > DMS (40 m). These great depths are surprisingly high, and worrying. Van der Linden & Uffink (1999) calculated with a hydrological model, no retardation nor biodegradation, that bentazone could have reached depths of about 30 m below ground surface, in 2000 (since first application in 1973). This could translate into (2012-1973)/(2000-1973) *30 = 43 m in 2010-2014, which is obviously an enormous underestimate (but also a too simple reasoning).

The observed depth differences are likely controlled by the first year of application, retardation factor and (bio)degradation. This aspect deserves further investigation!

Second, for most pesticides and metabolites the greatest depths are observed in pumping wells (GWP), followed by observation wells (GWO) and ultimately by the well field (GWR). The differences between GWP and GWO is even larger, because by taking the top of the well screen, the actual depth of GWPs with their long well screens is even greater compared to GWOs with their short well screen. Obviously, a pumping well pulls down the young polluted groundwater, and an observation well does not. The lower concentrations of well fields compared to individual wells is related to reduction of the pumping rate (contribution) by the more polluted wells.

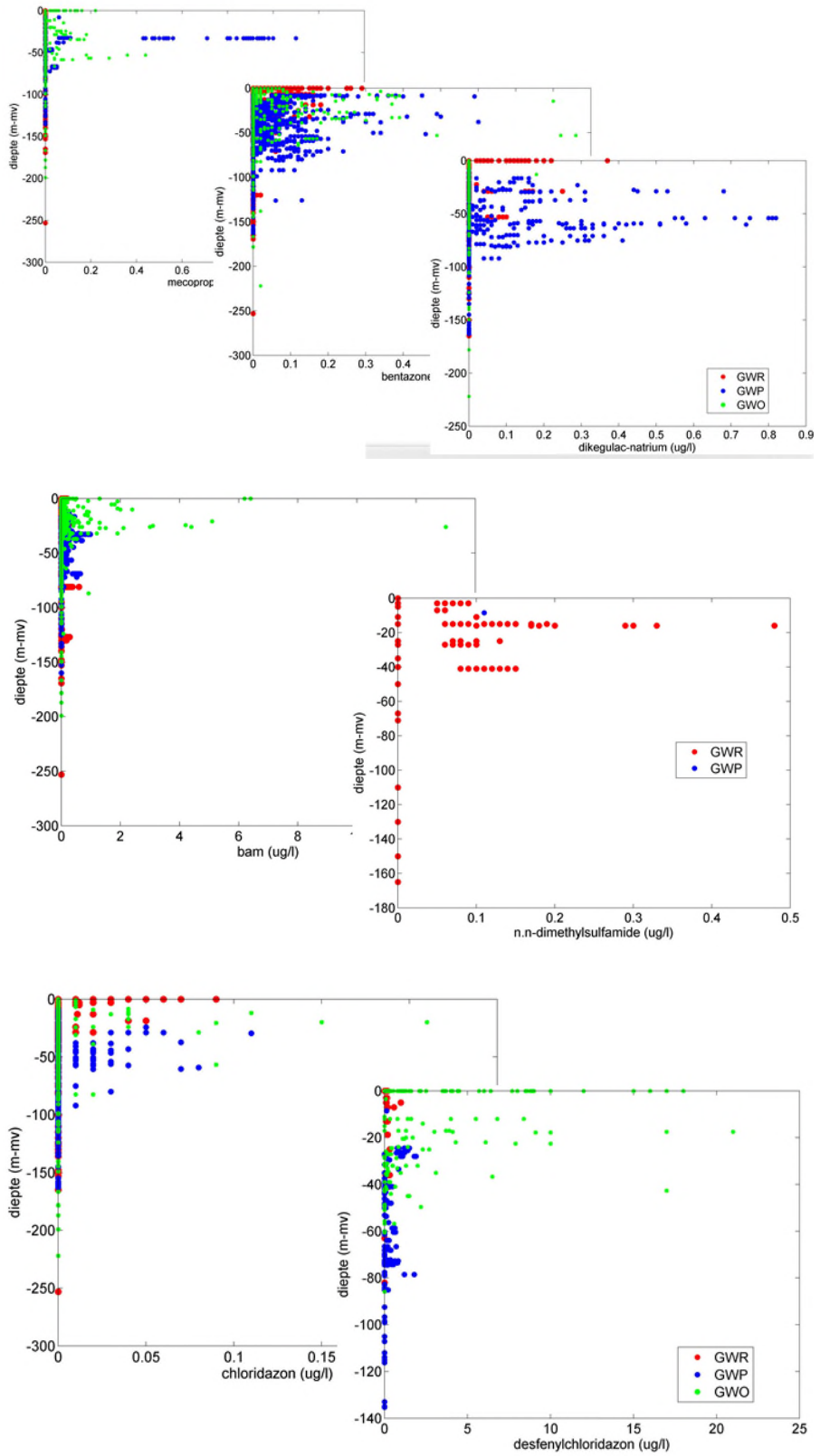


FIGURE 6-1. Relation between pesticide concentration in groundwater 2010-2014 and observation depth, distinguishing between monitoring wells (GWO), pumping wells (GWP) and public supply well fields (GWR). The depth to the top of the well screen is taken, with respect to ground surface (MV).

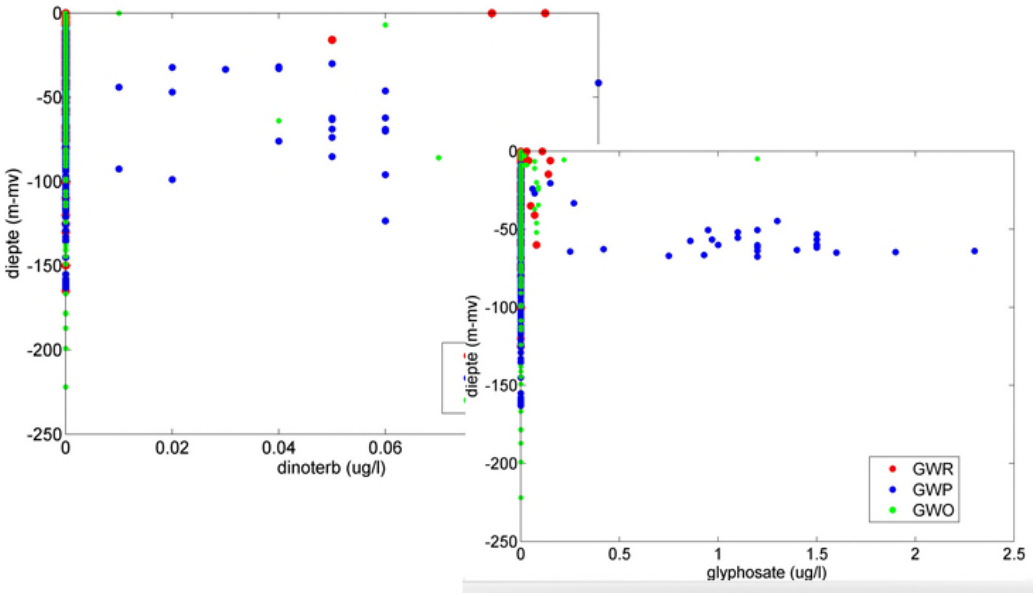


Figure 6-2. Relation between pesticide concentration in groundwater 2010-2014 and observation depth, distinguishing between monitoring wells (GWO), pumping wells (GWP) and public supply well fields (GWR). The depth to the top of the well screen is taken, with respect to ground surface (MV).

Details on the depth distribution of chloridazon with its 2 metabolites desphenyl chloridazon and methyl desphenyl chloridazon, and 1,2-dichloropropane (1,2-DCP; an impurity of 1,3-dichloropropene, which is the active substance in soil fumigant DD, also called Telone II) are shown in Figure 6-3, for selected monitoring wells of well field Gasselte in Drenthe. Van der Moot (2014) mentioned that chloridazon and DD have been applied since ~1965, with the difference that the impurity 1,2-DCP strongly diminished since 1981 and that the use of DD in groundwater protection zones was banned as of 1986.
We conclude the following from the patterns in Figure 6-3. The order of increasing penetration depth is MD-chloridazon < D-chloridazon = NO_3 < 1,2-DCP.

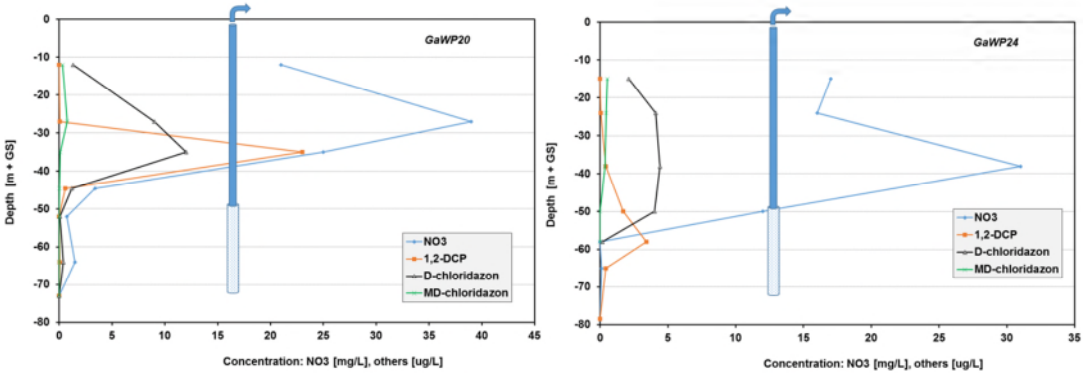


Figure 6-3. Depth plot of the concentration of NO_3, 1,2-dichloropropane, desphenyl-chloridazon and methyl-desphenyl chloridazon in 2 observation wells of well field Gasselte in 2014 (based on data from WMD). The designed well shows the position of the pumping well screens (shallowest top and deepest base). Concentrations in the pumping wells were: NO_3 = 0, 1,2-DCP=0-2.1, D-chloridazone = 0-1.8, and MD-chloridazon = 0-0.12 µg/L.

The retardation coefficient is close to 1 for all 4 compounds, which makes the following interpretation easier. The reconstructed 1,2-DCP input curve (Figure 6-19) is more or less reflected in the groundwater depth profile, however, with a possible reduction where the water becomes anoxic. The peak therefore could indicate, in well GaWP20, peak input year 1973, which translates into 35 m in 2014-1973 = 0.85 m/year. A similar calculation for well GaWP24 seems more hazardous, because denitrification may have suppressed the concentration levels below a depth of 38 m. D-chloridazon follows the NO_3 profile best, indicating that denitrification leads to its (bio)degradation, whereas (bio)degradation is probably negligible as long as NO_3 is hardly reduced. The concentration of MD-chloridazon declines earlier than that of D-chloridazon, which points at slow (bio)degradation in NO_3-stable environment.
The concentrations in the pumping wells (subtitle Figure 6-3) roughly correspond with the depth profiles in the monitoring wells.

6.5 Relation to redox environment

Pesticides may transform or breakdown or (bio)degrade during transport through the soil, either in the unsaturated zone, an aquitard or aquifer. The transformation rate depends on the pesticide structure and on environmental conditions such as temperature, pH, soil organic carbon, soil moisture content and redox environment.
The redox environment refers to the most important microbial terminal electron accepting process (TEAP) taking place, e.g. at sampling depth within the aquifer or upgradient, during the breakdown of organic matter (Stumm and Morgan, 1996). Oxygen, nitrate, hydroxides of manganese(IV) and iron(III), sulfate and carbon dioxide can be used as electron acceptors in order to gain energy for microbial maintenance and growth. Discrete groundwater chemistry zones, indicative of different redox environments, are often found along flow lines in aquifers, going from more oxidized to more reduced conditions (Appelo, 1993; Lovley and Chapelle, 1995).

For each sample in the dataset the redox level was established varying from (sub)oxic to reduced (anoxic) to deeply anoxic (Table6-5). Also mixed redox states were identified, for example in raw water where oxygen-rich and oxygen-depleted water mix. Mixed redox states are indicated by a redox index of e.g. 2.4, 3.5, 5.7 and 6.7 (Table 6-5).

For each of the top 20 detected pesticides (incl. metabolites) we studied the relation between the concentration of the pesticide and the redox level of the water samples, by relating their concentration to the corresponding redox states 1-7. For a maximum of 171 pesticides (incl. metabolites) the available data of concentrations and redox states was sufficient to obtain information on their relation. The results are shown for the top 20 pesticides (incl. metabolites) in Table 6-6, discerning between sampling type (GWR, GWP, GWO) and origin (G, AR, RBF).

Table 6-5 Practical criteria for the determination of the redox index (after Stuyfzand 2012). Concentrations in mg/L.

Level	Unmixed redox environment	Redox cluster	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
1	Oxic	(sub)oxic	$O_2 \geq 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2	O2-reducing		$1 \leq O_2 < 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
3	NO_3-reducing		< 1	≥ 1	< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
4	Mn-reducing	anoxic	< 1	< 1	≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
5	Iron reducing		< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.2
6	Sulfate reducing	deeply anoxic	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	0.2 - 0.5
7	Methanogenic		< 1	< 1			< 0.2 $(SO4)_O$		≥ 0.5

Level	Mixed redox environment	Mix of levels	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
2.4	O2 – Mn	2 + 4	≥ 1		≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2.5	O2 – Fe	2 + 5	≥ 1			≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2.6	O2 – H_2S	2 + 6	≥ 1				0.2-0.8 $(SO4)_O$	yes	< 0.1
2.7	O_2 – CH_4	2 + 7	≥ 1				< 0.2 $(SO4)_O$		> 0.1
3.5	NO_3 – Fe	3 + 5	< 1	≥ 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	<0.1
3.6	NO_3 – H_2S	3 + 6	< 1	≥ 1			0.2-0.8 $(SO4)_O$	yes	< 0.1
3.7	NO_3 – CH_4	3 + 7	< 1	≥ 1			< 0.2 $(SO4)_O$		<0.1
3.7	NO_3 – CH_4	3 + 7	< 1	≥ 1					> 0.1
5.6	Fe – H_2S	5 + 6	< 1	< 1		≥ 0.1	0.2-0.8 $(SO4)_O$	yes	< 0.1
5.6	Fe – H_2S	5 + 6	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	yes	0.2 - 0.5
5.7	Fe – CH_4	5 + 7	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$		≥ 0.5
6.7	H_2S – CH_4	6 + 7	< 1	< 1			< 0.2 $(SO4)_O$	yes	< 0.5
6.7	H_2S – CH_4	6 + 7	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	≥ 0.5

yes/no = yes/no clear H_2S-smell in field, or H2S ≥ / < 0.1 mg/L. If data unavailable not a criterion

$(O_2)_{SAT}$: see Eq.10.1. $(SO_4)_0$ = original SO4 concentration [mg/L], see text

Table 6-6. Linear correlation coefficient (R) between the top 20 pesticides incl. metabolites on the one hand, and 6 macroparameters 5 of which are related to the redox environment,on the other hand. The 6 rows refer to groundwater samples subdivided into groups according to sampling type (GWR, GWP, GWO) and origin (G, AR, RBF). The final row gives the conclusion on the significance of the correlation as based on criteria given in the main text. R values >0.3 and <-0.3 are very significant thanks to the high number of samples.

sample type / origin	2-chloro-aniline	AMPA	BAM	benta-zone	bromacil	carben-dazim	chlorotolu-rone	chlorida-zone	desfenyl chlorida-zone	methyl-desfenyl chlorida-zone	diethylto-luamide (DEET)	dikegu-lac-sodium	dimetho-morf	dinoterb	diurone	glufosi-nate-ammo-nium	glyfosate	isopro-turone	meco-prop (MCPP)	DMS
Redox level																				
GWR	0.32	-0.29	-0.31	0.18	-0.02	-0.06	0.09	0.19	0.17	0.07	0.21	0.00	-0.30	-0.02	-0.08	0.14	-0.08	0.12		
GWP		-0.05	-0.33	-0.15	-0.09	-0.10	-0.06	-0.02	-0.07	0.05	-0.07	-0.05		-0.04	-0.25		-0.04	-0.12	-0.08	
GWO		-0.06	-0.08	0.05	-0.02	0.06	-0.05	0.08	-0.07	-0.03	-0.06	-0.03		0.01	-0.07		-0.06	-0.21	0.11	
G		-0.01	-0.09	-0.03	-0.04	0.03	0.00	0.03	-0.05	0.00	-0.04	0.00		-0.01	-0.06		-0.03	-0.02	0.04	
AR		-0.44	0.37	0.18	0.10	-0.07	0.01	0.13	0.23	0.00		0.00	-0.30		0.22		-0.09	0.05		
RBF	0.14	-0.56	-0.16	0.34	0.00	-0.06	0.20	0.42	0.23	0.20	0.08	-0.04			-0.07	0.25	-0.66	-0.01		
Redox #	anoxic	(sub)oxic		?	(sub)oxic	?	?	anoxic	?	?	?	?	?	?	(sub)oxic	?	(sub)oxic	?	?	(sub)oxic
pH																				
GWR	0.03	-0.03	-0.22	-0.06	-0.03	0.22	0.03	0.02	0.03	-0.01	0.03	0.01	-0.10	0.00	0.12	-0.07	-0.01	0.02		0.26
GWP		0.01	0.00	0.04	0.04	0.04	0.04	0.04	-0.36	-0.07	0.05	0.09		-0.01	0.20	0.03	0.00	0.09	0.04	0.19
GWO		0.06	-0.23	0.09	0.01	0.13	0.11	0.08	-0.20	-0.18	0.01	0.02		0.01	-0.01		0.03	0.19	0.11	
G		0.02	-0.18	0.02	0.02	-0.01	0.02	0.01	-0.30	-0.14	0.00	0.08		0.00	-0.02	0.00	0.00	0.03	0.04	0.13
AR		-0.39	-0.24	-0.06	0.04	-0.47	0.02	-0.10	0.00				-0.10		0.06	0.09		0.03		
RBF	0.07	0.27	0.14	0.09		0.36	0.26	0.16		0.17	0.27	0.02			0.47	-0.15	0.47	0.54		0.29
pH	?	?	?	?	?	?	pos	pos	?	neg	pos	?	?	?	?	?	?	pos	?	pos
NO3																				
GWR	-0.12	-0.14	0.05	-0.07	0.02	-0.23	-0.02	-0.03	0.01	0.11	-0.02	0.06	0.15	0.07	-0.08	-0.06	0.03	-0.05		0.38
GWP		-0.02	0.20	-0.18	0.22	-0.04	-0.02	-0.02	-0.13	-0.07	0.04	-0.08		0.04	-0.08	-0.06	-0.05	-0.04	-0.03	0.41
GWO		-0.06	0.13	-0.07	0.02	-0.08	-0.06	-0.04	0.55	-0.12	-0.05	-0.07		0.12	0.01		0.10	-0.07	-0.06	
G		0.01	0.10	-0.13	0.11	-0.01	-0.01	-0.01	0.63	-0.01	0.02	-0.05		0.05	-0.01	-0.02	-0.02	-0.02	-0.02	0.56
AR		-0.34	0.15	-0.13	0.04	-0.17	0.04	-0.19	0.07				0.15		-0.03	0.22	0.00	0.01		
RBF	-0.23	-0.11	-0.13	-0.07	0.00	0.08	-0.23	-0.29			-0.22	-0.36			-0.31	-0.14	-0.03	-0.38		0.11
NO3	?	neg	pos	neg	pos	neg	neg	neg	pos	?	?	neg	?	?	neg	?	?	neg	?	pos
Fe																				
GWR	0.11	0.01	0.05	0.27	-0.03	-0.20	-0.02	0.03	-0.11	-0.02	0.02	0.09	-0.09	-0.02	-0.10	-0.02	0.01	0.05		-0.21
GWP		-0.04	-0.05	0.23	-0.06	-0.04	-0.03	0.01	0.40	0.26	-0.02	-0.01		0.08	-0.16	-0.01	0.07	-0.04	-0.03	-0.30
GWO		-0.08	-0.06	0.01	-0.05	-0.13	-0.09	-0.05	0.11	0.08	-0.04	0.05		0.03	-0.01		-0.06	-0.13	0.04	
G		-0.03	-0.04	0.19	-0.05	-0.02	-0.01	-0.02	0.18	0.16	-0.02	-0.05		0.05	-0.01	-0.01	0.05	0.00	-0.01	-0.26
AR		0.02	0.07	-0.08	-0.01	-0.22	-0.02	-0.06	0.10				-0.09		-0.10	-0.02	-0.01	0.00		
RBF	-0.03	-0.10	0.05	0.25		-0.21	-0.09	0.09		-0.12	0.07	0.18			0.13	-0.06	0.01	0.11		-0.30
Fe	?	?	?	pos	?	neg	?	?	pos	?	?	?	?	?	neg	?	?	?	?	neg
NH4																				
GWR	0.56	-0.07	-0.11	0.44	-0.02	-0.20	0.11	0.50	-0.15	0.01	0.55	0.03	-0.22	0.01	0.00	-0.06	0.01	0.24		0.00
GWP		0.09	0.16	0.10	-0.04	-0.04	-0.05	0.02	-0.26	-0.09	0.02	-0.02		-0.01	0.14	-0.04	0.07	-0.07	-0.03	0.01
GWO		-0.01	0.00	0.07	0.00	-0.01	-0.02	0.12	0.30	0.00	1.00	-0.01		0.48	0.03		-0.01	-0.15	0.01	
G		0.00	0.01	0.06	0.00	0.00	0.00	0.07	0.27	0.00	0.99	-0.01		0.14	0.04	0.00	0.00	0.01	0.00	0.16
AR		-0.02	0.32	0.17	0.02	-0.47	-0.03	-0.03	0.02				-0.22		-0.12	-0.11	-0.10	-0.01		
RBF	0.63	-0.01	-0.11	0.31		-0.25	-0.09	0.48		-0.08	0.42	0.02			-0.28	-0.10	0.11	-0.18		
NH4	?	?	?	pos	?	neg	?	pos	?	?	pos	?	?	?	?	?	?	?	?	?
CH4																				
GWR	-0.12	-0.18	-0.07	0.00				-0.05	-0.70		0.17				-0.02	-0.07	0.00	-0.01		-0.58
GWP		0.04	0.04	-0.11	-0.02	-0.02	-0.03	-0.05	-0.34	-0.02	-0.04	-0.08		0.09	0.40	-0.03	0.23	-0.05	-0.03	-0.41
GWO		-0.02	-0.06	-0.05	-0.02	-0.04	0.00	-0.04	-0.60	-0.03	0.09	-0.01		0.05	0.06	0.00	-0.02	-0.05	-0.11	
G		0.00	-0.02	-0.09	-0.01	-0.01	-0.01	-0.03	-0.06	-0.03	0.00	-0.05		0.07	0.24	-0.01	0.16	-0.02	-0.03	-0.39
AR																				
RBF	0.12	-0.01	-0.08	-0.02		-0.09	-0.03	-0.06			0.02	-0.06			0.02		-0.02	-0.09		
CH4	?	?	?	?	?	?	?	?	neg	?	?	?	?	?	?	?	?	?	?	neg

Table 6-6 not only shows the relation with the redox level, but also with pH, NO_3, Fe, NH_4 and CH_4, the latter 4 of which determine the redox level (together with O_2 and SO_4). The correlation of pesticide concentration with each of the 6 macroparameters was considered significant when the following criteria were met: (a) data available for ≥4 of 6 data rows (GWR, GWP, GWO, G, AR and RBF), (b) n-1 data rows are either positive or negative, and (c) at least one data row shows R ≥0.15 or R ≤-0.15.

The main problem in interpreting the relation between redox index (1-7) and pesticide levels, in a huge mixed population of data, is that the older, deeper groundwater samples are often (deeply) anoxic but too old to possibly contain pesticides! The same problem pertains to the relation between pH and pesticide concentrations in a huge mixed population of data. Nevertheless, it seems likely that AMPA, BAM, bromacil, diurone, glyphosate and DMS survive better in a (sub)oxic environment, and 2-chloroaniline and chloridazone in an anoxic environment.

6.6 Artificially recharged surface waters (AR)

AR systems

Artificial recharge was taking place in the period 2010-2014 on 12 sites (Figure 6-4). Basin recharge is strongly dominating over deep well recharge (ATR) systems, which all together (sites 1 and 6 only), produce 8 Mm^3/a. Important characteristics of AR systems are: multibarrier present, selective intake, dual intake possibility (e.g. either Rhine or Meuse River, Lake IJssel or Rhine River), pretreatment near intake, detention in recharge basins (on average 2-5 days), infiltration in sandy or gravelly (site 12 only) areas, no unsaturated zone (site 13 excluded), aquifer passage for a modal distance and travel time of 40-110 m and 30-100 days, and admixing of ambient groundwater in the recovery system (on average 5-15%). Further system details are given by Stuyfzand (1986, 1993) and Stuyfzand & Lüers (2000).

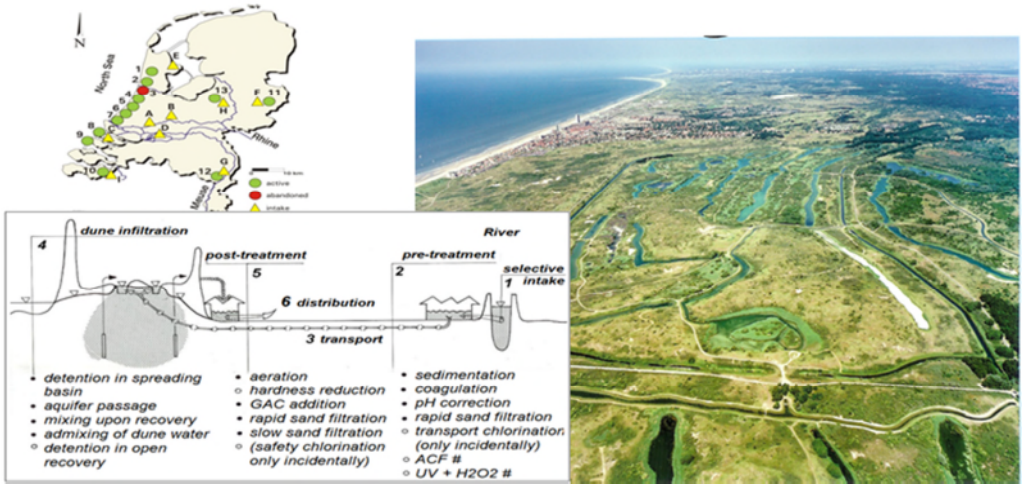


FIGURE 6-4. Basin artificial recharge in the Netherlands since 1940, in the period 2010-2014 producing on 12 sites ~200 Mm^3/a (~16% of national drinking water supply). Figure s from Stuyfzand (in prep), photo showing the Amsterdam dune catchment area from MAR calender.

Data on system scale

We conclude from Table 6-2, that concentrations and frequency of detection in infiltrated surface waters are generally higher than in groundwater, especially for 2-chloroaniline, AMPA, bentazone, carbendazim, chloridazone, desphenyl chloridazone, diethyltoluamide (DEET), dikegulac, dimethomorph, diurone, glyphosate, isoproturone and DMS. Compared to RBF, AR systems show on average a lower detection frequency (AMPA, carbendazim, desfenyl chloridazone, dimethomorph and gluphosinate ammonium excluded), mostly with a lower concentration while all maxima remain below the drinking water standards. The better quality of AR systems compared to RBF systems is mainly thanks to the selective intake, pretreatment, detention time in basins and more aerobic aquifer passage.

TABLE 6-7. Overview of statistical parameters of the 20 most detected pesticides (incl. metabolites indicated in red) in artificially recharged surface water, with distinction based on provenance of infiltration water: Meuse River downgradient (input Meijendel), Rhine River (Input Leiduin), Rhine/Meuse estuary (Haringvliet intake), Meuse River upstream (Lateral Canal).

Origin / type	Statistics	2-chloro-aniline	AMPA	BAM	benta-zone	bromacil	carbend azim	chloroto-lurone	chlorida zone	desfenyl chlorida zone	methyl-desfenyl chlorida zone	diethylto-luamide (DEET)	dikegu-lac-sodium	dimetho morf	dinoterb	diurone	glufosi-nate-ammo-nium	glyfosate	isoprotu rone	meco-prop (MCPP)	DMS
Input Meijen-del	Average		0.661	0.017	0.011	0.000	0.023	0.000	0.003	*0.181*		0.002		0.094	0.000	0.011		0.000	0.007		
	sd		0.254	0.007	0.016	0.000	0.015	0.000	0.010	*0.047*		0.007		0.540	0.004	0.016		0.000	0.010		
	Max		1.10	0.03	0.08	0.00	0.08	0.00	0.05	*0.35*		0.03		4.00	0.03	0.11		0.00	0.04		
	no. samples		19	19	62	66	59	64	65	*17*		64		64	62	64		19	64		
	no samples>DL		19	18	25	0	56	0	6	*17*		5		7	1	32		0	25		
Schev raw	Average		0.002	0.006	0.002	0.000	0.005	0.000	0.001	0.221		0.000		0.010	0.000	0.002		0.000	0.000		
	sd		0.015	0.007	0.006	0.001	0.007	0.000	0.003	0.311		0.000		0.029	0.000	0.004		0.000	0.002		
	Max		0.12	0.02	0.03	0.01	0.02	0.00	0.01	0.99		0.00		0.18	0.00	0.01		0.00	0.02		
	no. samples		65	26	64	66	67	67	74	8		47		97	19	67		65	67		
	no samples>DL		1	11	6	1	27	0	5	8		0		12	0	16		0	2		
Katwijk raw	Average		0.000	0.001	0.002	0.000	0.015	0.000	0.000	0.136		0.000		0.014	0.000	0.003		0.000	0.000		
	sd		0.000	0.004	0.008	0.000	0.008	0.000	0.002	0.028		0.000		0.029	0.000	0.005		0.000	0.000		
	Max		0.00	0.01	0.03	0.00	0.04	0.00	0.01	0.19		0.00		0.10	0.00	0.02		0.00	0.00		
	no. samples		20	8	56	61	52	56	38	8		21		97	18	56		20	56		
	no samples>DL		0	1	5	0	46	0	1	8		0		19	0	12		0	0		
Monster raw	Average		0.000	0.003	0.007	0.000	0.016	0.000	0.001	0.133		0.000		0.041	0.000	0.004		0.000	0.001		
	sd		0.000	0.005	0.011	0.000	0.006	0.001	0.002	0.017		0.000		0.056	0.000	0.007		0.000	0.003		
	Max		0.00	0.01	0.03	0.00	0.02	0.01	0.01	0.15		0.00		0.26	0.00	0.02		0.00	0.02		
	no. samples		20	8	56	63	52	55	40	8		23		99	19	55		20	55		
	no samples>DL		0	2	16	0	49	1	2	8		0		43	0	18		0	4		
Leiduin input	Average		0.399		0.000	0.000	0.013	0.004	0.000					0.000	0.000	0.002		0.007	0.013		
	sd		0.141		0.004	0.000	0.010	0.011	0.000					0.000	0.000	0.005		0.020	0.023		
	Max		0.71		0.03	0.00	0.03	0.05	0.00					0.00	0.00	0.02		0.06	0.10		
	no. samples		9		64	64	58	64	26					24	63	64		9	64		
	no samples>DL		9		1	0	41	9	0					0	0	10		1	23		
Leiduin output	Average	0.000		0.001		0.000	0.001	0.000	0.000						0.000	0.000			0.001		
	sd	0.000		0.003		0.000	0.006	0.000	0.000						0.000	0.000			0.003		
	Max	0.00		0.02		0.00	0.03	0.00	0.00						0.00	0.00			0.01		
	no. samples	20		65		16	22	21	9						15	21			21		
	no samples>DL	0		4		0	1	0	0						0	0			2		
Haring-vliet intake	Average		0.436	0.003	0.000	0.000	0.001		0.000	0.132	0.004	0.004	0.000		0.000	0.000	0.002	0.026	0.003	0.000	0.003
	sd		0.197	0.009	0.000	0.000	0.006		0.000	0.039	0.014	0.012	0.000		0.000	0.000	0.007	0.025	0.018	0.000	0.013
	Max		0.85	0.04	0.00	0.00	0.05		0.00	0.23	0.05	0.06	0		0.00	0.00	0.03	0.10	0.13	0.00	0.05
	no. samples		65	53	64	63	62		12	11	12	59	18		27	63	63	65	63	54	16
	no samples>DL		65	5	0	0	1		0	11	1	8	0		0	0	5	42	2	0	1
Ouddorp raw	Average		0.050		0.000	0.000									0.000	0.000	0.000	0.000	0.000	0.000	
	sd		0.037		0.000	0.000									0.000	0.000	0.000	0.000	0.000	0.000	
	Max		0.16		0.00	0.00									0.00	0.00	0	0.00	0.00	0.00	
	no. samples		38		19	13									19	19	37	38	19	19	
	no samples>DL		33		0	0									0	0	0	0	0	0	
Input (Lateral canal)	Average		1.194	0.007	0.000	0.000	0.001	0.000	0.006	0.243	0.000	0.023	0.000		0.000	0.002	0.000	0.097	0.005	0.000	0.000
	sd		0.889	0.013	0.000	0.000	0.009	0.000	0.019	0.097	0.000	0.064	0.000		0.000	0.011	0.004	0.076	0.018	0.000	0.000
	Max		4.20	0.04	0.00	0.00	0.06	0.00	0.08	0.67	0	0.44	0		0.00	0.08	0.04	0.41	0.07	0.00	0.00
	no. samples		104	46	48	52	48	52	34	31	31	52	42		51	52	99	104	52	47	23
	no samples>DL		104	10	0	0	1	0	3	31	0	19	0		0	1	1	90	4	0	0
Heel raw Galgen-berg	Average		0.020	0.016	0.000	0.000	0.000	0.000	0.000	0.180	0.000	0.000	0.000		0.000	0.000	0.001	0.003	0.000	0.000	0.098
	sd		0.025	0.018	0.000	0.000	0.000	0.000	0.000	0.028	0.000	0.000	0.000		0.000	0.000	0.004	0.015	0.000	0.000	0.013
	Max		0.07	0.06	0.00	0.00	0.00	0.00	0.00	0.20	0	0.00	0		0.00	0.00	0.02	0.07	0.00	0.00	0.12
	no. samples		22	19	28	20	12	22	11	2	2	20	12		14	22	22	22	22	21	12
	no samples>DL		10	10	0	0	0	0	0	2	0	0	0		0	0	1	1	0	0	12
Heel raw Langven + Reut	Average		0.013	0.013	0.000	0.000	0.000	0.000	0.000	0.235	0.000	0.000	0.000		0.000	0.001	0.000	0.000	0.000	0.000	0.130
	sd		0.025	0.018	0.000	0.000	0.000	0.000	0.000	0.049	0.000	0.000	0.000		0.000	0.006	0.000	0.000	0.000	0.000	0.011
	Max		0.08	0.06	0.00	0.00	0.00	0.00	0.00	0.27	0	0.00	0		0.00	0.03	0	0.00	0.00	0.00	0.15
	no. samples		22	20	28	20	12	22	11	2	2	20	12		14	22	21	22	22	21	12
	no samples>DL		6	8	0	0	0	0	0	2	0	0	0		0	1	0	0	0	0	12
Rhine	% >DL (in+out)		96	8	1	0	30	11	0	100	8	14	0	0	0	6	5	38	16	0	6
Meuse	% >DL (in+out)		51	41	15	0	59	0	6	100	0	10	0	23	1	24	1	33	10	0	51

Rhine River water (AR input and output) shows on average more frequent detections than Meuse River water (AR input and output) for AMPA, chlorotolurone, methyl desfenyl chloridazone, DEET, glufosinate ammonium and isoproturone, but less frequent detections for BAM, bentazone, carbendazim, chloridazone, dimethomorph (? no data Rhine), diurone and DMS (Table 6-7).

System performance

The performance of individual AR systems can be deduced from the data in Table 6-7, where the mean concentrations of 20 pesticides and metabolites have been listed for the input (pretreated surface water before entering the basins) and output (raw recovered water incl. admixed ambient groundwater). The AR systems included are: the 3 dune systems Katwijk, Scheveningen and Monster of Dunea (input from Meuse River), the dune system Leiduin of Waternet (input from Lek River), the dune system Ouddorp of Evides (input from Haringvliet = 70% Rhine + 30% Meuse River), and gravel pit lake Heel of WML (input from Meuse River via Lateral Canal).

We can calculate the system's performance (%□C) as follows (Stuyfzand & Lüers 2000):

$$\%\Delta C = 100\frac{C_{IN}-\frac{C_{OUT}}{(1-f_D)}}{C_{IN}} \quad (6\text{-}1)$$

$$C_{IN} = aC_{IN,y} + bC_{IN,y-1} + cC_{IN,y-2} + \cdots \ldots + nC_{IN,y-n} \quad (6\text{-}2)$$

where: C_{IN}, $C_{IN,y-n}$, C_{OUT} = mean concentration in input, input n years prior to period considered, and output, respectively [µg/L]; f_D = fraction of ambient groundwater with supposed concentration = 0 [-]; a-n = fraction contributing to input concentration 0 to n years before period considered [-].

As we are averaging over a 5 years period, we can approximate %□C by taking a = 1 and b=c=n=0. It should be realized that %□C holds for the total of all subsystem performances, each of which normally leading to a concentration decline:

$$\%\Delta C = \%\Delta C_{BAS} + \alpha\%\Delta C_{MUD} + \beta\%\Delta C_{AQU,S} + \gamma\%\Delta C_{AQU,A} + (1-\beta-\gamma)\%\Delta C_{AQU,SA} + \%\Delta C_{MIX} \quad (6\text{-}3)$$

where: a = fraction passing the mud layer; always <1 [-]; ß = fraction only residing in (sub)oxic aquifer [-]; □ = fraction only residing in anoxic aquifer [-]; $_{BAS}$ = residence in recharge basin (atmospheric inputs, evaporation losses, photolysis, biodegradation, uptake); $_{MUD}$ = passage of the water/soil interface (filtration, sorption, (bio)degradation); $_{AQU,S}$, $_{AQU,A}$, $_{AQU,SA}$ = passage of (sub)oxic aquifer only, anoxic aquifer only, first (sub)oxic then anoxic aquifer (sorption, (bio)degradation); and $_{MIX}$ = admixing of ambient groundwater.

The field data also allow for an estimate of the overall average half-life (in the system as a whole), being:

$$T½ = \frac{-0.3\ t\ R_{OMP}}{log\frac{C_{OUT}}{C_{IN}(1-f_D)}} \quad (6\text{-}4)$$

where: t = modal travel time from input to output [d]; R_{OMP} = retardation factor of organic micropollutant, see Table 6-15 [-].

Results of calculation of %□C and T½ for the top 14 pesticides (incl. metabolites), in the AR systems of Leiduin, Katwijk, Scheveningen, Monster, Ouddorp and Heel (with 2 subsystems) are shown in Table 6-8. There were no data for 2-chloroaniline, bromacil, methyl desfenylchloridazone, dikegulac-sodium, mecoprop and DMS. The percentage admixed ambient groundwater (%mix) and modal travel time in the whole system (t50) are based on various sources.

TABLE 6-8. Overview of the calculated % ΔC and T½ for the top 14 pesticides (incl. metabolites indicated in red), in the AR systems of Leiduin, Katwijk, Scheveningen, Monster, Ouddorp and Heel (2 subsystems). Based on data in Table 6-7, and equations 6-1 and 6-4 respectively.
No data for 2-chloroaniline, bromacil, methyl desfenylchloridazone, dikegulac-sodium, mecoprop and DMS. The percentage admixed ambient groundwater (%mix) and modal travel time in the whole system (t50) are based on various sources. In = 0 means input = 0 (not detected), no calculations possible. 9999.0 = infinite half-life deduced from no concentration reduction, however, mostly not reliable due to extremely low concentrations.

Hydrol. para-meter	AR-site	AMPA	BAM	benta-zone	carben-dazim	chloroto-luron	chlorida-zone	desfenyl chlorida-zone	diethylto-luamide (DEET)	dimetho-morf	dinoterb	diurone	glufosi-nate-ammo-nium	glyfosate	isopro-turone
	R=	1.0	1.14	1.0	1.2	1	1.7	1	1.65	3.0	9.23	1.0	1	1.11	2.8
%mix	%ΔC [%]														
16	Scheveningen	99.7	59.5	78.6	74.1	In = 0	69.1	0.0	100.0	87.6	100.0	72.3		In = 0	92.7
15	Katwijk	100.0	91.3	75.8	24.5	In = 0	87.4	11.2	100.0	83.0	100.0	72.2		In = 0	100.0
8	Monster	100.0	83.9	36.4	23.0	In = 0	77.9	20.2	100.0	52.2	100.0	56.8		In = 0	85.5
14	Leiduin				87.7	100.0	In = 0				In = 0	100.0			91.2
12	Ouddorp	86.9		In = 0							In = 0	In = 0	100.0	100.0	100.0
34	Heel Galgenberg	97.1	0.0	In = 0	100.0	In = 0	100.0	0.0	100.0		In = 0	100.0	0.0	94.1	100.0
44	Heel Langv+Reut	98.0	0.0	In = 0	100.0	In = 0	100.0	0.0	100.0		In = 0	0.0	100.0	100.0	100.0
	Likely mean %ΔC	97	47	64	68	100	78	6	100	74	100	67	67	98	96
t50 [d]	T½ [d]														
70	Scheveningen	8.5	61.0	31.4	42.9		70.0	9999.0	< 153.8	69.4	< 860.3	37.6			51.8
70	Katwijk	< 91.2	22.6	34.1	206.5		39.6	405.6	< 150.4	81.8	< 841.1	37.8			< 255.2
50	Monster	< 56.7	21.6	76.3	158.4		38.9	152.7	< 93.5	140.3	< 522.9	41.2			50.1
90	Leiduin				35.6	< 114.7						< 114.7			71.6
110	Ouddorp	37.4											< 134.5	< 149.2	< 376.4
365	Heel Galgenberg	68.2	9999.0		< 1089.8		< 1543.9	9999.0	< 1498.5			< 908.2	9999.0	93.3	< 2542.9
400	Heel Langv+Reut	70.4	9999.0		< 2925.8		< 4144.9	9999.0	< 4023			9999.0	< 2438.2	< 2706.4	< 6826.8
	Likely mean T½	46	35	47	111	< 114.7	50	406	<100	97	< 522.9	39	< 134.5	93	58
	Confidence	+ +	+	- -	+	-	+	-	+	++	- -	+	-	+	++
	T½ [d] literature #	37 / <37		? / >2200	>365 / 25							240 / 25			

#: X / Y = (sub)oxic / anoxic. AMPA see Hopman et al. 1995; bentazone + carbendazim see Stuyfzand et al. 2007; diurone see Stuyfzand & Luers 1996.

The following conclusions are drawn:

- The estimated confidence levels in Table 6-8 vary from very low (--) to very high (++). A high confidence level was given when the input concentration was significantly above the MDL, and when many or all AR systems gave about the same result;
- The removal performance of the AR systems (%□C) is for most pesticides / metabolites >64%. The highest removal rate (with a high confidence level) is observed for AMPA, DEET, glyfosate and isoproturone (>96% removal), the lowest for desfenylchloridazone (6%) and BAM (47%);
- The deduced half-lives with a high confidence level, for AMPA, carbendazim and diurone fit best with the indicated literature data for anoxic or partly (sub)oxic and anoxic systems. The AR systems are indeed displaying a mainly anoxic facies (Table 6-9), although with admixing of (sub)oxic water. This mixed redox is typical of AR systems and leads to clogging of the recovery system by iron hydroxides. Ouddorp and Heel are clearly more anoxic than Scheveningen, Katwijk, Monster and Leiduin.
- The short half-life of bentazone is probably biased by extremely low concentration levels (Table 6-7). Proof of nearly conservative behaviour (very long T½) is derived from other data (Figure 6-5).

TABLE 6-9. Mean concentration of the main redox sensitive parameters in AR systems (period 2010-2014). No data on CH_4. Leiduin has an open recollection system leading to reaeration.

AR system	O2	NO3	SO4	Fe	Mn	NH4
	mg/L					
Scheveningen	1.8	3.9	46.5	0.53	0.10	0.41
Katwijk	2.8	5.2	47.4	0.41	0.06	0.14
Monster	2.3	4.0	50.5	0.22	0.06	0.14
Leiduin	8.9	2.7	46.0	0.34	0.09	0.10
Ouddorp	2.5	1.3	38.5	2.79	0.13	0.33
Heel Galgenberg		2.2	58.5	2.27	0.13	0.12
Heel Langv+Reut		0.1	58.0	4.41	0.52	0.37

Data on flow line scale

Pesticides have been measured in monitoring wells along various transects between an infiltration basin and recovery system, and also between infiltration and recovery wells of ATR systems (among others Smeenk 1986, Stuyfzand & Lüers 1996, Stuyfzand et al 2007, De la Loma Gonzáles et al. 2013a,b).

In November 1994- June 1995, 5 such transects (2 RBF and 3 AR) were sampled twice and analyzed on 300 dissolved species among which about 20 pesticides (Stuyfzand & Lüers 1996). The results are summarized in Table 6-10, excluding dicamba and 8 chlorophenoxycarbonic acids (2,4,5-T, 2,4,5-TP, 2,4-D, 2,4-DB, 2,4-DP, 4-chlorophenoxy acetic acid, MCPA and MCPB) all of which showing concentrations below an MDL of ca. 0.03 µg/L. It is concluded that AMPA, atrazine and simazine were the main pesticides detectable in the studied AR systems in those years. The data do not allow for hard conclusions on biodegradation due to seasonal fluctuations in the input.

TABLE 6-10. Mean concentration levels of selected pesticides as measured in 1994-1995 along 5 monitoring transects, 2 of which RBF and 3 AR (data from Stuyfzand & Lüers 1996).
The green cells are 0.5 MDL. 0 = not detected or not analyzed. Redox: O = oxic, SO = (sub)oxic, A = anoxic, DA = deeply anoxic.

Site	Section	Obs. point	Distance	t50	Redox	AMPA	bentazon	glyphosat	MCPP	atrazine	DEET	diurone	desethyla	simazine
			m	d	level	µg/L								
Opperduit	RBF-1	O	0	0	O	0.54	0.02	0.06	0.03	0.07	0	0	0.01	0.01
		A	10	450	A	0.015	0.03	0.02	0.015	0.005	0.01	0.005	0.005	0.005
		B	100	900	A	0.05	0.03	0.02	0.015	0.005	0.02	0.005	0.005	0.005
		C	220	1800	DA	0.06	0.33	0.06	0.04	0.005	0.03	0.005	0.005	0.005
		D	675	2900	DA	0.08	1.96	0.02	0.13	0.01	0.01	0.01	0.01	0.01
		R	810	3650	A	0	0.17	0	0	0	0	0	0	0
Eng. Werk	RBF-2	O	0	0	O	0.8	0.02	0.05	0.03	0.07	0	0	0.01	0.02
		A	16	180	SO	0.06	0.03	0.02	0.015	0.04	0.01	0.01	0.01	0.01
		B	82	310	SO	0	0.03	0	0.015	0.03	0.005	0.005	0.005	0.005
		C	135	510	A	0.18	0.03	0.02	0.015	0.01	0.01	0.005	0.005	0.005
		D	394	1170	A	0.015	0.03	0.02	0.015	0.005	0.005	0.005	0.005	0.005
		E	447	1240	A	0	0.03	0	0.015	0.005	0.005	0.005	0.005	0.005
		R	815	2200	A	0	0.12	0	0.03	0.005	0	0	0	0.005
Wijk a/Z	AR-1	O	0	0	O	0.015	0.02	0.02	0.015	0.03	0.005	0.005	0.005	0.005
		A	2	8	SO	0.015	0.03	0.02	0.015	0.01	0.005	0.005	0.005	0.005
		B	17	24	SO	0.06	0.03	0.02	0.015	0.01	0.005	0.005	0.005	0.005
		C	32	32	SO	0.015	0.03	0.02	0.015	0.005	0.005	0.005	0.005	0.005
		R	41	40	Mix	0.015	0.03	0.02	0.015	0.005	0.005	0.005	0.005	0.005
Katwijk	AR-2	O	0	0	O	0.08	0.02	0.02	0.015	0.04	0.005	0.005	0.005	0.005
		A	10	14	SO	0.07	0.03	0.02	0.015	0.03	0.005	0.005	0.01	0.005
		B	35	36	SO	0.05	0.03	0.02	0.015	0.05	0.005	0.005	0.005	0.02
		C	100	73	SO	0.04	0.03	0.02	0.015	0.05	0.005	0.005	0.01	0.02
		D	225	260	DA	0	0.03	0	0.015	0.005	0.005	0.005	0.005	0.005
		R	90	70	Mix	0.06	0	0.02	0	0.02	0.005	0	0	0.02
Scheveninç	AR-3	O	0	0	O	0.17	0.09	0.02	0.015	0.05	0.005	0.005	0.005	0.02
		A	2	22	SO	0.26	0.03	0.02	0.015	0.07	0.005	0.005	0.005	0.02
		B	16	32	SO	0.3	0.03	0.02	0.015	0.03	0.005	0.005	0.005	0.01
		C	29	42	SO	0.25	0.03	0.02	0.015	0.02	0.005	0.005	0.005	0.01
		D	80	70	SO	0.04	0.03	0.02	0.015	0.03	0.005	0.005	0.005	0.02
		R	65	70	Mix	0.08	0	0.02	0	0.05	0.005	0	0	0.03

In July-August 2005 and August-September 2006 other 9 AR monitoring transects were sampled and analyzed on about 200 dissolved compounds (Van Rooyen 2006, Segers 2007, Stuyfzand et al. 2007) among which 19 pesticides (in 2006 only). The results are summarized in Table 6-11, excluding the 14 not-detected pesticides (MDL = 0.03 µg/L): 2,4,5-T, 2,4,5-TP (fenoprop), 2,4-D, 2,4-DB, 2,4-dinitrophenol, 2,4-DP (dichlorprop), dinoseb, dinoterb, DNOC, MCPA, MCPB, metamitron, metribuzin, and pirimicarb. It is concluded that atrazine and dimethenamide show negligible concentrations, and that bentazone, MCPP and carbendazim were more prominent. Bentazone and MCPP were present in much older, anoxic infiltrate (Fig. 6-5), demonstrating their resistance against (bio)degradation. Carbendazim was mainly present in (sub)oxic infiltrated water in concentrations of 0.01-0.06 µg/L. In anoxic environment, carbendazim rapidly degraded, which Stuyfzand et al (2007) translated into T½ = 25 d.

Table 6-11. Concentration levels of selected pesticides as measured in August-September 2006 along 9 monitoring transects, 2 of which ATR and 7 BAR. Data from Stuyfzand & Lüers (1996). 0 = not detected or not analyzed. Redox: O = oxic, (S)O = (sub)oxic, A = anoxic, DA = deeply anoxic.

Site code	Monitoring point	Distance in aquifer [m] [A]	Depth [m+MSL]	Travel time [d or y]		Redox Environment [B]	Atrazin	Dimethenamide	Bentazone	MCPP	Carbendazim
		m	m+MSL	d or y			µg/L				
Castricum, PWN (24 August 2006)											
Icas (BAR)	Pond 5	0	4	0	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.013
	L5388-1	1.4	0.8	2	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.012
	L5391-1	9.1	-0.1	7	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
	L5393-1	29	-0.4	16	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.015
	L5393-3	36	-7.3	25	d	(S)O					
	PCQ414	64	-3	56?	d	A (mix)	< 0.01	< 0.01	0.06	< 0.05	< 0.01
Dwat (ATR)	W780-3	10	-67.3	18	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.018
	W779-3	30	-97.3	43	d	A					
	W778-3	73	-66.8	103	d	A	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
Old (BAR)	W799-3	34	-34.4	3?	y	A					
	W096-3	120	-52.2	25.3	y	A	< 0.01	< 0.01	0.37	0.2	< 0.01
	W618-10	340	-52	>26	y	A	< 0.01	< 0.01	0.55	0.13	< 0.01
	W793-3	320	-36	>36	y	A/DA	< 0.01	< 0.01	< 0.05	0.08	< 0.01
Zandvoort, Waternet (6 September 2006)											
Basin 6	Basin 6	0	6	0	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.031
	10J537-5	3.6	4.9	2	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.02
	10J536-4	96	-2.8	49	d	(S)O	0.011	< 0.01	< 0.05	< 0.05	0.037
	10J537-1	3.6	-8.1	75	d	A	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
	10J536-1	96	-13.8	351	d	A	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
Basin 12	Basin 12	0	7	0	d	(S)O					
	24H337-7	2.5	4.2	8	d	mix					
	10J539-5	6	4.1	14	d	(S)O					
	24H335-7	30	5.1	30	d	(S)O					
	10J538-5	57	4	57	d	(S)O					
Van der Vliet (BAR)	24H478-4	95	-1.9	3.5	y	A	0.011	< 0.01	< 0.05	< 0.05	< 0.01
	24H478-3	95	-12.3	6.6	y	A	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
	24H481-3	375	-12.9	18.8	y	A	< 0.01	< 0.01	0.18	< 0.05	< 0.01
	24H482-3	500	-11.1	18.8	y	A	< 0.01	< 0.01	0.15	< 0.05	< 0.01
	24H481-2	375	-19.9	>26	y	A	< 0.01	< 0.01	0.11	0.25	< 0.01
Scheveningen, Dunea (31 August 2006)											
Pond 13.1 (BAR)	Pond 13.1	0	-	0	d	(S)O	< 0.01	0.011	< 0.05	< 0.05	0.062
	pb195	3	-1.9	20	d	DA	< 0.01	< 0.01	< 0.05	< 0.05	0.044
	pb194	16	-1.9	30	d	(S)O	< 0.01	0.011	< 0.05	< 0.05	0.043
	pb193	31	-1.9	40	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.062
	TC-1	37	-2	48	d	(S)O					
Waalsdorp (ATR)	Input	0	-	0	d	(S)O	0.011	0.011	< 0.05	< 0.05	0.013
	WE-34	23	-33.9	21	d	(S)O	< 0.01	< 0.01	< 0.05	< 0.05	0.017
	WG-32	64	-31.4	48	d	A	< 0.01	< 0.01	< 0.05	< 0.05	0.011
	Eff	120	-34	112	d	A					
Old (BAR)	TA-4	2	-16.1	1.7	y	DA	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
	K-33	100	-33	7.9	y	A	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
	A-54	58	-54	11.4	y	DA	< 0.01	< 0.01	0.06	< 0.05	< 0.01
						MIN	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01
						MAX	0.01	0.01	0.55	0.25	0.06
						Total number of detections in 30 observations	3	3	7	4	14

[A]: horizontal distance (in flow direction) to basin bank or injection well

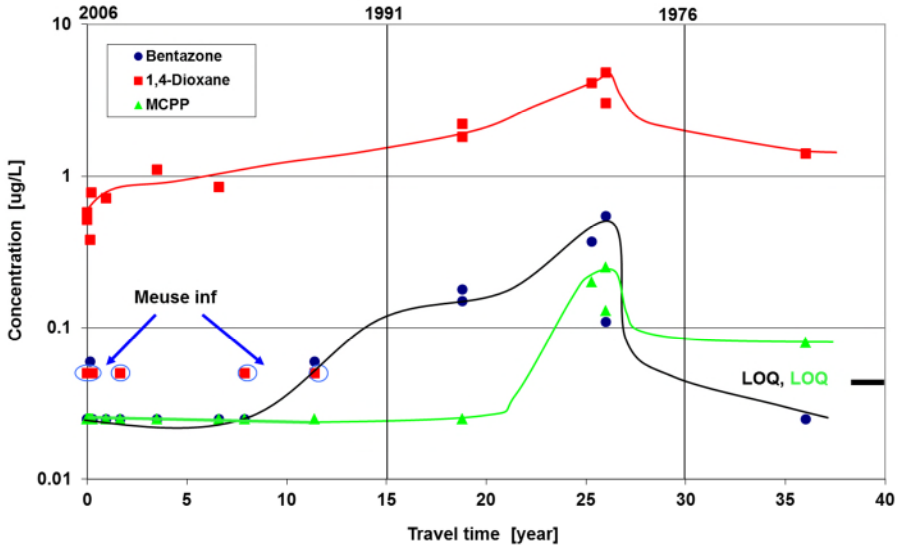


Figure 6-5. Concentration of bentazone, mecoprop (MCPP) and 1,4-dioxane in the basin artificial recharge systems of Waternet, PWN and Dunea as function of travel time. Based on a survey in 2006 (Stuyfzand data files).

The monitoring transect of Pond 13.1 north of Scheveningen (Figure 6-6) was resampled in 2011 (De la Loma Gonzáles et al. 2013b), with the results for pesticides and some macroparameters shown in Table 6-12. We conclude that the pesticide concentrations were very low again, with AMPA, nicosulfuron and terbuthylazine showing the highest concentrations levels, but not surviving anoxic environments. Chloridazone and DEET seem to have had higher concentrations in the past while surviving anoxic conditions.

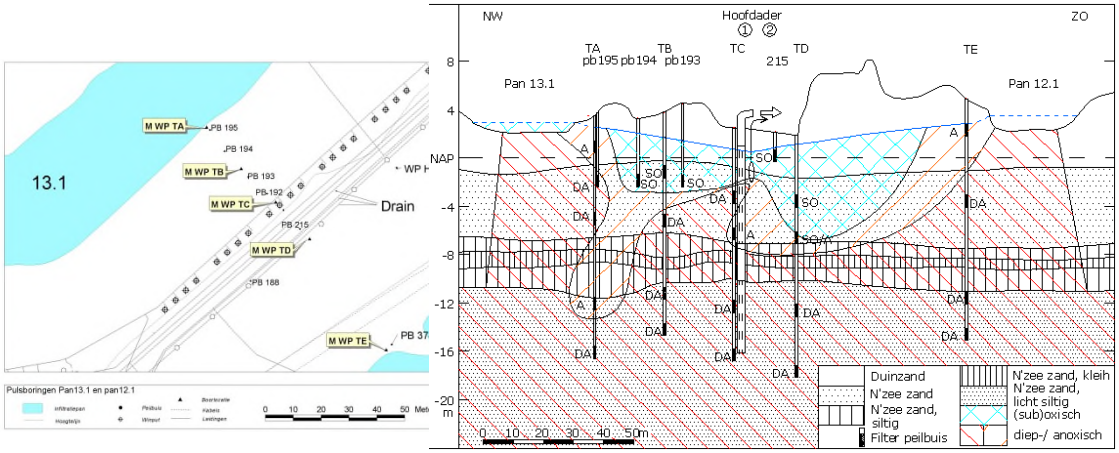


Figure 6-6. Location and cross section of the investigated row of monitoring wells in between recharge basins 12.1 and 13.1 in recharge area Meijendel north of Scheveningen (Dunea). Cross section from Segers (2007). Redox levels in 2006: SO = suboxic, A = anoxic, DA = deeply anoxic.

Table 6-12. Pesticides and some macroparameters in the water samples of November 2011, from recharge area Meijendel. - = substance not detected. Based on data in De la Loma Gonzáles et al. 2013b.

Parameter	Unit	Brakel Intake	Basin 13.1	PB-195	PB-193	TC1-f1	TA-f4	Mixed Raw	Drinking water
Travel time	day	-2	0	22	42	48	600	>60	>60
Redox		oxic	oxic	suboxic	suboxic	anoxic	deeply an	anoxic	oxic
pH		8.3	8.5	7.7	7.8	7.8	7.9	7.8	8.4
TEMP	°C	24.1	24.6	20.7	18.2	17.2	14.1	17.6	16.3
O2	mg/L	9.5	11.6	1.6	2.4	1.7	1.7	1.8	9.3
CH4	µg/L	<10	13	<10	<10	<10	210	40	<10
Cl	mg/L	37	40	38	40	41	43	45	47
SO4	mg/L	41.6	42.3	40	43.2	41.1	24.1	42.6	42.1
HCO3	mg/L	148	110	187	200	198	239	204	182
NO3	mg/L	8	1.5	0.2	0.2	0.4	0.2	3.4	4.7
TOC	mg/L	5.2	5.3	3.3	2.8	2.7	3.1	2.6	2.3
NH4	mg/L	<0.02	0.04	<0.02	<0.02	<0.02	1.3	0.28	<0.02
Fe	mg/L	<0.05	<0.05	<0.05	<0.05	0.14	0.88	0.22	<0.05
Mn	mg/L	0.02	<0.01	0.01	<0.01	0.01	0.13	0.08	<0.01
Pesticides									
AMPA	µg/L	0.689	-	0.13	-	-	-	-	-
bentazone	µg/L	0.02	0.02	0.02	0.02	0.03	0.03	0.01	<d.l.
carbendazim	µg/L	0.016	0.012	-	0.016	0.023	-	0.012	-
chloridazone	µg/L	<0.01	<0.01	<0.01	<0.01	0.01	0.08	<0.01	<0.01
DEET	µg/L	0.03	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
dimethenamid-P	µg/L	0.01	0.01	0.01	0.02	0.02	<0.01	<0.01	<0.01
dimethomorph (E,Z	µg/L	0.06	0.02	<0.01	<0.01	<0.01	<0.01	0.03	<0.01
diurone	µg/L	0.024	-	0.01	0.01	0.02	n.a.	-	
linurone	µg/L	0.02	-	-	-	-	-	-	-
MCPA	µg/L	0.048	-	-	-	-	-	-	-
mecoprop (MCPP)	µg/L	0.026	-	-	-	-	-	-	-
metolachlor	µg/L	0.02	0.01	0.01	0.02	0.02	<0.01	<0.01	<0.01
nicosulfuron	µg/L	0.08	0.08	0.07	0.07	-	-	-	-
terbuthylazine	µg/L	0.05	0.05	0.05	0.07	0.03	-	-	

Yet another data set refers to a monitoring transect in the basin AR area Ouddorp of Evides, sampled in 2011 (De la Loma Gonzáles et al. 2013a; Figure 6-7). We conclude that the 5 pesticides investigated are all close to or below MDL.

Sample:	Unit	Canal 7	10-664	10-663	Drain 5M
Distance	m	0	44	83	100
t50	d	0	34	93	108
Redox state		Oxic	SO4 red	Fe red	Mix
Temp	oC		12.9	12.8	10.1
pH	Field	7.66	7.56	7.38	7.33
Fe	mg/L	<0.01	2.7	0.21	0.2
Mn	mg/L	<0.01	0.03	0.07	0.09
NH4	mg/L	0.04	0.3	0.34	0.17
Cl	mg/L	129	110	184	127
SO4	mg/L	65	40	75	50
HCO3	mg/L	193	264	281	279
NO3	mg/L	5.4	<0.2	<0.2	0.5
CH4	µg/L	<10	<10	<10	<10
Bentazone	µg/L	0.01	0.01	0.01	0.01
Carbendazim	µg/L	0.01	<0.01	<0.01	<0.01
Diuron	µg/L	<0.01	0.01	0.01	<0.01
Isoproturon	µg/L	<0.01	0.01	0.01	0.01
DEET	µg/L	0.01	0.01	<0.01	<0.01

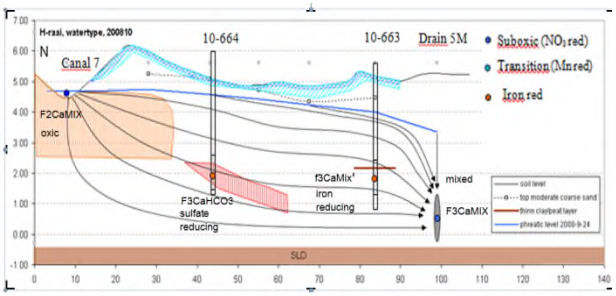


Figure 6-7. Pesticides detected in water samples from the Ouddorp recharge area (Evides), taken on 8 November 2011. Table based on data in De la Loma Gonzáles et al. 2013a, Cross section from Aggenbach (??).

6.7 River bank filtrate

RBF systems

River bank filtration for drinking water supply was taking place in the period 2010-2014 on ~22 sites (Figure 6-8), together producing ~100 Mm^3/a. This forms about 9% of the total annual drinking water in the Netherlands. Important characteristics of RBF systems are: no selective intake, no pretreatment, no unsaturated zone (site 80 = Roosteren excluded), aquifer passage for a modal (!) distance and travel time of 130-3500 m and 0.8-20 years,

and admixing of ambient groundwater in the recovery system (on average 2-60%). Further system details are given by Stuyfzand (1985, 1989, 1991) and Stuyfzand & Lüers (1996).

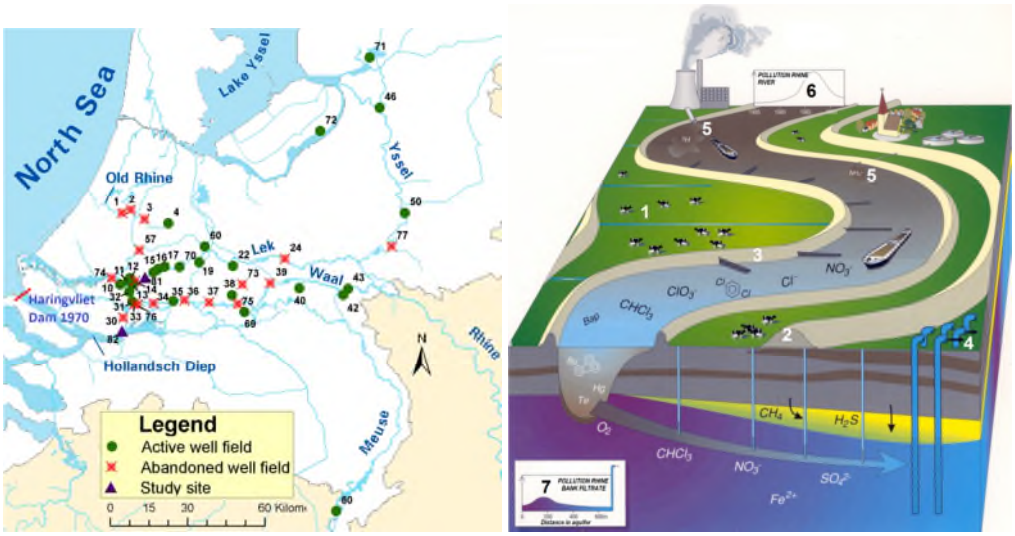


Figure 6-8. River bank filtration (RBF) in the Netherlands, a proven technology since 1876. Total amount of RBF contributing to drinking water supply ~9 %. Left panel from Stuyfzand in prep., right panel from Stuyfzand & Lüers 1996. Sites: 17 = Rodenhuis; 46 = Engelse Werk (Zwolle); 81 = Opperduit.

Data on system scale

Data on system scale refer to the raw river bank filtrate collected by the well field. Data on pesticides and some macroparameters are presented in Table 6-13, for 11 well fields, 10 of which managed by Oasen and 1 (Engelsche Werk) by Vitens. We conclude that bentazone, chloridazone, desphenyl-chloridazone and 2-chloroaniline are the most prominent, and that the RBF systems are all predominantly deeply anoxic with admixing of anoxic water. This redox environment favours the survival of these compounds indeed. A high percentage of river bank filtrate (%RBF in Table 6-13) and a not long travel time (such as for De Steeg deep) result in high concentrations for a.o. bentazone, as observed elsewhere.

Trends in the concentration of bentazone and dikegulac in the raw water of RBF well fields Schuwacht (15 on Figure 6-8) and de Laak (60 on Figure 6-8) in the period 1994-2006 are shown in Figure 6-9. They show a declining trend for both in Schuwacht, a well field with relatively short travel times (1.8-3.8 year), and an increasing trend for De Laak, a well field with relatively long travel times (32-200 year).

Table 6-13. Mean concentration of 8 pesticides (incl. metabolites) and some macroparameters in the raw water from 11 RBF well fields, in period 2010-2014. Age data from drs. H. Timmer (Oasen, pers. comm.).

RBF Well field	%RBF	Age 10-50%	Cl	SO4	HCO3	NO3	PO4	Fe	Mn	NH4	CH4	benta-zone	chloro-tolu-rone	chlori-dazone	chlori-dazone desphe-nyl	DEET	diurone	isopro-turone	2-chloro-aniline
	%	year	mg/L								µg/L	µg/L							
Hendrik Ido Ambac	86	3-8	95.4	53.6	216		2.34	5.14	0.72	1.55		0.07				0.03		0.02	0.08
Kamerik			78.5	42.1	388		1.59	8.35	0.52	3.67	1975	0.06				0.01			
De Laak	46	32-200	39.1	26.4	275		0.47	1.01	0.11	0.66	980	0.10							
Lekkerkerk-Schuw	93	1.8-3.8	89.2	48.6	230	1.2	1.69	2.77	0.84	1.80	535	0.03	0.01	0.06	0.16	0.01	0.01	0.02	0.09
Lekkerkerk-Tiend	100	10-25	107.7	44.2	233		2.25	5.47	0.49	5.57	1047	0.24		0.08	0.14	0.02		0.01	0.13
De Put	96	3.6-7.6	88.6	50.0	221		1.49	2.41	0.48	3.53		0.13	0.01	0.04	0.19	0.01	0.01	0.02	0.10
Rodenhuis	100	3.3-10	88.2	57.0	204	1.2	0.46	1.79	0.57	0.90		0.08	0.01	0.04	0.20	0.01	0.01	0.02	0.06
Ridderkerk			116.5	24.3	309			5.03	0.45	7.49	5150	0.06		0.06	0.10	0.02		0.01	0.08
De Steeg	90	4.2-83	93.7	63.8	250		0.48	2.50	0.82	0.95	92	0.15		0.04	0.11	0.01		0.01	0.06
De Steeg	96	48-210	21.4	10.3	316	1.3	0.61	1.21	0.07	1.00	3625	0.05							
Engelsche Werk	57	6-16	71.3	53.5	209	1.4	0.52	6.01	0.50	0.44		0.06	0.01	0.02	0.15	0.01	0.02	0.02	0.06

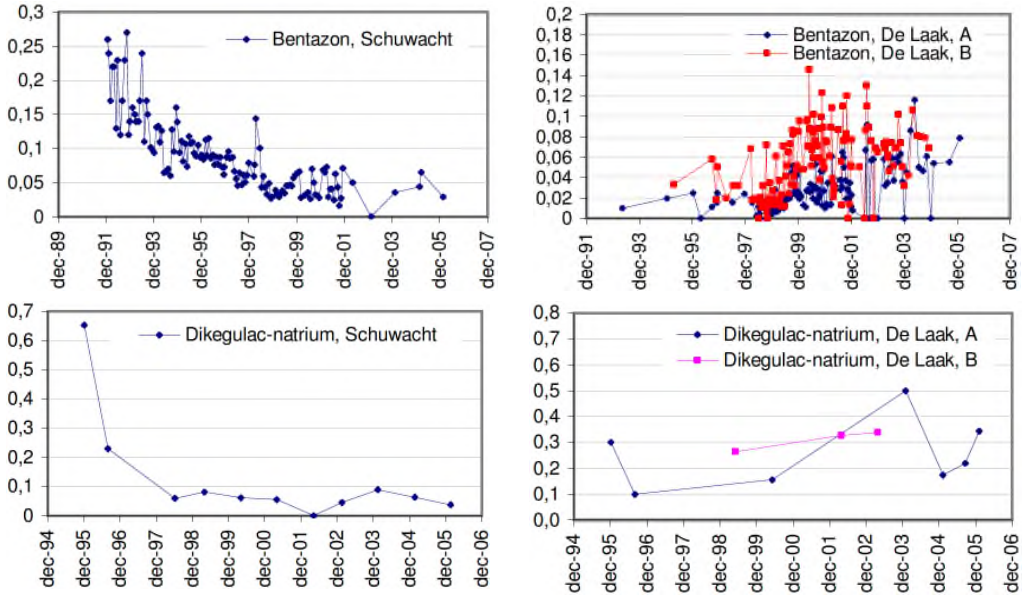


Figure 6-9. Trends in the concentration of bentazone and dikegulac in the raw water of RBF well fields Schuwacht (15 on Figure 6-8) and de Laak (60 on Figure 6-8) in the period 1994-2006 (fragment from Segers 2007).

Data on flow line scale

Pesticide data for 2 monitoring transects, namely one near Opperduit (site 81 in Figure 6-8) and the other near PSWF Engelse Werk (site 46 in Figure 6-8) are shown in Table 6-10 (Stuyfzand & Lüers 1996). The data on dicamba and 8 chlorophenoxycarbonic acids are not shown, because all of them were below detection (MDL 0.03 µg/L). We conclude that AMPA is largely removed during the first 180-450 days of aquifer passage, but that some AMPA may still be present after longer transit times, without much difference between (sub)oxic and anoxic redox environment. This corresponds with the half-lives deduced in Table 6-8. Bentazone (and MCPP) showed higher concentrations in the older river bank filtrates, which agrees with the data from AR flow lines (Figure 6-5). Atrazine and simazine showed survival but slow (bio)degradation in (sub)oxic environment. Their concentration in anoxic environment was below detection, but that zone followed prolonged passage through the (sub)oxic zone, which hampers the deduction of T½ in the anoxic zone.

RBF monitoring transect Engelsche Werk (Figure 6-10) is still in use, and was recently addressed by Stuyfzand et al. (2012). The new data collected in the period 2000-2010 showed a significant advance of the (sub)oxic zone with respect to the survey in 1994-1995, but data on pesticides were not supplied for the 2000-2010 survey. The expansion of the (sub)oxic zone is due to (i) the significantly improved quality of the Rhine River, and (ii) aquifer leaching by the oxic IJssel water. This expansion is important because it has an impact on the (bio)degradation of pesticides and metabolites.

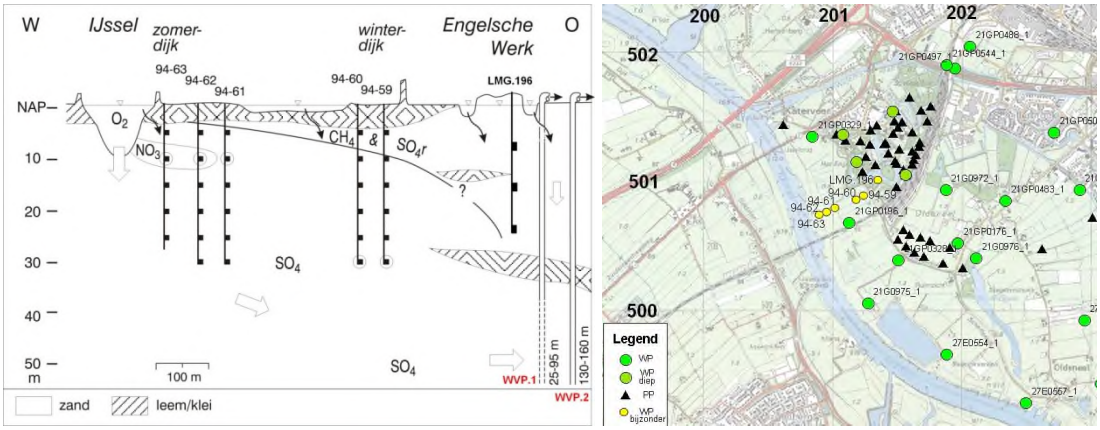


Figure 6-10 Monitoring transect Engelsche Werk (also RBF-2 in Table 6-10) with the spatial extent of the redox zones in 1994-1995. O_2 = oxic; NO_3 = suboxic; SO_4 = anoxic Fe-reducing; SO_4r = deeply anoxic, SO4 reducing; CH_4 = methanogenic. A survey in 2011 of well 94-61 showed anoxic river bank filtrate in the upper well screen and (sub)oxic river bank filtrate in de deeper 4 well screens!

Yet another important operational RBF monitoring transect is the one near Rodenhuis (Figure 6-11) which Oasen is sampling on a quasi annual basis in order to custody general trends in Rhine bank filtrate. The data collected in the period 1999-2005 were investigated by Segers (2006) for the first time, and subsequently the data from 1999-2013 were evaluated and modeled by Hamann et al. (2016). The data show in general very low pesticide and metabolite concentrations (<0.03 µg/L).

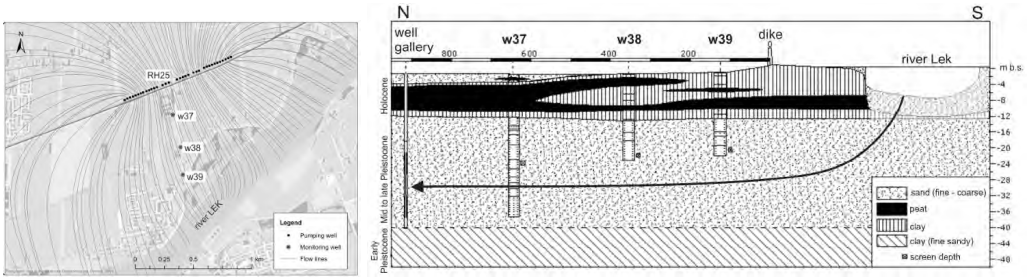


Figure 6-11. Hydrogeological conditions and position of the monitoring wells along transect Rodenhuis (modi□ed from Segers (2006). The arrow indicates the hypothetical groundwater □ow.

6.8 Modelling methods

Pesticide inputs from the plough layer

Modelling of the pesticide leaching from the arable soil horizons (the plough layer) down to about 1 meter depth, is complex. Various models have been developed for evaluating the environmental fate of plant protection products (www.pesticidemodels.eu) and are used for registration of plant protection products on a European and national level.
Modelling of pesticides in the groundwater compartment generally starts with the output from the leached arable soil horizons. This means that many processes acting at the soil atmosphere interface and in the upper soil, such as volatilization, photochemical degradation and plant interception and uptake do not need to be addressed at all.

In order to keep the model simple and practical, the output from the upper meter is set at 100%, which can easily be changed into a specific concentration (to be supplied by e.g. GeoPearl), as we assume the following: (i) the calculated concentrations downgradient do not participate in any dissolution or precipitation reaction, (ii) sorption is linear, fully reversible and immediate, and (iii) (bio)degradation follows first order decay, with the same constant for the dissolved and sorbed fraction.

The hydrological response curve of a well (field)

The so-called hydrological response curve (HRC) is defined as the cumulative frequency distribution of travel times to a well (field). This HRC is of great value to predict concentration trends in the well (field) since the pesticide (or any pollutant) has been applied. An example of the HRC is shown in Figure 6-13.

The purpose is to predict or simulate the behaviour of pesticides within a phreatic (very vulnerable) to semi-confined (moderately vulnerable) groundwater catchment area, given a 100% input from the plough zone, as a step input for either a specific site at radial distance r_x or for the whole catchment area. The well field is schematized into one single centralized well, with an aggregated pumping rate, mean well screen depth, a concentric catchment area, an unsaturated zone and a saturated aquitard on top of the pumped aquifer, which is underlain by an aquiclude (Figure 6-12). Flow is assumed vertical and parallel in both the unsaturated zone and aquitard, but horizontal and radial in the aquifer.

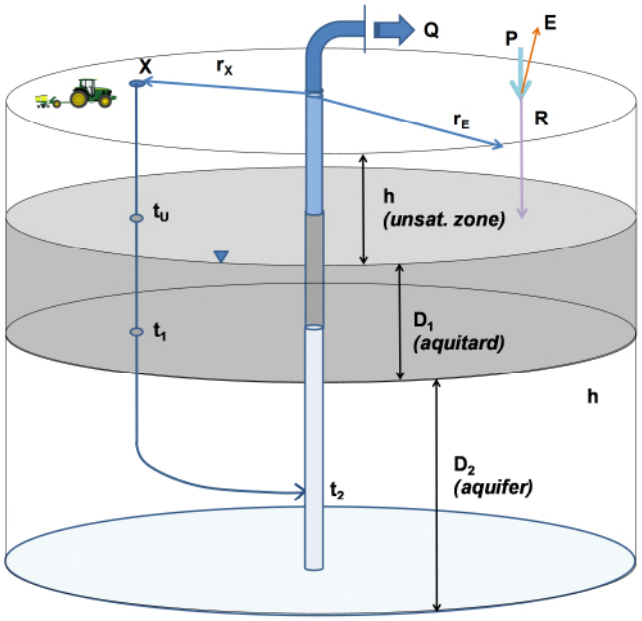


Figure 6-12. Schematic of a circular groundwater catchment area for a well (field) with divide at distance r_E, uniform recharge R, and an unsaturated zone, aquitard and aquifer. The well screen is fully penetrating. Travel time sections along a flow path from site X at radial distance r_x refer to the whole unsaturated zone (t_U, vertical parallel flow), the whole aquitard (t_1; vertical parallel flow) and the aquifer (t_2, predominantly horizontal radial flow).

A simplified hydraulic model provides the total travel time from land surface to the well (field), by adding up the travel time in each of the 3 discerned zones (Figure 6-12). We discern 2 situations: a phreatic aquifer (D_1=0 in Fig.6-12) and a semiconfined aquifer leaky at its top (D_1 >0 in Fig.6-12).

The phreatic case:

In the phreatic case, the total travel time from land surface to the well (field) is the sum of the travel time in the unsaturated zone and saturated aquifer, t_U and t_2, both a function of r_X (Fig.6-12):

$$t_{TOT} = t_U + t_2 \qquad (6\text{-}5)$$

$$t_U = \frac{h\theta + n_U c_F}{R} \qquad (6\text{-}6)$$

$$t_2 = \frac{n_2 D_2}{R} \ln \frac{1}{1-\left(\frac{r_X}{r_E}\right)^2} = \frac{n_2 D_2}{R} \ln \left[\frac{Q}{Q - \pi R r_X^2}\right] \qquad (6\text{-}7)$$

where: Q = pumping rate of well (field) [m^3/d]; t_{TOT} = total travel time from ground level to well (field) [d]; t_U , t_2 = mean travel time in unsaturated zone and saturated aquifer, respectively [d]; n_U, n_2 = effective porosity of unsaturated zone and aquifer, respectively [volume fraction]; h, D_1, D_2 = mean total thickness of unsaturated zone, aquitard and aquifer, respectively [m]; R = groundwater recharge [m/d]; r_X, r_E = radial distance to well (field), from X and groundwater divide, respectively [m]; □ = mean moisture content unsaturated zone [volume fraction]; c_F = thickness full-capillary fringe [m].

For details on equations 6-6 to 6-7, see Van Lanen (1984) and Stuyfzand (2015), respectively. The right hand equation of Eq.6-7 is obtained from its left hand part by inserting r_E =

√(Q/(πR). If the aquitard is lacking, then it suffices to enter $D_1 = 0$, and all calculations pertain to a phreatic (unconfined) aquifer. If the well screen is located at some depth below the top of the aquifer, then in case of a phreatic aquifer that upper part of the aquifer can be considered an aquiclude with very low vertical flow resistance by setting c_V = 1 day.

Inserting $(r_X/r_E)^2 = 0.01P_X$ in Eq.6-7, with P_X = percentile X [0-99.999), yields:

$$t_2 = \frac{n_2 D_2}{R} \ln[\frac{1}{1-0.01P_X}] \quad (6\text{-}8)$$

This equation can be directly used, after adding t_U, to calculate the HRC.

The approximate depth of entrance in the well screen (d_X in m – top of aquifer) for a ring of flowlines depends on r_X as follows:

$$d_X = D_2(\frac{r_X}{r_E})^2 \quad (6\text{-}9)$$

The following equation holds for a conservative pollutant from a fully penetrating well in a homogeneous, isotropic aquifer (such as in Figure 6-12), with initial concentration in the aquifer (and in both the unsaturated zone and aquitard) being zero:

$$C_t = C_{IN}(1 - e^{\frac{-R\,(t-t_U-t_1)}{D_2 n_2}}) \quad \text{if } t - t_U - t_1 > 0, \text{ else } C_t = 0 \quad (6\text{-}10)$$

where: C_{IN} = average (constant) input concentration for unsaturated zone since start of application at t =0 [%]; C_t = concentration in output of well in zone 2 after time t since start; t = time since start of pollutant application (entrance into system) [d].

The semiconfined case:

In the semiconfined case, the total travel time from land surface to the well (field) is the sum of the travel time in the unsaturated zone (t_U), saturated aquitard (t_1) and saturated aquifer (t_2)

An average constant value needs to be taken for the thickness of the unsaturated zone (h) and aquitard (D_1), for the sake of simplicity. The lack of drawdown of the groundwater table in the aquitard, even in the vicinity of the well (field), can be explained by an intricate system of influent ditches and canals.

De Glee (1930) presented an analytical solution of the drawdown of the piezometric head in the aquifer, for this scenario. Peters (1985) used his solution to calculate the travel time in both the aquitard (t_1) and aquifer (t_2). We thereby obtain the following set of solutions:

$$t_{TOT} = t_U + t_1 + t_2 \quad (6\text{-}11)$$

$$t_1 = f\frac{2\pi\lambda^2 n_1 D_1}{Q K_0(\frac{r}{\lambda})} \quad (6\text{-}12)$$

$$t_2 = \frac{2\pi\lambda^2 n_1 D_1}{Q} \int_0^{r/\lambda} \frac{dr}{K_1(r)} \quad (6\text{-}13)$$

$$\int_0^{r/\lambda} \frac{dr}{K_1(r)} = 1.0872\,(\frac{r}{\lambda})^3 - 1.7689(\frac{r}{\lambda})^2 + 1.5842(\frac{r}{\lambda})^1 - 0.2544 \quad (6\text{-}14)$$

where: t_1 = travel time in saturated aquitard [d]; n_1 = effective porosity of aquitard [volume fraction]; h = mean constant thickness of unsaturated zone [m]; D_1 = mean total thickness of aquitard (saturated) [m]; $\lambda = \sqrt{(K_2 D_2 c_V)}$ = leakage factor [m]; c_V = mean resistance of aquitard to vertical flow [d]; $K_0(x)$ = modified Bessel function of the second kind and zero order (= besselk(x,0) function in Excel); $K_1(r)$ = modified Bessel function of the second kind and first order (= besselk(x,1) function in Excel); f = fraction of aquitard contacted, to account for gaps in aquitard [-].

The approximation of the integral in Eq.6-13 by Eq.6-14 is based on its plot against r/□ as provided by Peters (1985).

The HRC for the semiconfined case as presented here, cannot be approached by an equation similar to Eq.6-8. As stated by Bear (1979), the ratio Q_r/Q_0 indicates for every distance r the portion of the well's discharge (Q_0) flowing through the aquifer, so that:

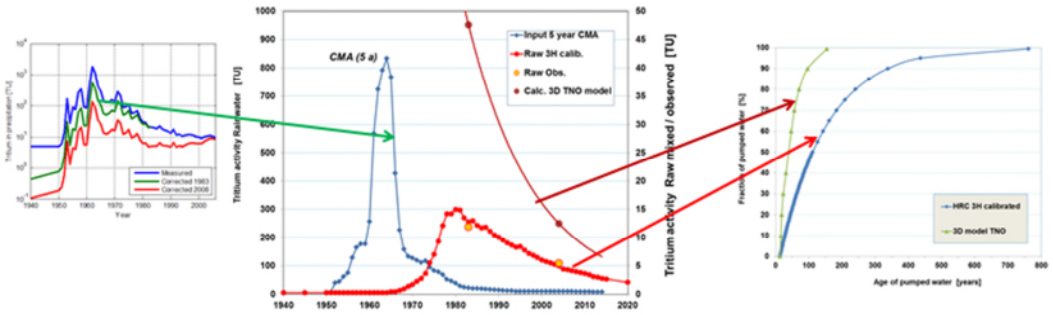
$$P_r = 100\frac{Q_r}{Q_0} = 100\,[1 - \left(\frac{r}{\lambda}\right) K_1\left(\frac{r}{\lambda}\right)] \qquad (6\text{-}15)$$

The more difficult to estimate parameters for calculating the HRC are: □, R, K_2D_2 and c_V. It can then be very helpful to use an independent validation by comparing the measured concentration in the output (from the well) of a conservative tracer, with its output as calculated by the HRC combined with the known concentration input time series. An interesting possibility is offered by tritium, if measured in the mixed well field output at any time after 1964, and if tritium is well above the detection limit. Examples are give by Mendizabal and Stuyfzand (2009), and more recently, in a further elaborated form, by Stuyfzand (2015). Some details of the latter case, for well field Noordbargeres in Drenthe, are shown in Figure 6-13.

If the isohypses of the groundwater table or a 3D model indicate that the groundwater catchment area deviates from a circular form with the well (field) at its center, then the above given travel time calculations remain valid under specific conditions by applying a multiplication factor $1/F_a$, after a simple shape transformation (Stuyfzand 2015). This implies multiplying the radial distance of the groundwater divide so as to fit the observed shape, while keeping both surface areas equal and recording the multiplication factor F_a for each compass angle (Figure 6-14).

Retardation and (bio)degradation

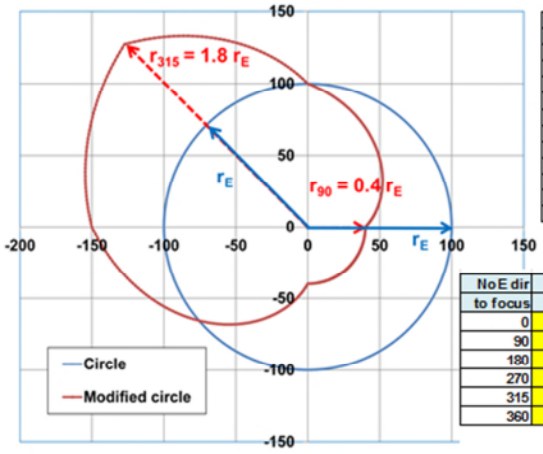
As stated before, many processes acting at the soil atmosphere interface and in the upper soil, do not need to be addressed at all. The only processes therefore remaining, are sorption and (bio)degradation.



HRC #	Ground Surface	GWT	Screen depth Upper	Screen depth Lower	R	Aquifer Top	Aquifer Base	eff. por	Soil Moisture	3H [T.U.] Meas	3H [T.U.] calc '83	3H [T.U.] Meas	3H [T.U.] calc '04	t-UNS
	m ASL				m/a	m ASL		n	V	1983	HRC	2004	HRC	year
1	22.0	14.6	-24.3	-36.7	0.300	14.6	-38	0.30	0.15	11.9	47.6	5.5	12.8	4.0
9	*22.0*	*14.6*	*-24.3*	*-36.7*	*0.300*	*14.6*	*-110*	*0.34*	*0.15*	*11.9*	*12.8*	*5.5*	*5.0*	*4.0*

#	t-UNS	HRC %Y	HRC %Y	PHREATIC HRC P	P	P	P	P	P	P	P	P	P	P
	year	30	51	0	10	20	30	40	50	60	70	80	90	99.5
1	4.0	38.5	64.1	13.1	15.8	18.2	22.9	31.3	38.7	47.2	56.4	71.0	96.3	154.0
9	*4.0*	*12.4*	*24.5*	*13.0*	*27.9*	*44.5*	*63.4*	*85.2*	*110.9*	*142.4*	*183.0*	*240.3*	*338.2*	*761.2*

Figure 6-13. Verification and calibration of the HRC of a well field, on 3H data (based on Stuyfzand 2015). The measured annual tritium input curve (left panel) is first corrected for radioactive decay to 1983 (= date of first sample from well field) and subsequently its 5 years centralized moving average (CMA) is calculated (blue curve in middle panel). The red curve in the middle panel is the well field's tritium output (raw) as calculated on the basis of the calibrated hydrological response curve (HRC #9), together with 2 yellow dots representing the measured tritium activity in 1983 and 2004, respectively.
The calibrated HRC parameters are given on row #9 in the table below, with the resulting match between measured and calculated tritium. The dark red curve refers to the calculated tritium activities on the basis of the HRC derived from a 3D groundwater flow model (HRC #1 in table). Obviously, that model results in a bad match for tritium, and the resulting HRC yields too short travel times (right panel). The most likely reason for the bad tritium performance of the 3D model, is that the aquifer thickness was taken too small (compare HRC #2 with #1).



NoE dir to focus	Multipl. factor F	Circle x	Circle y	Modified x	Modified y	Area circle	Area Modif
0	1.00	0	100	0	100	0.0087	0.0087
1	0.99	2	100	2	99	0.0087	0.0086
2	0.99	3	100	3	99	0.0087	0.0085
3	0.98	5	100	5	98	0.0087	0.0084
4	0.97	7	100	7	97	0.0087	0.0083
5	0.97	9	100	8	96	0.0087	0.0082
6	0.96	10	99	10	95	0.0087	0.0080
7	0.95	12	99	12	95	0.0087	0.0079
8	0.95	14	99	13	94	0.0087	0.0078
9	0.94	16	99	15	93	0.0087	0.0077
10	0.93	17	98	16	92	0.0087	0.0076

NoE dir to focus	Multipl. factor F	Circle x	Circle y	Modified x	Modified y	Area circle	Area Modif
0	1.0	0.00	100.00	0.00	100.00	0.008727	0.008727
90	0.4	100.00	0.00	40.00	0.00	0.008727	0.001396
180	0.4	0.00	-100.00	0.00	-40.00	0.008727	0.001396
270	1.5	-100.00	0.00	-150.00	0.00	0.008727	0.019635
315	1.8	-70.71	70.71	-127.28	127.28	0.008727	0.028274
360	1.0	0.00	100.00	0.00	100.00	0.008727	0.008727
					Sum 0-360 =	3.14	3.18

Figure 6-14. Transforming the radial distance to the well field's abstraction center (x=y=0), for observation wells or spots within an observed, noncircular groundwater catchment area (circumference in red), in order to correct the drawdown and travel times as calculated for an equivalent circular groundwater catchment area (circumference in blue).

The radial distances within the observed, noncircular groundwater catchment area (rX and rE) are to be multiplied with factor F. The factor F was fixed here at each multiple of 90o (lower table) and was stepwise and clockwise linearly changed within each segment (upper table).

$R_{OMP} = t_{OMP} / t_{H2O}$	
$R_{OMP} = 1 + (f_{GL}\ f_{OC}\ f_{ND}\ K_{OC}) / (1 + f_B\ TOC\ 10^{-6}\ f_{ND}\ K_{OC})$	
Soil / aquifer parameters	
f_{GL} =	$\rho_S (1-n) / n$ with ρ_S = density solids [kg/L], n = porosity [-]
f_{OC} =	fraction of organic carbon in soil [by weight]
OMP characteristics	
K_{OC} =	distribution coefficient of OMP between organic carbon and water [L/kg]
	$= 10^B (K_{OW})^A$ where K_{OW} = octanol-water distribution coefficient
f_{ND} =	$1 / (1 + 10^{[pH - pKA]})$ = non dissociated fraction [-], with
	$pK_A = - \log K_A$ where K_A = 1st dissoc constant H-OMP <--> OMP + H^+
f_B =	TOC or DOC fraction available for OMP sorption [-]
Water matrix characteristics	
pH =	-log[H^+]
TOC =	Total Organic Carbon [mg/L] = mostly DOC in groundwater

Figure 6-15. Calculation of the retardation factor of organic micropollutants (R_{OMP}), with indication of the involved parameters.

Retardation of organic micropollutants (OMPs) such as pesticides is due to hydrophobic sorption mainly to soil organic carbon. It can be calculated using the classical approach (see Appelo & Postma 1993) with addition of the effects of (i) DOC-binding according to Kan & Tomson (1990) and (ii) OMP ionization (dissociation) according to Schellenberg et al. (1984). The resulting retardation factor R_{OMP} is defined and calculated as indicated in Figure 6-15. It is thus assumed that, upon dissociation, acid OMPs become anions that hardly sorb to the dominantly negatively charged soil or aquifer. Basic or cationic OMPs can be approached in a similar way, but positively charged OMPs remain more prone to sorption, thus complicating a simplified method.
K_{OC} values refer to a standard lab temperature (t_{REF} = 20-25°C) and should therefore be corrected when field temperature (t_{FIELD}) is different.
Pesticides may be broken down also below the plough layer, by (bio)chemical processes. This can be modelled in the easiest way by assuming first order decay similar to radionuclides, and an equal (bio)degradation rate for the adsorbed and dissolved fraction:

$$C_t = C_0 e^{-\lambda_B t_{H2O} R_{OMP}} = C_0\ 2^{\frac{-t_{H2O} R_{OMP}}{T½}} \qquad (6\text{-}16)$$

where: λ_B = decay constant of OMP during (bio)degradation [1/d]; T½ = half-life due to (bio)degradation = ln(2) / λ_B [d]; R_{OMP} = retardation factor for OMP according to Figure 6-15.

For a retarding and (bio)degrading compound in the output from a well in zone 2, Eq.6.10 transforms into:

if $t - (R_U t_U + R_1 t_1) \leq 0$ $\quad C_t = 0$

else : $$C_t = \frac{C_{IN,2}}{2^{R_2 t_2 / (T½)_2}} \left(1 - e^{\frac{-R\,(t - R_U t_U - R_1 t_1) R_2}{D_2 n_2}}\right) \qquad (6\text{-}17)$$

with: $$C_{IN,2} = \frac{C_{IN}}{2^{\frac{R_U t_U}{(T½)_U} + \frac{R_1 t_1}{(T½)_1}}}$$

where: $C_{IN,2}$ = average input concentration for saturated aquifer (zone 2) since abrupt pollutant breakthrough [%]; R = groundwater recharge [m/d]; R_U, R_1, R_2 = retardation factor for pollutant in unsaturated zone, aquitard (zone 1) and aquifer (zone 2), respectively [-]; $(T½)_2$ = half-life of pollutant in aquifer (zone 2) [d].

Half-lives strongly depend on the conditions in the aquifer, especially the redox conditions and temperature, but also the clay (lutum) content, pH and soil moisture content play a role. The effect of redox conditions is shown for a selection of 28 OMPs as function of the 3 main redox zones in Figure 6-18.

Tabulated T½ values refer to a specific temperature setting (t_{EXP}) and should therefore be corrected when extrapolated to a different environmental temperature (t_{FIELD}). This can be done by replacing the reaction rates r_{T1} and r_{T2} by $T½_{T2}$ and $T½_{T1}$ respectively, in the Arrhenius equation.
Half-lives obtained from the literature require serious inspection of the conditions in the field or lab under which they were determined. An interesting example of a pesticide for which strongly diverging and misleading half-lives were obtained, is the anionic, nonsorbing herbicide bentazone ($C_{10}H_{12}N_2O_3S$). In (sub)oxic up to deeply anoxic, natural groundwater and MAR systems in the Netherlands, bentazone has been observed to be one of the most persistent and omnipresent pesticides (this chapter). Nevertheless, many authors mention short half-lives in (sub)oxic environment, e.g. 14-60 d (Hopman et al. 1990), <30 d (Eureco 1990), and 1-2 d (Bosma et al. 1996). These values could be true for the unsaturated upper soil of cultivated land, but certainly are false for groundwater. Even in oxic slow sand filters, bentazone was not removed at all (Hrubec et al. 1991).

TRANSATOMIC.xlsx
TRANSATOMIC (version 1.3) is the acronym for TRANS Aquifer Transport Of MICropollutants. With TRANSATOMIC concentration changes are calculated with analytical solutions, for trace elements, radionuclides and organic micropollutants during aquifer passage and, if applicable, also during detention in a spreading basin or fluvial compartment prior to infiltration (Stuyfzand 2012). The processes addressed include volatilization, photolysis, filtration, advection, dispersion (+ diffusion), linear sorption and first order decay (by either radioactive decay or biodegradation), in a hydrologically stationary situation.
The following input signals are included: step, pulse, peak, sinusoidal (Figure 6-16), and any shape (but then with dispersion simplified). The output consists of a concentration-time plot at a specific distance, or a concentration-distance plot at a specific time, or a table giving quantitative information on the behaviour of various micropollutants for a given set of conditions.

Transport is calculated on a flow tube basis, which can be parallel (uniform) or radial. By defining a representative number of flow tubes and also assigning their individual flux contribution (using the HRC), the system's mixed output can be calculated. Parts of the model have been validated against a finite element model comparable to PHREEQC (which is less user-friendly), while other parts have been successfully applied to various test data sets.

TRANSATOMIC.xlsx facilitates a tiered approach for studying aquifer transport behaviour. The first tier (→ § 6.8) could be with a step input (0 to 100%) without dispersion for a single flowline (Figure 6-16), departing from a line source such as an AR basin, an RBF system or an infiltrating water course to a row of wells or a drain parallel to the banks. The second tier (→ § 6.9) could be with a step input without dispersion for a single flowline àn d for the whole well field, with an unsaturated zone on top of an aquitard and an aquifer below. The third tier (→ § 6.10) could be a pulse input with dispersion, in the line source setting as above.

And the fourth (→ § 6.11) could consist of a reconstructed generalized pesticide input curve, (simplified) dispersion àand aquifer leaching resulting in a downward shift of the (sub)oxic zone.

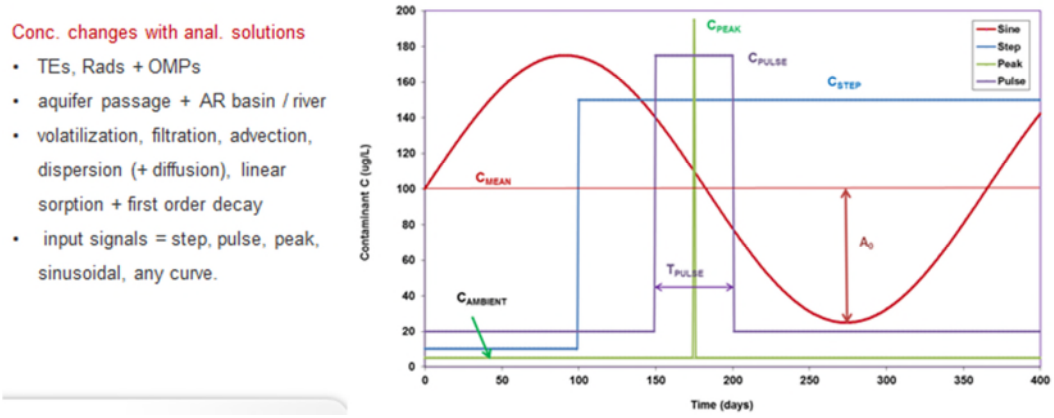


FIGURE 6-16. Schematic of the 4 main input signal types that can be addressed by TRANSATOMIC.xlsx (Stuyfzand 2016).

6.9 Modelling example of first tier: n pesticides from a line source

As the first tier, the behaviour is predicted for 5 pesticides with a step input from 0 to 100% without dispersion, in a steady, uniform flow system between a recharge basin and its recovery at 120 m distance with 120 days transit time in the mainly anoxic aquifer. The sandy system is without unsaturated zone, without aquitard, with f_{OC} = 0.001, porosity 0.38 and pH=7.5.

The results of calculation are shown in Figure 6-17. Differences in half-life and retardation factor clearly explain the differences in breakthrough time (0.33-55 year) and final breakthrough level (0-98%). The results match more or less the observations in AR systems, but recent concentration levels are often too low to detect the patterns calculated.

Anoxic vH2O = 1 m/d
Condition = breakthrough can be infinitesimal

Total distance = 120 m
Condition = given enough time for breakthrough

t since inf	ΔX = front distance in aquifer [m]				
year	AMPA	benta-zone	HCB	dimeth omorph	isopro-turone
T1/2 [d]	19	4400	8356	100	7
R	1.0	1.0	169	3.2	2.8
0.01	4	3.65	0.02	1.14	1.30
0.03	11	11	0	3.4	3.91
0.06	22	22	0	6.8	7.83
0.1	37	37	0	11	13.04
0.15	55	55	0	17	19.57
0.25	91	91	1	29	32.61
0.5	183	183	1	57	65.22
0.75	274	274	2	86	97.83
1	365	365	2	114	130.45
2	730	730	4	228	260.89
3.5	1278	1278	8	399	456.56
5	1826	1826	11	571	652.23
8	2922	2922	17	913	1043.57
9	3287	3287	19	1027	1174.02
10	3652	3652	22	1141	1304.46
17	6209	6209	37	1940	2217.6
20	7305	7305	43	2283	2609
30	10957	10957	65	3424	3913
40	14609	14610	87	4566	5218
50	18262	18262	108	5707	6522
75	27392	27394	162	8561	9783
100	36523	36525	217	11414	13045
120	43828	43830	260	13697	15654
200	73046	73050	433	22828	26089
500	182615	182624	1083	57070	65223
1000	365231	365249	2166	114141	130446

Dist X	$C_{X\text{-}max}$ = activity [% CIN]				
m	AMPA	benta-zone	HCB	dimeth omorph	isopro-turone
T1/2 [d]	19	4400	8356	100	7
R	1.0	1.0	169	3.2	2.8
0.01	100	100	100	100	100
0.03	100	100	100	100	99
0.06	100	100	100	100	98
0.1	100	100	100	100	97
0.15	99	100	100	100	96
0.25	99	100	100	99	93
0.5	98	100	99	99	87
0.75	97	100	99	98	81
1	96	100	99	98	76
2	93	100	97	96	57
3.5	88	100	95	93	38
5	83	100	93	90	25
8	75	100	89	84	11
9	72	100	88	82	8
10	69	100	87	80	6
17	54	100	79	69	1
20	48	100	76	64	0
30	33	100	66	51	0
40	23	99	57	41	0
50	16	99	50	33	0
75	6	99	35	19	0
100	3	98	25	11	0
120	1	98	19	7	0
200	0	97	6	1	8E-23
500	0	92	0	0	6E-59
1000	0	85	0	0	0

Distance [m]	Arrival in recovery [year]				
120	0.33	0.33	55.4	1.05	0.92

If tR / T1/2 > 300 then act = 0
= radionuclide or OMP in recovery

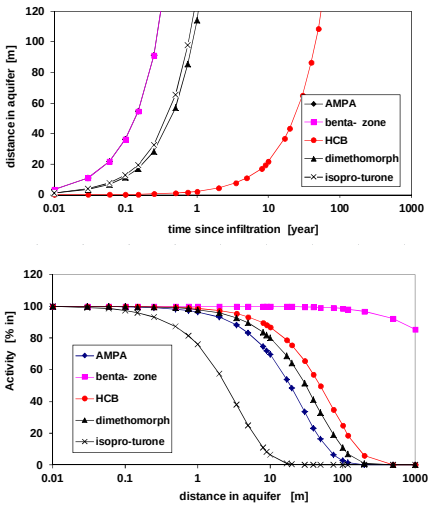


FIGURE 6-17. TRANSATOMIC predicted behaviour of 5 pesticides, with a step input from 0 to 100% without dispersion, in an anoxic AR system with recovery at 120 m distance and 120 days transit time in the aquifer. The upper plot is based on the data in the left table, the lower plot on the right table.

6.10 Modelling example of second tier: n pesticides towards a well field

As the second tier, the behaviour is predicted for a number of pesticides and metabolites with a step input (0 to 100%) without dispersion, for a single flowline (Figure 6-18) and for an entire well field (Fig.6-19; assuming a uniform pesticide application in the whole groundwater catchment area), with an unsaturated zone on top of an aquitard and an aquifer below. Flow is steady, uniform and vertical in the unsaturated zone and aquitard, but steady, radial and subhorizontal in the aquifer.

Single radial flowline towards well field

The results for a single flow line starting at ground level at 400 m from the well field and terminating in the central well, are shown in Figure 6-18, for 28 pesticides and metabolites. The conditions of the porous medium (very poor sands), infiltration water (TOC, DOC and pH), and hydrology are defined as indicated in Figure 6-18. The initial part of the flowline is in the (sub)oxic unsaturated zone (vertical, parallel), followed by a (sub)oxic aquitard (vertical, parallel) and anoxic aquifer (subhorizontal, radial) as depicted in Figure 6-12.
We conclude the following from Figure 6-18:

- aldicarb sulfoxide, metformin, methyldesphenylchloridazone and DMS show conservative behaviour (R=1, $T½ = 10^{99}$), so that they arrive with concentration 100% after 13 years (the travel time of the water) in the pumping well;
- other pesticides and metabolites that survive the underground passage to the well, are bentazone (79%), mecoprop (62%) and desphenyl chloridazone (7%). They show no retardation but some (bio)degradation;
- all other pesticides and metabolites do arrive in the well after 13-1649 years, but in negligible concentration (10^{-300} up to 10^{-3} %) due to rapid (bio)degradation or significant retardation combined with slower (bio)degradation;
- the above conclusions strongly rely on the conditions, of which the half-lives are the most uncertain.

Note that dispersion has been neglected and that only the defined flow line has been considered. It is calculated with Eq.6-9, that the studied flowline enters the well at 3.5 m below the aquifer top (which equals the top of the well screen).

Output from well field

For the well (field) where many flowlines mix, the breakthrough of 2 persistent pesticides (bentazone and mecoprop), 2 metabolites (desphenyl chloridazone and DMS) and 1,2-chloropropane (1,2-DP) is shown in Figure 6-19, based on the scenario defined in Figure 6-18 and based on calculations using Eq.6-17.

These compounds have in common that they are hardly/not retarded anywhere, and hardly/not degraded in the (sub)oxic zones (unsaturated zone and aquitard). The breakthrough starts after 33-42 years and is practically completed within about 700 years.

The situation as defined in Figure 6-18, is analogous to the situation of well field Noordbargeres (Drenthe).

N.B.: Yellow cells = input; All other cells = do not change, because output or text.

			Oxic unsaturated zone		Suboxic saturated zone		Anoxic saturated zone	
Porous medium	porosity [n]	soil moisture content θ [m3/m3] 0.15	0.38		0.3		0.35	
	rho solids [kg/L]	thickness full capil. fringe c [m] 0.4	2.65		2.65	Set D = 0, if zone is lacking	2.65	
	fOC= fraction organic carbo	0.1% = 0.001	0.001		0.0005		0.0005	
	D = thickness [m]	thickness unsaturated zone h [m]	7.4		29.6		95	
Infiltration water	DOC after inf [mg/L]	redox: fill in 1,2 or 3	10	redox: fill in 1,2 or 3	3.4	redox: fill in 1,2 or 3	3	
	TOC prior to inf [mg/L]	1	10	1	4.2	2	3	
	DOC/TOC prior to inf [-]	suboxic	1	suboxic	1	anoxic	1	
	pH-inf		5.0		6.0		6.7	
Hydrology	travel time H2O to wells(s) [tH2O	R [m/a] 0.3	1536	4.2 a	1737	4.8 a	1509	4.1 a
	Q_{OUT} well (field) [m3/h]	PV = Pore volume = T_{TOT} / t_{H2O}					470.0	
	Dist. site to well [m]	PV_C = PV contaminant = T_{TOT} / (t_{H2O} R_{OMP}); vertical piston flow		vertical piston flow		Radial, subhorizontal to PSWF	400	2091 = r [m]
	time since step input [a]	Ttot	45.00	16436 d	45.00	16436 d	45.00	16436 d

OMP abbrev.	OMP in full	OMP type	Koc calc	pKa	T1/2 [d] suboxic	T1/2 [d] anoxic	T1/2 [d] deeply anoxic	Oxic unsat. R_{OMP}	Front [m] after 45.00 a	PV_C [n] bottom unsat.	C_{IN} %	if PV_C ≥1 C_{OUT} %	Suboxic sat. R_{OMP}	Front [m] after 45.00 a	PV_C [n] bottom suboxic	C_{IN} %	if PV_C ≥1 C_{OUT} %	Anoxic sat. R_{OMP}	Front [m] after 45.00 a	PV_C [n] pumping well(s)	C_{IN} %	if PV_C ≥1 C_{OUT} %	Total tEQ PV_C =1 year
1,1,1-TE	1,1,1-trichloroethane	pesticide	177.8	99.0	273	560	4	1.8	>7	6.0	100.00	0.10	1.5	>37	3.0	0.10	0.00	1.4	>437	2.2	0.00	0.00	20.75
1,2-DEY	1,2-dichloorethylene	pesticide	150.0	99.0	28	720	720	1.6	>7	6.5	100.00	0.00	1.5	>37	3.2	0.00	0.00	1.4	>437	2.3	0.00	0.00	19.55
BAM	2,6-dichlorobenzamide	metabolit	33.0	99.0	35	660	1.E+99	1.1	>7	9.4	100.00	0.00	1.1	>37	4.5	0.00	0.00	1.1	>437	3.1	0.00	0.00	14.51
aldicarb-sulf	aldicarb-sulfoxide	metabolit		99.0	1.E+99	1.E+99	1.E+99	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.4	100.00	100.00	13.09
AMPA	aminomethylphosphonic ac	metabolit	0.0	99.0	37	19	9	1	>7	10.7	100.00	0.00	1.0	>37	5.0	0.00	0.00	1	>437	3.4	0.00	0.00	13
atrazine	atrazine	pesticide	70.8	1.7	140	20	10	1.0	>7	10.7	100.00	0.05	1.0	>37	5.0	0.05	0.00	1.0	>437	3.4	0.00	0.00	13.09
bentazone	bentazone	pesticide	0.3	2.9	1.E+99	4400	2200	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.4	100.00	78.84	13.09
bromacile	bromacile	pesticide	72.0	99.0	180	1.E+99	1.E+99	1.3	>7	8.2	100.00	0.04	1.2	>37	4.0	0.04	0.00	1.2	>437	2.8	0.00	0.00	16.19
carbendaz	carbendazim	pesticide	36.3	99.0	1.E+99	25	13	1.2	>7	9.2	100.00	100.00	1.1	>37	4.4	100.00	100.00	1.1	>437	3.1	100.00	0.00	14.66
chloridazo	chloridazone	pesticide	161.8	3.4	35	50	1.E+99	1.0	>7	10.5	100.00	0.00	1.0	>37	5.0	0.00	0.00	1.0	>437	3.4	0.00	0.00	13
D-chlorida	desphenylchloridazone	metabolit		99.0	1.E+99	400	200	1	>7	10.7	100.00	100.00	1	>37	5.0	100.00	100.00	1	>437	3.4	100.00	7.31	13
DEET	diethyltoluamide	metabolit	151.4	99.0	50	50	1.E+99	1.7	>7	6.5	100.00	0.00	1.5	>37	3.2	0.00	0.00	1.4	>437	2.3	0.00	0.00	19.61
Na-dikegul	dikegulac sodium	pesticide	2.9	99.0	195	1.E+99	1.E+99	1.0	>7	10.6	100.00	0.40	1.0	>37	5.0	0.40	0.00	1.0	>437	3.4	0.00	0.00	13.22
dimethomo	dimethomorph	pesticide	459.2	99.0	1.E+99	100	50	3.0	>7	3.6	100.00	100.00	2.4	>37	1.9	100.00	100.00	2.1	>437	1.4	100.00	0.00	32.86
dinoseb	dinoseb	pesticide	4140.1	5.0	123	10	5	9.9	>7	1.1	100.00	0.00	2.2	32.0	0.9	0.00	0.00	1.2	32.0	0.1	0.00	0.00	56.94
dinoterb	dinoterb	pesticide	1908.7	4.8	10	1.E+99	1.E+99	4.2	>7	2.6	100.00	0.00	1.4	>37	1.9	0.00	0.00	1.1	>437	1.6	0.00	0.00	28.41
diurone	diurone	pesticide	354.8	2.2	240	25	13	1.0	>7	10.7	100.00	1.17	1.0	>37	5.0	1.17	0.01	1.0	>437	3.4	0.01	0.00	13.10
glyphosate	glyphosate	pesticide	24.9	99.0	96	22	1.E+99	1.1	>7	9.7	100.00	0.00	1.1	>37	4.6	0.00	0.00	1.1	>437	3.2	0.00	0.00	14
HCB	hexachlorobenzene	pesticide	4.0E+04	99.0	986	8356	2557	160.4	0.5	0.1	100.00	0.00	120.8	0.5	0.0	0.00	0.00	96.7	0.5	0.0	0.00	0.00	1649
HCbuta	hexachlorobutadiene	pesticide	5011.9	99.0	183	112	720	22.5	3.5	0.5	100.00	0.00	16.4	3.5	0.1	0.00	0.00	13.3	3.5	0.0	0.00	0.00	227.58
isoprot	isoproturone	pesticide	421.9	99.0	23	986	1.E+99	2.8	>7	3.8	100.00	0.00	2.3	>37	2.0	0.00	0.00	2.0	>437	1.44	0.00	0.00	31.25
HCH-g	lindane	pesticide	1995.3	99.0	240	7	4	9.6	>7	1.1	100.00	0.00	7.2	22.4	0.6	0.00	0.00	5.9	22.4	0.05	0.00	0.00	98.80
MCPP	mecoprop	pesticide	1.3	3.8	1.E+99	2200	1100	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.44	100.00	62.15	13.10
metformin	metformin	pesticide	100.0	2.8	1.E+99	1.E+99	1.E+99	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.43	100.00	100.00	13.11
MD-chlorid	methyl-desphenylchloridaz	metabolit		99.0	1.E+99	1.E+99	1.E+99	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.44	100.00	100.00	13.09
DMS	n,n-dimethylsulfamide	metabolit		99.0	1.E+99	1.E+99	1.E+99	1.0	>7	10.7	100.00	100.00	1.0	>37	5.0	100.00	100.00	1.0	>437	3.44	100.00	100.00	13.09
o-chloroan	o-chloroaniline	metabolit	100.0	2.7	50	1.E+99	1.E+99	1.0	>7	10.7	100.00	0.00	1.0	>37	5.0	0.00	0.00	1.0	>437	3.43	0.00	0.00	13.10
simazine	simazine	pesticide	131.8	1.7	90	10	5	1.0	>7	10.7	100.00	0.00	1.0	>37	5.0	0.00	0.00	1.0	>437	3.44	0.00	0.00	13.10

FIGURE 6-18. TRANSATOMIC predicted behaviour of selected pesticides and metabolites along a single flowline, after first passing the oxic unsaturated zone, then the (sub)oxic saturated zone, and finally the anoxic saturated zone, where pumped out by a well. Dispersion neglected, step input (0 to 100%). Input concentration (C_{IN}) for unsaturated zone is output upper soil (plough layer, set at 100%), for suboxic saturated zone it is the output unsaturated zone (C_{OUT}), and for anoxic saturated zone it is the output from the suboxic saturated zone.
Output concentrations for each zone are given with respect to input from plough layer, and refer to moment when PV_C = 1 (i.e. when contaminant reached output). Position of contaminant front after time since step input (t_{TOT}=45 year) is indicated for each zone (>values = zone fully passed), giving the cumulative distance up to each zone. The number of pollutant pore volumes (PV_C), between input point and zone exit point is also indicated (<1 meaning not reached yet). The right most column shows when the contaminant reaches the well (field), i.e. the number of years for PV_C to become 1.0.

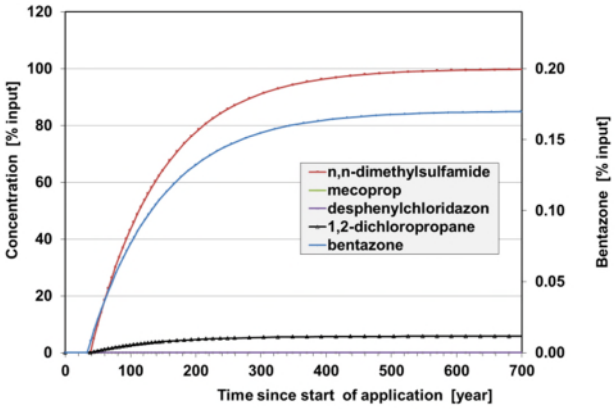


FIGURE 6-19. TRANSATOMIC predicted breakthrough of 2 persistent pesticides, 2 metabolites and 1,2-dichloropropane, based on the scenario defined in Figure 6-18 (step input 0 to 100%) and based on calculations using Eq.6-17. Breakthrough holds for the abstracted groundwater by the well (field).

It is calculated with Eq.6-9, that the not retarded pesticides introduced 45 years ago at 400 m distance from the well (field), must have reached a depth in the well (field) of 3.5 m below the aquifer top, which is equal to 40.5 m below ground level. For the well field as a whole, the maximum depth d_2 can be calculated by taking:

$$d_2 = D_2(1 - e^{\frac{-R\,(t - R_U t_U - R_1 t_1) R_2}{D_2 n_2}}) \qquad (6\text{-}18)$$

Inserting t=45 years yields d_2 = 9-11 m, corresponding with 46-48 m below ground level.

These calculations approximate what has been measured around well field Noorbargeres, where several pesticides and metabolites reached the indicated depth level (also in the pumping wells), but still are strongly diluted in the abstracted water by older unpolluted groundwater. Concentrations are therefore expected to rise.

6.11 Modelling example of third tier: a pesticide pulse, with dispersion

As the third tier, the behaviour is predicted for just one pesticide with a pulse input (0 to 100% back to 0%), with dispersion, for a single flowline (Figure 6-16) between a row of recovery wells parallel to the infiltrating water course. The analytical solution is based on the steady, uniform flow equation of Van Genugten & Alves (1982), however with incorporation of retardation and first order decay. Further scenario details are given in Figure 6-20, together with the resulting concentration plot as function of flow distance in the homogeneous aquifer at 4 specified times.

Along the 120 m long flowline the modeled dimethomorph pulse of 28 days in the infiltrating water course is clearly attenuated by dispersion, delayed by retardation and further reduced by (bio)degradation. In the well field at 120 m distance, the modeled dimethomorph pulse of 28 days in the infiltrating water course is further attenuated by mixing of fast with slow flowlines (Fig.6-21). The 28 days pulse is thereby reduced from 100 to maximum 0.5% while taking about 1 year to dissappear.
Short peaks of pesticide with a significant retardation and relatively short half-life are thus hardly visible in the mixed output of an AR or RBF well field. This is confirmed by practice.

with:		*Peak*	
C_{PEAK}	single peak concentration input	C_{PEAK}	100
C_{BL}	baseline concentration [mg/L]	$C_{BASELINE}$	0
t	time since start [d]		
T	Pulse duration [d]	T_{PEAK}	28
		Flow system	
$D = \alpha_L v_C + D_d/n$	longitudinal dispersion coefficient [m2/d]	D [m2/d]	0.4348879
n	effective porosity	n_E	0.38
α_L	longitudinal dispersivity [m]	α_L [m]	1
X	travel distance in aquifer [m]		
v_W	migration velocity of H2O or tracer [m/d]	v_W	1
v_C	migration velocity of contaminant [m/d]	v_C	0.4347826
D_d	Diffusion coefficient (m2/d)	D_d (m2/d)	0.00004
R	Retardation coefficient pollutant	R	2.3
T½	Half life [d]	T½	100

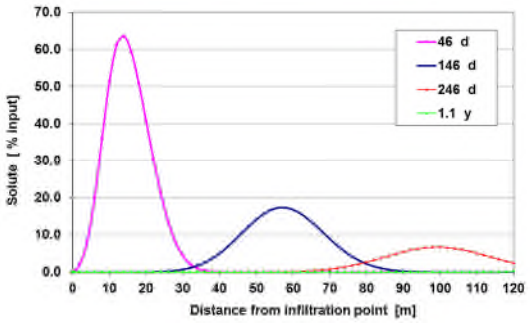


FIGURE 6-20. TRANSATOMIC predicted propagation of a dimethomorph pulse of 28 days through an anoxic homogeneous sandy aquifer towards a well at 120 m distance.

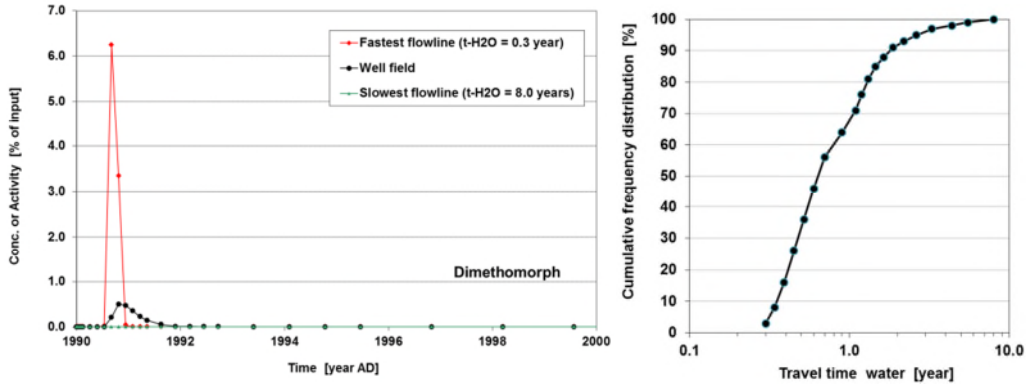


FIGURE 6-21. TRANSATOMIC predicted breakthrough of a dimethomorph pulse of 28 days through an anoxic homogeneous sandy aquifer towards a well field at 120 m distance with indicated HRC.

6.12 Modelling example of fourth tier: expanding (sub)oxic redox zone

The last tier consists of predicting the output of a well field with a reconstructed generalized pesticide input curve, simplified dispersion ànd aquifer leaching resulting in a downward shift of the (sub)oxic zone with consequences for the biodegradation rate. Essential is to know the hydrological response curve (HRC) of the well field, the depth of the redox boundary (between (sub)oxic and anoxic in this case) at a specific time (time of hydrogeochemical survey), and the velocity of the downward shift of this boundary (as deduced from the downward NO_3 front displacement or from a mass balance calculation). For details about this, see Stuyfzand (2015).

It is assumed that the retardation factor R_C be constant along each of the 100 flowlines, and in this case v_{H2O} = 1 m/d and the redox front displacement 0.1 m/year.

The concentration trend is calculated by averaging for each year the calculated ouput concentration for each of the 100 flowlines, which match the 100 percentiles of the HRC:

$$C_{HRC,y} = 0.01 \left\{ \begin{matrix} (C_{IN,y-R_C t_1}) 2^{-R_C(t_{1A}/T½_{1A} + t_{1B}/T½_{1B})} + \dots \dots \dots \\ . + (C_{IN,y-R_C t_{100}}) 2^{-R_C(t_{100A}/T½_{1A} + t_{100B}/T½_{1B})} \end{matrix} \right\} \quad (6.19)$$

$$t_{XA} = A + (t_y - t_{START})\, v_L / v_{H2O} \quad \text{[year]} \quad (6.20)$$

$$t_{XB} = t_X - t_{XA} \quad \text{[year]} \quad (6.21)$$

where: $C_{HRC,y}$ = with HRC predicted mean concentration of contaminant C for well field during year y; $(C_{IN,y\text{-}RCt1})$ = concentration of contaminant C in input for percentile 1 during year y minus $R_C t_1$ years; R_C = retardation factor for contaminant C along entire flowline [-]; t_X, t_{XA} , t_{XB} = total travel time to well field for percentile X according to HRC, the first part of it (up to redox boundary), and remaining part to well field,respectively [year]; $T½_{1A}$, $T½_{1B}$ = half-life of contaminant C, for section A (1st part of flowline) and section B (remaining part of flowline) [year]; A = mean travel time from ground surface down to redox boundary in aquifer zone A [year]; t_y = year for which t_{XA} is determined; t_{START} = year of hydrogeochemical sampling on which redox front position was determined; v_L = leaching rate as determined by NO_3

propagation or mass balance; v_{H2O} = mean vertical flow velocity of groundwater in aquifer zone A [year].

This way, each year after t_{START} the travel time in the (sub)oxic zone (t_{XA}) increases at the expense of the travel time in the anoxic zone (t_{XB}). Dispersion has been taken into account very roughly by calculating the centralized 5 years moving average of annual mean input concentrations. This aspect still needs to be refined.

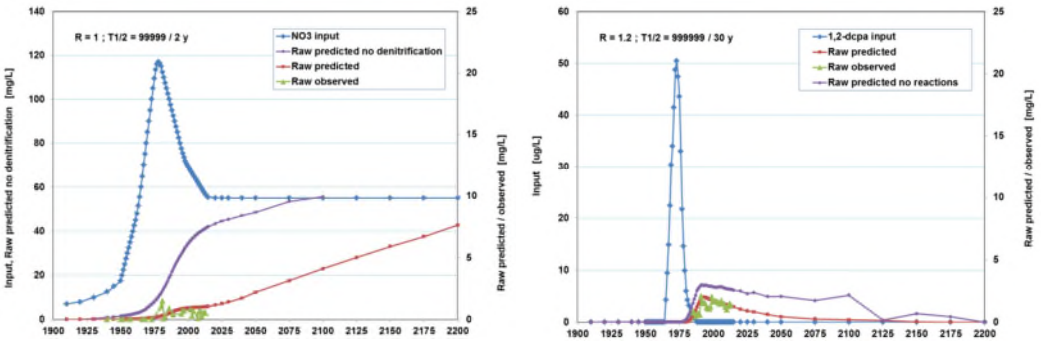


FIGURE 6-22. Concentration trends for NO_3 (left) and 1,2-dichloropropane (right), including their reconstructed input, the observed values in the output (raw water well field Noordbargeres) and the TRANSATOMIC predicted output based on yes and no reactions (denitrification and biodegradation resp.) and the tritium calibrated HRC. Predictions assume leaching leads to a redox boundary above which no denitrification occurs, and below which T½ = 2 years for NO_3. Redox boundary dropped by 0.1 m / year since 1910. For details see Stuyfzand (2015).

The modelling results are shown for NO_3 and 1,2-dichloropropane (an impurity in the herbicide 1,2-chloropropene) in Figure 6-22. They illustrate the importance of denitrification for the NO_3 prediction, and the improved prediction of 1,2-dichloropropane by incorporating the slowly expanding (sub)oxic zone.

6.13 Summary and conclusions

In this chapter, the data on groundwater collected in 2010-2014 (and some earlier data) have been explored, and a new, tiered modelling approach of pesticide behaviour in groundwater catchment areas has been presented. The huge data base (with 143,500 samples from public supply catchment areas) comprised groundwater from monitoring wells (GWO), pumping wells (GWP), drains (DR), public supply well fields (GWR) and surface water taken in for AR, and with different groundwater origins (local groundwater = G, river bank filtrate = RBF, artificially recharged water = AR).
The 321 pesticides that were never detected (<MDL = <Minimum Detection Limit) were excluded, leaving 155 pesticides and 16 metabolites to focus on.

It is concluded that BAM, bentazone, desphenyl chloridazone and DMS are the most frequently detected (in 32-53% of all samples), followed by AMPA, dikegulac, isoproturone and mecoprop (in 6-11% of all samples). There is a significant difference between autochthonous groundwater (G) and infiltrated surface waters (AR and RBF). Pesticides are more uniformly present and less retained in AR and RBF systems than in groundwater systems.

There are distinct differences in maximum depth reached, from deep to shallow: bentazone (125 m) > dinoterb (100 m) > dikegulac (90 m) > BAM, chloridazone, desphenyl chloridazone

(80 m) > mecoprop (70 m) > glyphosate (65 m) > DMS (40 m). These great depths are surprisingly high, testifying of little or no retardation, hardly any (bio)degradation, and prolonged application. For most pesticides and metabolites the greatest depths are observed in pumping wells (GWP), which pull down the young polluted groundwater, not in observation wells.

The search for significant relations between main constituents and pesticides yielded disappointing results, even after separating the origins (G, AR, RBF). The main problems with huge, mixed data populations are that (i) the older, deeper groundwater samples are often too old to possibly contain pesticides, (ii) non synchronosity of trend reversals blurs the relations, and (iii) further a priori subdivisions are needed to separate e.g. infiltrated Rhine River from infiltrated Meuse River water and areas with specific agricultural activities. Nevertheless, the data indicate that AMPA, BAM, bromacil, diurone, glyphosate and DMS survive better in a (sub)oxic environment, and 2-chloroaniline and chloridazone in an anoxic environment. Also, significant linear correlations of the top 20 pesticides incl. metabolites with main constituents were occasionally found for NH_4, PO_4, redox level, NO_3, DOC and Cl/Br. These relations require further investigation.

Compared to RBF, AR systems showed on average a lower detection frequency mostly with a lower concentration while all maxima remained below the drinking water standards. The better quality of AR systems compared to RBF systems is mainly thanks to the selective intake, pretreatment, detention time in basins and more aerobic aquifer passage.
The removal performance of the AR systems (corrected for admixing of dune water) was for most pesticides / metabolites >64%. The highest removal rate (with a high confidence level) was observed for AMPA, DEET, glyfosate and isoproturone (>96% removal), the lowest for desfenylchloridazone (6%) and BAM (47%). The deduced half-lives with a high confidence level, for AMPA, carbendazim and diurone fit best with the indicated literature data for anoxic or partly (sub)oxic and anoxic systems. The AR systems are indeed displaying a mainly anoxic facies, although with admixing of (sub)oxic water.

The predominantly (deeply) anoxic RBF systems displayed a predominance of the following pesticides: bentazone, chloridazone, desphenyl-chloridazone and 2-chloroaniline. Trends in the concentration of bentazone and dikegulac in 1994-2006 showed a declining trend in Schuwacht, a well field with relatively short travel times (1.8-3.8 year), and an increasing trend for De Laak, a well field with relatively long travel times (32-200 year).

Pesticide data on flow line scale since the 1980s have been evaluated for AR and RBF systems, based on surface water input and infiltrated water as sampled from monitoring wells along various transects. The data reveal that only few pesticides are observed and then at relatively low concentrations. More prominent were bentazone, MCPP and carbendazim, the first 2 in much older, anoxic infiltrate, demonstrating their resistance against (bio)degradation and reflecting a declining input trend. Carbendazim was mainly present in (sub)oxic infiltrated water, and rapidly degraded in anoxic environment with T½ = ~25 d.

Modelling of pesticides in the groundwater compartment starts with setting the input equal to the output from the upper 1 meter arable soil (to be derived from other models such as Geopearl), and assuming (i) sorption to be linear and immediate, and (ii) (bio)degradation to follow first order decay as function of 3 redox classes ((sub)oxic, anoxic and deeply anoxic). The modelling was done with TRANSATOMIC.xlsx, to analytically model the TRANS Aquifer Transport Of MICropollutants. For this project the model was extended to also include (next to uniform flow) predictions for a whole well field, where flow is assumed vertical and

parallel in both the unsaturated zone and upper aquitard, but horizontal and radial in the aquifer below.

With TRANSATOMIC.xlsx a tiered approach is offered for studying aquifer transport behaviour. This is demonstrated for pesticides in 4 tiers of increasing complexity. The first is a simple step input (0 to 100%; example with 5 pesticides) without dispersion for a single flowline, departing from a line source such as an AR basin, RBF system or infiltrating water course towards a row of wells or a drain parallel to the banks. The calculated differences between pesticides match various observations.

The second tier is a step input (example with 28 pesticides incl. metabolites) without dispersion for any single flowline ànd for a whole well field, with an unsaturated zone on top of an aquitard and the aquifer below. This approach yields a first estimate of those pesticides that may reach the well (field) with which retardation and biodegradation. This provides an interesting rapid screening tool for admission of pesticides in addition to models that test for behavior within the plough layer (above the groundwater compartment).

The third tier is a pulse input (example 28 days) with dispersion, in the line source setting as for tier 1. It shows that for instance a 28 days pulse can still be noticed along a 120 m long single flowline, but reduces to <1% when mixed with other flowlines in a well field.

And the fourth tier is a reconstructed generalized NO_3 and pesticide input curve, with (simplified) dispersion ànd aquifer leaching resulting in a downward shift of the (sub)oxic zone. They illustrate the importance of denitrification for the NO_3 prediction, and the improved prediction of 1,2-dichloropropane by incorporating the slowly expanding (sub)oxic zone.

The added value of TRANSATOMIC and its tiered approach is, that (i) in one Excel program a tool box is offered for several scenario's of varying complexity, (ii) these tools are really easy to use, and (iii) they generate in some cases direct answers for a multitude of pesticides (and other dissolved species).

Future research should continue with monitoring of old and new pesticide and metabolite behaviour along well defined flow paths, in G, AR and RBF systems with due attention paid to among others the main redox sensitive species, pH, temperature and EC. For some persistent pesticides and metabolites it could be attempted to date groundwater by correlating peaks in groundwater to (reconstructed) peaks in input. The locations where a worrying great depth penetration of pesticides and metabolites was observed (up to 125 m BLS), should be identified and analyzed for the conditions that facilitated this.

7 Conclusions

In 67% of the 221 abstraction areas covering groundwater and surface water bodies in the Netherlands, pesticides have been detected. 65 pesticides and 6 metabolites were prioritized based on the extensive dataset (4,176 sampling sites over 2010-2014) according to their presence in drinking water or their presence in drinking water sources in 90 percentile concentrations above the drinking water quality standard of 0.1 µg/L (1 µg/L for human toxicological non-relevant metabolites). Dependent on the local land-use, soil and water system characteristics these compounds are relevant for uptake in monitoring programs. Examples of pesticides that were present in drinking water are: growth regulator dikegulac, the herbides glyphosate, bentazone, glufosinate-ammonium, bromacil, the fungicide dimethomorf and the insecticide oxamyl. Examples of pesticides that have exceeded the threshold of 0.1 µg/L in drinking water sources are the herbicides MCPA, MCPP, terbutylazine, isoproturon and the fungicides etridiazole and tolclofos-methyl. A large part of the monitored pesticides however have no priority for extensive further monitoring according to their concentrations below 1/10th the drinking water standard or below the detection limit. These compounds have recently no priority for uptake in intensive monitoring programs; however, it is recommended to monitor these compounds with low frequency (once in five years).

There is a significant difference between detected pesticide concentrations in autochthonous groundwater (G) and infiltrated surface waters (AR and RBF). Pesticides are more uniformly present and less retained in artificial recharge (AR) and river bank filtrate (RBF) systems than in groundwater systems. The data indicate that AMPA, BAM, bromacil, diurone, glyphosate and DMS survive better in a (sub)oxic environment, and 2-chloroaniline and chloridazone in an anoxic environment. Also, significant linear correlations of the top 20 pesticides including metabolites with main constituents were occasionally found for NH_4, PO_4, redox level, NO_3, DOC and Cl/Br. These relations require further investigation.

We signalled 50 mobile and persistent recently authorised pesticides on the market since 2005. A novel LC-MS/MS method for the simultaneous detection and sensitive quantification for 24 recently authorized pesticides on the market was developed and validated in drinking- and surface water. More than half of the compounds (15) were detected in 128 samples at locations susceptible for pesticide contamination in The Netherlands and in Belgium. Most compounds have been detected in the surface water samples; only two out of 90 groundwater samples contained recently authorized pesticides. In surface water, six of these pesticides already exceed the drinking water standard of 0.1 µg/L: the herbicide fluxapyroxad, the insecticides thiamethoxam and acetamiprid and the fungicides fluopyram, fluxastrobin and mandipropamid. The insecticide clothianidine, a neonicotinoid insecticide, was detected in groundwater above the drinking water standard of 0.1 µg/L. The analysed recently authorised pesticides detected in the water samples in concentrations above the basic guideline value of 0.1 µg/L, were assessed for human health effects using the value for the acceptable daily intake (ADI).

8 Literature

Adriaanse, 2008. Development of an assessment methodology to evaluate agricultural use of plant protection products for drinking water production from surface waters. Alterra.

Appelo, C.A.J. and D. Postma 2005. Geochemistry, groundwater and pollution. 2nd edition, AA Balkema Publ., Rotterdam, 649p.

Brinkmann, F.J.J., den Engelsman, G., Wammes, J.I.J., Willemsen, W.H., 1995. Metingen van de gehalten aan diaceton-keto-gulonzuur (dikegulac) in grensoverschrijdend rivierwater gedurende het tijdvak 1 oktober 1990 tot en met 30 juni 1994. RIVM, De Bilt, p. 28.

Ctgb, 2014. Evaulation manual for the Authorisation of Plant protection products and Biocides according to Regulation (EC) No 1107/2009. NL part. Plant protection products. chapter 6 Fate and behaviour in the environment: behaviour in surface water and sediment. Version 2.0. .

De la Loma Gonzáles B., K.J. Raat, L.M. Puijker en D. Vughs 2013a. Broad screening of emerging organic contaminants in the Ouddorp artificial recharge system. KWR report BTO 2013.???(s), 43p.

De la Loma Gonzáles B., K.J. Raat, L.M. Puijker en D. Vughs 2013b. Occurrence and fate of (emerging) organic substances in the Scheveningen artificial recharge system. KWR report BTO 2013.233(s), 52p.

Dolan, T., Howsam, P., Parsons, D.J., Whelan, M.J., 2013. Is the EU drinking water directive standard for pesticides in drinking water consistent with the precautionary principle? Environmental Science and Technology 47, 4999-5006.

Dolan, T., Howsam, P., Parsons, D.J., Whelan, M.J., 2014. Impact of European water framework directive article 7 on drinking water directive compliance for pesticides: Challenges of a prevention-led approach. Water Policy 16, 280-297.

Drinkwaterbesluit, 2011.

EC (European Commission), 2005. Review report for the active substance clothianidin. Finalised in the Standing Committee on the Food Chain and Animal Health at its meeting on 27 January 2006 in view of the inclusion of clothianidin in Annex I of Council Directive 91/414/EEC. SANCO/10533/05-Final, 18 January 2005.

EC (European Commission), 2006. Review report for the active substance thiamethoxam. Finalised in the Standing Committee on the Food Chain and Animal Health at its meeting on 14 July 2006 in view of the inclusion of thiamethoxam in Annex I of Council Directive 91/414/EEC. SANCO/10390/2002-rev. Final, 14 July 2006.

EFSA (European Food Safety Authority), 2014. Reasoned opinion on the review of the existing maximum residue levels (MRLs) for clothianidin and thiamethoxam according to Article 12 of Regulation (EC) No 396/2005. EFSA Journal 2014;12(12):3918, 120 pp. doi:10.2903/j.efsa.2014.3918.

EFSA (European Food Safety Authority), 2016. Conclusion on the peer review of the pesticide risk assessment of the active substance acetamiprid. EFSA Journal 2016;14(11):4610,26 pp. doi:10.2903/j.efsa.2016.4610.

EFSA PPR Panel (EFSA Panel on Plant Protection Products and their Residues), 2013. Scientific Opinion on the developmental neurotoxicity potential of acetamiprid and imidacloprid. EFSA Journal 2013;11(12):3471, 47 pp. doi:10.2903/j.efsa.2013.3471.

EFSA Scientific Report (2006) 64, 1-71, Conclusion regarding the peer review of the pesticide risk assessment of the active substance metconazole.

EFSA Scientific Report (2007) 102, 1-84, Conclusion regarding the peer review of the pesticide risk assessment of the active substance fluoxastrobin.

Emke, E., 2007. New pesticides. An anlytical survey. KWR Watercycle Research Institute, Nieuwegein, The Netherlands, p. 78.

European Commision, 2000. EU Water Framework Directive - integrated river basin management for Europe, 2000/60/EC. Brussels, Belgium.

European Commission, 1998. The Drinking Water Directive, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption Brussels, Belgium, pp. 32-54.

European Commission, 2016. EU Pesticide database. Active substances. Reguation (EC) No 1107/2009.

European Food Safety Authority; Conclusion on the peer review of the pesticide risk assessment of the active substance bixafen. EFSA Journal 2012;10(11):2917. [87 pp.] doi:10.2903/j.efsa.2012.2917.

European Food Safety Authority; Conclusion on the peer review of the pesticide risk assessment of the active substance fluxapyroxad (BAS 700 F). EFSA Journal 2012;10(1):2522. [90 pp.] doi:10.2903/j.efsa.2012.2522.

European Food Safety Authority; Conclusion on the peer review of the pesticide risk assessment of the active substance [fluopyram]. EFSA Journal 2013;11(4):3052. [76 pp.] doi:10.2903/j.efsa.2013.3052.

European Food Safety Authority; Conclusion on the peer review of the pesticide risk assessment of the active substance mandipropamid. EFSA Journal 2012;10(11):2935. [76 pp.] doi:10.2903/j.efsa.2012.2935.

European Food Safety Authority; Reasoned opinion on the review of the existing maximum residue levels (MRLs) for fluoxastrobin according to Article 12 of Regulation (EC) No 396/2005. EFSA Journal 2012;10(12):3012. [42 pp.] doi:10.2903/j.efsa.2012.3012.

FOCUS, 2001. FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. In: Scenarios, F.W.G.o.S.W. (Ed.), p. 245.

González-Rodríguez, R.M., Rial-Otero, R., Cancho-Grande, B., Gonzalez-Barreiro, C., Simal-Gándara, J., 2011. A review on the fate of pesticides during the processes within the food-production Chain. Crit. Rev. Food Sci. Nutr. 51, 99-114.

Hamann, E., P.J. Stuyfzand, J. Greskowiak, H. Timmer & G. Massmann 2016. The fate of organic micropollutants during long-term/long-distance river bank filtration. Sci Total Envir. (STOTEN), 545-546, 629-640.

Heuvelink, G.B.M., Burgers, S.L.G.E., Tiktak, A., Den Berg, F.V., 2010. Uncertainty and stochastic sensitivity analysis of the GeoPEARL pesticide leaching model. Geoderma 155, 186-192.

Hopman, R., 1995.

Hopman, R., C.G.E.M. van Beek,H.M.J. Jansen and L.M. Puijker 1990. Pesticides and the drinking water supply in the Netherands. Kiwa Meded. 113, 176p.

Hopman, R., van beek, C.G.E.M., janssen, H.M.J., Puijker, L.M., 1990. Pesticides and the Drinking water Supply in the Netherlands. KIWA.

Kan A.T. and M.B. Tomson, 1990. Ground water transport of hydropho¬bic organic compounds in the presence of dissolved organic matter. Env. Toxicol. and Chem. 9, 253-263

Linders, J.B.H.J., Van der Linden, A.M.A., Stienstra, Y.J., 2010. Surface water intended for the abstraction of drinking water after use of plant protection products on hard surfaces – Evaluation of plant production products. With corrigendum by Van der Linden (2012) RIVM.

Lovley, D.R., Chapelle, F.H., 1995. Deep subsurface microbial processes. Reviews of Geophysics 33, 365-381.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment 473–474, 619-641.

Peters, J.H. 1985. Pesticides in groundwater catchment areas. Kiwa Meded. 95, 142p (in Dutch).

Prommer H., and V.E.A. Post. 2010. A Reactive Multicomponent Model for Saturated Porous Media, Version 2.0, User's Manual, http://www.pht3d.org.

Reemtsma, T., Berger, U., Arp, H.P.H., Gallard, H., Knepper, T.P., Neumann, M., Quintana, J.B., Voogt, P.D., 2016. Mind the Gap: Persistent and Mobile Organic Compounds - Water Contaminants That Slip Through. Environmental Science and Technology 50, 10308-10315.

RIWA, 2016a. De kwaliteit van het Maaswater in 2015. RIWA-Maas.

RIWA, 2016b. Jaarpport 2015. De Rijn. RIWA-Rijn.

Schellenberg K., Leuenberger C., Schwarzenbach R.P.,1984. Sorption of chlorinated phenols by natural sediments and aquifer materials, Environ. Sci. Technol. 18, 652-657.

Schreiner, V.C., Szöcs, E., Bhowmik, A.K., Vijver, M.G., Schäfer, R.B., 2016. Pesticide mixtures in streams of several European countries and the USA. Science of the Total Environment 573, 680-689.

Segers W.C.J. 2006. Vóórkomen en gedrag van geneesmiddelen, röntgencontrastmiddelen, MTBE en enkele prominente organische microverontreinigingen in Rijnoeverfiltraat. Thematic Research MSc program VU University Amsterdam, 101p.

Segers W.C.J. 2007. Vóórkomen en gedrag van 'emerging substances' tijdens duininfiltratie. M.Sc. thesis VU University Amsterdam, 145p.

Sjerps, R.M.A., ter Laak, T.L., Zwolsman, J.J.G., 2016a. Effect van klimaatverandering en vergrijzing op waterkwaliteit en drinkwaterfunctie van Maas en Rijn. Vakblad H2O, 10.

Sjerps, R.M.A., ter Laak, T.L., Zwolsman, J.J.G., 2016b. Ontwikkeling waterkwaliteit bij innamepunten van oppervlaktewater voor de drinkwatervoorziening. KWR Watercycle Research Institute, Nieuwegein, The Netherlands, p. 107.

Smeenk J.G.M.M. 1984. Organische microverontreinigingen en duininfiltratie. In Stuyfzand, P.J. (ed) Microverontreiniging en duininfiltratie. KIWA Meded. 81, 106-216.

Stumm, W., Morgan, J.J., 1996. Aquatic chemistry. Third edition. . John Wiley & Sons, Inc., New York.

Sturm S, J. Kiefer, D. Kollotzek and J.M. Rogg 2010. Aktuelle Befunde der Metaboliten von Tolylfluanid und Chloridazon in den zur Trinkwasserversorgung genutzten Grundwasservorkommen Baden-Württembergs. GWF-Wasser Abwasser Oct.2010, 950-959.

Stuyfzand, P.J. & F. Lüers 1996. Gedrag van milieugevaarlijke stoffen bij oeverinfiltratie en kunstmatige infiltratie; effecten van bodempassage gemeten langs stroombanen. Kiwa-Meded. 125, 272p.

Stuyfzand, P.J. & F. Lüers 2000. Balans van milieugevaarlijke stoffen in natuurterreinen met en zonder kunstmatige infiltratie. Kiwa-Meded. 126, 241p.

Stuyfzand, P.J. 1985. Hydrologie, herkenning en datering van Rijnoevergrondwater. Ch.2 in KIWA Meded. 89.

Stuyfzand, P.J. 1986. Macroparameters bij duininfiltratie ; kwaliteitsveranderingen van oppervlaktewater bij kunstmatige infiltratie in de Nederlandse kustduinen. KIWA-Meded. 82,345 p.

Stuyfzand, P.J. 1989. Hydrology and water quality aspects of Rhine bank ground water in The Netherlands. J. Hydrol. 106, 341-363.

Stuyfzand, P.J. 1991a. Sporenelementen in Rijnoever-grondwater in het rivierengebied. Ch.8 in KIWA-Meded. 118, 129-154.

Stuyfzand, P.J. 1991b. Sporenelementen in duinwater en kunstmatig geïnfiltreerd oppervlaktewater in de kuststreek. Ch.9 in KIWA-Meded. 118, 155-184.

Stuyfzand, P.J. 1993. Hydrochemistry and hydrology of the coastal dune area of the Western Netherlands. Ph.D Thesis Vrije Univ. Amsterdam, published by KIWA, ISBN 90-74741-01-0, http://dare.ubvu.vu.nl/handle/1871/12716, 366 p.

Stuyfzand P.J. 2012. TRANSATOMIC (TRANS Aquifer Transport Of MICropollutants), a computer program set in Excel, for predicting concentration changes with analytical solutions, for trace elements, radionuclides and organic micropollutants during aquifer passage and during detention in a spreading basin or fluvial compartment. Updated in April 2017.

Stuyfzand, P.J. 2015. Model based monitoring van puttenvelden: meetnetoptimalisatie via systeemanalyse en hydrogeochemische modellering, met Noordbargeres als voorbeeld. KWR rapport BTO-2015.021, 127p.

Stuyfzand, P.J., Lüers, F., 1996. Gedrag van milieugevaarlijke stoffen bij oeverinfiltratie en kunstmatige infiltratie. Effecten van bodempassage gemeten langs stroombanen. KIWA, VEWIN.

Swartjes, F.A., Van Der Linden, A.M.A., van Der Aa, N.G.F.M., 2016. Bestrijdingsmiddelen in grondwater bij drinkwaterwinningen: huidige belasting en mogelijke maatregelen. RIVM, p. 124.

Tiktak, A., Boesten, J.J.T.I., Van Der Linden, A.M.A., Vanclooster, M., 2006. Mapping ground water vulnerability to pesticide leaching with a process-based metamodel of EuroPEARL. J. Environ. Qual. 35, 1213-1226.

Van Beek C.G.E.M. 1987. Landbouw en drinkwatervoorziening; oriënterend onderzoek naar de beïnvloeding van de grondwaterkwaliteit door bemesting en het gebruik van bestrijdingsmiddelen. Onderzxoek 1982-1987. Kiwa Meded. 99.

Van der Linden A.M.A., H.F.R. Reijnders, M.C. Zijp and A.M. Durand-Huiting 2007. Residuen van gewasbeschermingsmiddelen in het grondwater. Een analyse voor de KRW. RIVM Rapport 607310001/2007, 56p.

Van der Linden AMA, Uffink GJM. 1999. Dilution of pesticides in groundwater during advective dispersive transport. In: Del Re AAM, Brown C, Capri E, Errera G, Evans SP, Trevisan M (eds). Human and environmental exposure to xenobiotics. Proceedings of the XI Symposium Pesticide Chemistry. September 11 - 15, 1999.

Van der Moot N.L. 2014. Chloridazon-desfenyl in het ruwwater van Gasselte, Noordbargeres en Valtherbos. WMD notitie, 9p.

van Eerdt, M.M., Spruijt, J., van der Wal, E., van Zeijts, H., Tiktak, A., 2014. Costs and effectiveness of on-farm measures to reduce aquatic risks from pesticides in the Netherlands. Pest Management Science 70, 1840-1849.

Van Leerdam, R., Adriaanse, P., 2009. Evaluation of agricultural use of plant protection products for drinking water production from surface waters in the Netherlands - User□s manual of DROPLET to calculate concentrations at drinking water abstraction points. .

Van Rooyen N. 2006. Gedrag van 'vergeten stoffen' tijdens bodempassage na duininfiltratie. KWR-rapport KWR 2006.015, 125p.

VERORDENING (EG) Nr. 1107/2009 VAN HET EUROPEES PARLEMENT EN DE RAAD van 21 oktober 2009, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:309:0001:0050:NL:PDF

Vijver, M.G., Kruijne, R., Van 'T Zelfde, M., Van Der Linden, A.M., Tamis, W.L., De Snoo, G.R., 2011. Similarities and differences between measured and predicted concentrations of pesticides in Dutch surface waters. Communications in agricultural and applied biological sciences 76, 879-889.

Attachment I

Classified pesticides and metabolites using prioritization scheme

High priority, priority, potential priority and low priority pesticides (P) and metabolites (M).

CAS	Compound	Class	Number of measure-ments > detection limit	Number of measure-ments	Percentage (%) > detection limit	Detected in drinking water	90 percentile concentrations in sources of drinking water
1646-88-4	aldicarb-sulfon (P)	high priority	13	5080	0.3	yes	0.06
1066-51-9	aminomethylfosfonzuur (M)	high priority	1414	5987	23.6	yes	1.21
1912-24-9	Atrazine (P)	high priority	57	9068	0.6	yes	0.05
2008-58-4	BAM (M)	high priority	2257	5653	39.9	yes	0.24
101-27-9	Barban (P)	high priority	3	291	1.0	yes	0.01
25057-89-0	bentazon (P)	high priority	2396	10301	23.3	yes	0.14
319-84-6	beta-hexachloorcyclohexaan (P)	high priority	2	3931	0.1	yes	0.02
314-40-9	Bromacil (P)	high priority	216	8903	2.4	yes	3.38
10605-21-7	Carbendazim (P)	high priority	1014	7384	13.7	yes	0.03
16118-49-3	Carbetamide (P)	high priority	10	862	1.2	yes	0.02
6339-19-1	desfenylchloridazon (M)	high priority	460	752	61.2	yes	3.50
60-57-1	Dieldrin (P)	high priority	3	2434	0.1	yes	0.02
134-62-3	diethyltoluamide (P)	high priority	415	6230	6.7	yes	0.06
52508-35-7	dikegulac-natrium (P)	high priority	467	6512	7.2	yes	0.39
110488-70-5	Dimethomorf (P)	high priority	168	1503	11.2	yes	1.70
330-54-1	Diuron (P)	high priority	558	5095	11.0	yes	0.04
72-20-8	Endrin (P)	high priority	10	2445	0.4	yes	0.04
158062-67-0	Flonicamid (P)	high priority	113	2688	4.2	yes	0.18
77182-82-2	glufosinaat-ammonium (P)	high priority	74	5427	1.4	yes	0.05
1071-83-6	glyfosaat (P)	high priority	593	6839	8.7	yes	0.20
34123-59-6	Isoproturon (P)	high priority	608	6888	8.8	yes	0.07
17254-80-7	methyl-desfenylchloridazon (M)	high priority	154	4682	3.3	yes	0.93
171118-09-5	Metolachlor ESA (M)	high priority	56	65	86.2	yes	0.22

74223-64-6	metsulfuron-methyl (P)	high priority	7	914	0.8	yes	0.03
3984-14-3	N,N-dimethylsulfamide (M)	high priority	277	612	45.3	yes	0.27
111991-09-4	Nicosulfuron (P)	high priority	92	5728	1.6	yes	0.09
23135-22-0	Oxamyl (P)	high priority	33	6111	0.5	yes	0.19
72-55-9	p,p'-DDE (P)	high priority	1	1723	0.1	yes	
51-03-6	piperonyl-butoxide (P)	high priority	12	2569	0.5	yes	0.08
148-79-8	thiabendazool (P)	high priority	56	1997	2.8	yes	0.06
23564-05-8	Thiophanate-methyl (P)	high priority	12	621	1.9	yes	0.60
142469-14-5	tritosulfuron (P)	high priority	3	1526	0.2	yes	0.17
94-82-6	2,4-DB (P)	priority	2	6208	0.0	0	0.15
95-51-2	2-chlooraniline (P)	priority	82	2333	3.5	0	0.12
116-06-3	Aldicarb (P)	priority	3	1221	0.2	0	0.10
1646-87-3	aldicarb-sulfoxide (P)	priority	8	5504	0.1	0	0.27
131860-33-8	Azoxystrobin (P)	priority	3	1482	0.2	0	0.30
470-90-6	cis-chloorfenvinfos (P)	priority	2	737	0.3	0	0.13
121552-61-2	Cyprodinil (P)	priority	19	445	4.3	0	0.20
75-99-0	Dalapon (P)	priority	3	417	0.7	0	0.13
1596-84-5	Daminozide (P)	priority	1	353	0.3	0	1.40
2327-02-8	DCFU (P)	priority	1	975	0.1	0	0.50
1194-65-6	Dichlobenil (P)	priority	9	3815	0.2	0	0.32
60-51-5	dimethoaat (P)	priority	8	2346	0.3	0	0.31
88-85-7	Dinoseb (P)	priority	3	3455	0.1	0	0.50
2593-15-9	etridiazool (P)	priority	46	393	11.7	0	0.73
161326-34-7	Fenamidone (P)	priority	26	356	7.3	0	0.99
67564-91-4	fenpropimorf (P)	priority	3	2468	0.1	0	0.13
103361-09-7	Flumioxazin (P)	priority	1	353	0.3	0	0.26
239110-15-7	Fluopicolide (P)	priority	12	388	3.1	0	0.12
133-07-3	Folpet (P)	priority	2	393	0.5	0	2.10
35554-44-0	Imazalil (P)	priority	9	862	1.0	0	0.16
94-74-6	MCPA (P)	priority	289	9852	2.9	0	0.15
7085-19-0	Mecoprop (P)	priority	236	3600	6.6	0	0.54
57837-19-1	Metalaxyl (P)	priority	23	5023	0.5	0	0.29
67129-08-2	metazachloor (P)	priority	16	3678	0.4	0	0.12
2032-65-7	Methiocarb (P)	priority	55	741	7.4	0	0.14
72-43-5	Methoxychloor (P)	priority	1	1255	0.1	0	0.15
19937-59-8	Metoxuron (P)	priority	3	3579	0.1	0	0.11
150-68-5	Monuron (P)	priority	8	7466	0.1	0	0.28
66840-71-9	N,N-Dimethyl-N'-tolylsulfonyldiamide (P)	priority	1	5411	0.0	0	0.16
76738-62-0	Paclobutrazol (P)	priority	49	479	10.2	0	0.14
311-45-5	paraoxon-ethyl (P)	priority	1	737	0.1	0	0.20
23103-98-2	primicarb (P)	priority	8	2150	0.4	0	0.37
114-26-1	Propoxur (P)	priority	5	1637	0.3	0	1.30
87392-12-9	s-metolachloor (P)	priority	6	2358	0.3	0	0.18

99105-77-8	sulcotrione (P)	priority	4	2374	0.2	0	0.12
110-01-0	Tetrahydrothiofeen (P)	priority	16	1443	1.1	0	0.50
57018-04-9	tolclofos-methyl (P)	priority	104	2182	4.8	0	0.30
55219-65-3	Triadimenol (P)	priority	5	698	0.7	0	0.40
153719-23-4	Thiamethoxam (P)	priority	126	10488	1.2	0	0.10
3567-62-2	1-(3,4-dichloorfenyl)-3-methylureum (P)	potential priority	56	12900	0.4	0	0.02
93-76-5	2,4,5-T (P)	potential priority	12	11459	0.1	0	0.03
94-75-7	2,4-D (P)	potential priority	22	5561	0.4	0	0.09
120-36-5	2,4-DP (P)	potential priority	8	8522	0.1	0	0.04
50-30-6	2,6-dichloorbenzoezuur (P)	potential priority	15	1290	1.2	0	0.04
534-52-1	2-methyl-4,6-dinitrofenol (P)	potential priority	33	5244	0.6	0	0.07
2327-02-8	3,4-dichloorphenylureum (P)	potential priority	13	1017	1.3	0	0.06
122-88-3	4-chloorfenoxyazijnzuur (P)	potential priority	1	3363	0.0	0	0.05
1214-39-7	6-benzyladenine (P)	potential priority	4	353	1.1	0	0.04
30560-19-1	Acephate (P)	potential priority	1	479	0.2	0	0.01
3337-71-1	Asulam (P)	potential priority	2	514	0.4	0	0.04
86-50-0	azinphos-methyl (P)	potential priority	1	1872	0.1	0	0.04
33213-65-9	beta-endosulfan (P)	potential priority	1	6591	0.0	0	0.02
188425-85-6	Boscalid (P)	potential priority	130	1124	11.6	0	0.03
1563-66-2	Carbofuran (P)	potential priority	9	6090	0.1	0	0.02
13360-45-7	chloorbromuron (P)	potential priority	2	3306	0.1	0	0.02
2136-79-0	chloorthal (P)	potential priority	1	622	0.2	0	0.02
15545-48-9	chloortoluron (P)	potential priority	165	7944	2.1	0	0.05
1698-60-8	chloridazon (P)	potential priority	250	7258	3.4	0	0.06
2921-88-2	chlorpyrifos (P)	potential priority	25	518	4.8	0	0.07
81777-89-1	Clomazone (P)	potential priority	3	3482	0.1	0	0.03
210880-92-5	clothianidin (P)	potential priority	3	479	0.6	0	0.04
21725-46-2	Cyanazine (P)	potential priority	2	1651	0.1	0	0.02
30125-63-4	desethylerbutylazine (M)	potential	12	583	2.1	0	0.27

		priority					
1007-28-9	desisopropylatrazine (M)	potential priority	12	6573	0.2	0	0.12
30614-22-3	desmethylprimicarb (P)	potential priority	1	479	0.2	0	0.04
1014-69-3	Desmetryn (P)	potential priority	2	2521	0.1	0	0.07
333-41-5	Diazinon (P)	potential priority	3	2189	0.1	0	0.02
1918-00-9	Dicamba (P)	potential priority	3	3422	0.1	0	0.08
62-73-7	dichloorvos (P)	potential priority	2	1981	0.1	0	0.08
35367-38-5	diflubenzuron (P)	potential priority	1	479	0.2	0	0.01
50563-36-5	Dimethachloor (P)	potential priority	1	904	0.1	0	0.03
87674-68-8	Dimethenamide (P)	potential priority	106	1593	6.7	0	0.06
163515-14-8	Dimethenamide-P (P)	potential priority	43	4798	0.9	0	0.09
1420-07-1	Dinoterb (P)	potential priority	43	6287	0.7	0	0.06
2497-07-6	disulfoton-sulfoxide (P)	potential priority	1	479	0.2	0	0.01
26225-79-6	ethofumesaat (P)	potential priority	49	1705	2.9	0	0.09
13194-48-4	ethoprofos (P)	potential priority	2	2487	0.1	0	0.05
126833-17-8	fenhexamid (P)	potential priority	9	862	1.0	0	0.03
101-42-8	fenuron (P)	potential priority	4	603	0.7	0	0.05
120068-37-3	Fipronil (P)	potential priority	4	408	1.0	0	0.02
142459-58-3	Flufenacet (P)	potential priority	1	686	0.1	0	0.08
2164-17-2	fluometuron (P)	potential priority	2	556	0.4	0	0.02
69377-81-7	Fluroxypyr (P)	potential priority	26	3582	0.7	0	0.06
66332-96-5	Flutolanil (P)	potential priority	4	608	0.7	0	0.03
944-22-9	fonofos (P)	potential priority	2	547	0.4	0	0.02
98886-44-3	Fosthiazate (P)	potential priority	1	598	0.2	0	0.03
51276-47-2	glufosinaat (P)	potential priority	1	174	0.6	0	0.06
69806-34-4	Haloxyfop (P)	potential priority	1	2595	0.0	0	0.07
51235-04-2	Hexazinon (P)	potential priority	3	1504	0.2	0	0.08

138261-41-3	Imidacloprid (P)	potential priority	84	5799	1.4	0	0.08
55406-53-6	Joodpropynylcarbamaat (P)	potential priority	1	540	0.2	0	0.03
143390-89-0	Kresoxim-Methyl (P)	potential priority	4	1578	0.3	0	0.07
2164-08-1	Lenacil (P)	potential priority	1	2210	0.0	0	0.05
330-55-2	Linuron (P)	potential priority	134	9279	1.4	0	0.06
41394-05-2	Metamitron (P)	potential priority	19	4649	0.4	0	0.07
172960-62-2	Metazachlor Esa (M)	potential priority	51	54	94.4	0	0.14
18691-97-9	Methabenzthiazuron (P)	potential priority	33	3762	0.9	0	0.02
10265-92-6	Methamidophos (P)	potential priority	1	142	0.7	0	0.01
2032-65-7	Methiocarb (P)	potential priority	16	702	2.3	0	0.04
2032-65-7	Methiocarb (P)	potential priority	6	1584	0.4	0	0.07
16752-77-5	Methomyl (P)	potential priority	2	1091	0.2	0	0.07
161050-58-4	Methoxyfenozide (P)	potential priority	2	479	0.4	0	0.05
#N/A	Methyl (P)	potential priority	1	274	0.4	0	0.01
3060-89-7	Metobromuron (P)	potential priority	1	2869	0.0	0	0.02
51218-45-2	Metolachloor (P)	potential priority	174	4179	4.2	0	0.09
152019-73-3	Metolachlor Oxa (M)	potential priority	46	59	78.0	0	0.13
21087-64-9	Metribuzine (P)	potential priority	10	4288	0.2	0	0.10
2212-67-1	Molinaat (P)	potential priority	2	796	0.3	0	0.09
1746-81-2	Monolinuron (P)	potential priority	2	2869	0.1	0	0.02
4710-17-2	N,N-Dimethylaminosulfanilide (M)	potential priority	64	6131	1.0	0	0.22
301-12-2	Oxydemeton-Methyl (P)	potential priority	1	479	0.2	0	0.01
50-29-3	P,P'-Ddt (P)	potential priority	2	2106	0.1	0	0.05
298-00-0	Parathion-Methyl (P)	potential priority	4	1633	0.2	0	0.08
66063-05-6	Pencycuron (P)	potential priority	2	671	0.3	0	0.01
82-68-8	Pentachloornitrobenzeen (Pcnb) (P)	potential priority	1	1972	0.1	0	0.03

23505-41-1	Pirimifos-Ethyl (P)	potential priority	1	1185	0.1	0	0.03
7287-19-6	Prometryn (P)	potential priority	1	2553	0.0	0	0.07
24579-73-5	Propamocarb (P)	potential priority	78	763	10.2	0	0.05
23950-58-5	Propyzamide (P)	potential priority	5	4634	0.1	0	0.06
123312-89-0	Pymetrozine (P)	potential priority	28	641	4.4	0	0.10
175013-18-0	Pyraclostrobin (P)	potential priority	3	884	0.3	0	0.07
55512-33-9	Pyridate (P)	potential priority	2	479	0.4	0	0.03
53112-28-0	Pyrimethanil (P)	potential priority	5	694	0.7	0	0.06
74051-80-2	Sethoxydim (P)	potential priority	1	479	0.2	0	0.01
122-34-9	Simazine (P)	potential priority	53	9482	0.6	0	0.03
107534-96-3	Tebuconazool (P)	potential priority	5	1512	0.3	0	0.02
886-50-0	Terbutryn (P)	potential priority	6	2486	0.2	0	0.05
5915-41-3	Terbutylazine (P)	potential priority	334	8901	3.8	0	0.09
111988-49-9	Thiacloprid (P)	potential priority	3	958	0.3	0	0.06
39184-59-3	Thiofanox Sulfone (P)	potential priority	2	4408	0.0	0	0.04
39184-27-5	Thiofanoxsulfoxide (P)	potential priority	2	4408	0.0	0	0.06
52-68-6	Trichlorfon (P)	potential priority	1	194	0.5	0	0.03
126535-15-7	Triflusulfuron-Methyl (P)	potential priority	1	398	0.3	0	0.02
34681-24-8	Butocarboximsulfoxide (P)	potential priority	7	5388	0.1	0	0.29
52888-80-9	Prosulfocarb (P)	potential priority	7	444	1.6	0	0.09
34681-23-7	Butoxycarboxim (M)	low priority	1	866	0.1	0	0.01
0	2-Amido-3,5,6-Trichlo-4-Cyanobenzenesulphonic Acid (R417888) (M)	low priority	1	1	100.0	0	0.08
6190-65-4	Desethylatrazine (M)	low priority	56	7393	0.8	0	0.05
1231244-60-2	Metazachloor-C-Metaboliet (M)	low priority	51	54	94.4	0	0.08

Pesticides (P) and metabolites (M) never detected above detection limit.

CAS-number	Compound

2327-02-8	1-(3,4-Dichloorfenyl)Ureum(Dcpu) (P)
13142-64-8	1-(3-Chloor-4-Methylfenyl)Ureum (P)
140-38-5	1-(4-Chloorfenyl)Ureum (P)
34123-57-4	1-(4-Isopropylfenyl)-3-Methylureum (P)
56046-17-4	1-(4-Isopropylfenyl)Ureum (P)
93-72-1	2,4,5-Tp (P)
607-99-8	2,4,6-Tribroomanisol (P)
21702-84-1	2,4-Dibroomanisol (P)
2398-37-0	3-Broomanisol (P)
16655-82-6	3-Hydroxycarbofuran (P)
122-83-3	4-Cpa (P)
71751-41-2	Abamectin (P)
94-81-5	Acequinocyl (P)
160430-64-8	Acetamiprid (P)
74070-46-5	Aclonifen (P)
959-98-8	A-Endosulfan (P)
319-84-6	A-Hch (P)
15972-60-8	Alachloor (P)
309-00-2	Aldrin (P)
834-12-8	Ametryn (P)
120923-37-7	Amidosulfuron (P)
2032-59-9	Aminocarb (P)
60207-31-0	Azaconazool (P)
35575-96-3	Azamethiphos (P)
120162-55-2	Azimsulfuron (P)
2642-71-9	Azinfos-Ethyl (P)
41318-75-6	Bde-028 (P)
5436-43-1	Bde-047 (P)
60348-60-9	Bde-099 (P)
189084-64-8	Bde-100 (P)
182677-30-1	Bde-138 (P)
68631-49-2	Bde-153 (P)
25059-80-7	Benazolin-Ethylester (P)
22781-23-3	Bendiocarb (P)
149877-41-8	Bifenazaat (P)
42576-02-3	Bifenox (P)
82657-04-3	Bifenthrin (P)
28434-00-6	Bioallethrin (P)
55179-31-2	Bitertanol (P)
2104-96-3	Bromophos (P)
4824-78-6	Bromophos-Ethyl (P)
18181-80-1	Bromopropylate (P)
1689-84-5	Bromoxynil (P)
3408-97-7	Bromuron (P)

41483-43-6	Bupirimaat (P)
69327-76-0	Buprofezin (P)
34681-10-2	Butocarboxim (P)
3766-60-7	Buturon (P)
133-06-2	Captan (P)
63-25-2	Carbaryl (P)
786-19-6	Carbofenthion (P)
5234-68-4	Carboxin (P)
128639-02-1	Carfentrazone-Ethyl (P)
104390-56-9	Cga 108906 (M)
Onbekend	Cga 354742 (M)
171118-09-5	Cga 354743 (M)
Onbekend	Cga 369873 (M)
Onbekend	Cga 50266 (M)
87764-37-2	Cga 62826 (P)
470-90-6	Chloorfenvinfos (P)
101-21-3	Chloorprofam (P)
2921-88-2	Chloorpyrifos (P)
39475-55-3	Chloorpyrifos-Ethyl (P)
5598-13-0	Chloorpyrifos-Methyl (P)
1967-16-4	Chlorbufam (P)
71422-67-8	Chlorfluazuron (P)
2675-77-6	Chloroneb (P)
1897-45-6	Chlorothalonil (P)
1982-47-4	Chloroxuron (P)
1861-32-1	Chlorthaldimethyl (P)
142891-20-1	Cinidon-Ethyl (P)
5103-71-9	Cis-Chloordaan (P)
23783-98-4	Cis-Fosfamidon (P)
1024-57-3	Cis-Heptachloorepoxide (P)
61949-76-6	Cis-Permethrin (P)
105512-06-9	Clodinafop-Propargyl (P)
74115-24-5	Clofentezine (P)
1702-17-6	Clopyralid (P)
56-72-4	Cumafos (P)
101205-02-1	Cycloxydim (P)
68359-37-5	Cyfluthrin (Som) (P)
68085-85-8	Cyhalothrin, Lambda- (P)
57966-95-7	Cymoxanil (P)
52315-07-8	Cypermethrin (P)
94361-06-5	Cyproconazool (P)
66215-27-8	Cyromazine (P)
319-86-8	Delta-Hexachloorcyclohexaan(Delta-Hch) (P)
52918-63-5	Deltametrin (P)

298-03-3	Demeton-O (P)
126-75-0	Demeton-S (P)
919-86-8	Demeton-S-Methyl (P)
17040-19-6	Demeton-S-Methylsulfon (P)
13684-56-5	Desmedipham (P)
97-17-6	Dichlofenthion (P)
1085-98-9	Dichlofluanid (P)
81859-29-2	Dichloran (P)
115-32-2	Dicofol (P)
141-66-2	Dicrotophos (P)
87130-20-9	Diethofencarb (P)
119446-68-3	Difenoconazool (P)
14214-32-5	Difenoxuron (P)
83164-33-4	Diflufenican (P)
5221-53-4	Dimethirimol (P)
83657-24-3	Diniconazole (P)
298-04-4	Disulfoton (P)
2497-06-5	Disulfoton-Sulfone (P)
2497-07-6	Disulfoton-Sulfoxide (P)
3347-22-6	Dithianon (P)
1593-77-7	Dodemorf (P)
2439-10-3	Dodine (P)
17109-49-8	Edinfenfos (P)
6108-10-7	E-Hch (P)
119791-41-2	Emamectine (P)
1031-07-8	Endosulfansulfaat (P)
106325-08-0	Epoxiconazool (P)
759-94-4	Eptam (Eptc) (P)
66230-04-4	Esvenvaleraat (P)
29973-13-5	Ethiofencarb (P)
53380-23-7	Ethiofencarb Sulfon (P)
53380-22-6	Ethiofencarb Sulfoxide (P)
563-12-2	Ethion (P)
23947-60-6	Ethirimol (P)
126801-58-9	Ethoxysulfuron (P)
38260-54-7	Etrimphos (P)
96-45-7	Etu (Ethyleenthio-Ureum) (P)
131807-57-3	Famoxadone (P)
22224-92-6	Fenamifos (P)
31972-44-8	Fenamiphos-Sulfone (P)
31972-43-7	Fenamiphos-Sulfoxide (P)
60168-88-9	Fenarimol (P)
299-84-3	Fenchloorphos (P)
122-14-5	Fenitrothion (P)

72490-01-8	Fenoxycarb (P)
74738-17-3	Fenpiclonil (P)
39515-41-8	Fenpropathrin (P)
111812-58-9	Fenpyroximate (P)
115-90-2	Fensulfothion (P)
14255-72-2	Fensulfothion-Sulfone (P)
55-38-9	Fenthion (P)
3761-42-0	Fenthion-Sulfone (P)
3761-41-9	Fenthion-Sulfoxide (P)
145701-23-1	Florasulam (P)
69335-91-7	Fluazifop (P)
69806-50-4	Fluazifop-Butyl (P)
79622-59-6	Fluazinam (P)
113036-88-7	Flucycloxuron (P)
101463-69-8	Flufenoxuron (P)
77501-90-7	Fluoroglycofen-Ethyl (P)
193740-76-0	Fluoxastrobin (P)
81406-37-3	Fluroxypyr Meptyl (P)
907204-31-3	Fluxapyroxad (P)
173159-57-4	Foramsulfuron (P)
2310-17-0	Fosalon (P)
732-11-6	Fosmet (P)
3878-19-1	Fuberidiazole (P)
57646-30-7	Furalaxyl (P)
65907-30-4	Furathiocarb (P)
58-89-9	G-Hch (Lindaan) (P)
69806-40-2	Haloxyfop-Methyl (P)
118-74-1	Hcb (Hexachloorbenzeen) (P)
76-44-8	Heptachloor (P)
1024-57-3	Heptachloorepoxide (P)
23560-59-0	Heptenofos (P)
86479-06-3	Hexaflumuron (P)
78587-05-0	Hexythiazox (P)
81405-85-8	Imazamethabenzmethyl (P)
173584-44-6	Indoxacarb (P)
144550-36-7	Iodosulfuron-Methyl-Natrium (P)
1689-83-4	Ioxynil (P)
36734-19-7	Iprodion (P)
140923-17-7	Iprovalicarb (P)
28159-98-0	Irgarol (P)
297-78-9	Isobenzan (P)
465-73-6	Isodrin (P)
141112-29-0	Isoxaflutole (P)
91465-08-6	Lambda-Cyhalothrin (P)

2164-08-1	Lenacil (P)
103055-07-8	Lufenuron (P)
121-75-5	Malathion (P)
94-81-5	Mcpb (P)
135590-91-9	Mefenpyr-Dietyl (P)
208465-21-8	Mesosulfuron-Methyl (P)
104206-82-8	Mesotrione (P)
70630-17-0	Metalaxyl-M (P)
9002-91-9	Metaldehyde (P)
62610-77-9	Methacrifos (P)
950-37-8	Methidathion (P)
556-61-6	Methylisothiocyanaat (Mitc) (P)
7786-34-7	Mevinfos (P)
298-01-1	Mevinfos-Cis (P)
2385-85-5	Mirex (P)
6923-22-4	Monocrotophos (P)
88671-89-0	Myclobutanil (P)
555-37-3	Neburon (P)
10552-74-6	Nitrothal-Isopropyl (P)
53-19-0	O,P-Ddd (P)
3424-82-6	O,P'-Dde (P)
789-02-6	O,P'-Ddt (P)
1113-02-6	Omethoaat (P)
90-43-7	O-Phenylphenol (P)
77732-09-3	Oxadixyl (P)
144651-06-9	Oxasulfuron (P)
5259-88-1	Oxycarboxin (P)
27304-13-8	Oxy-Chloordaan (P)
72-54-8	P,P'-Ddd (P)
950-35-6	Paraoxon-Methyl (P)
56-38-2	Parathion (P)
56-38-2	Parathion-Ethyl (P)
66246-88-6	Penconazool (P)
40487-42-1	Pendimethalin (P)
87-86-5	Pentachloorfenol (P)
52645-53-1	Permethrin(Sum) (P)
13684-63-4	Phenmedipham (P)
9004-65-3	Phenmedipham Metabolite (Mhpc) (M)
298-02-2	Phoraat (P)
2588-04-7	Phorate-Sulfone (P)
2588-03-6	Phorate-Sulfoxide (P)
13171-21-6	Phosphamidon (P)
14816-18-3	Phoxim (P)
1918-02-1	Picloram (P)

137641-05-5	Picolinafen (P)
117428-22-5	Picoxystrobin (P)
243973-20-8	Pinoxaden (P)
29232-93-7	Pirimiphos-Methyl (P)
30614-22-3	Primicarb, Desmethyl- (M)
67747-09-5	Prochloraz (P)
32809-16-8	Procymidon (P)
122-42-9	Profam (P)
139001-49-3	Profoxydim (P)
1610-18-0	Prometon (P)
1918-16-7	Propachloor (P)
139-40-2	Propazine (P)
60207-90-1	Propiconazool (P)
60207-90-1	Propiconazool_Cis (P)
60207-90-1	Propiconazool_Trans (P)
94125-34-5	Prosulfuron (P)
178928-70-6	Prothioconazool (P)
13457-18-6	Pyrazophos (P)
88283-41-4	Pyrifenox (P)
95737-68-1	Pyriproxyfen (P)
422556-08-9	Pyroxsulam (P)
2797-51-5	Quinoclamine (P)
124495-18-7	Quinoxyfen (P)
76578-14-8	Quizalofop-Ethyl (P)
100646-51-3	Quizalofop-P-Ethyl (P)
Onbekend	R611965 (M)
Onbekend	R611965 (M)
122931-48-0	Rimsulfuron (P)
83-79-4	Rotenone (P)
7286-69-3	Se-Butylazine (P)
168316-95-8	Spinosad (P)
148477-71-8	Spirodiclofen (P)
141776-32-1	Sulfosulfuron (P)
3689-24-5	Sulfotep (P)
1918-18-9	Swep (P)
112410-23-8	Tebufenozide (P)
119168-77-3	Tebufenpyrad (P)
117-18-0	Tecnazeen (P)
297-78-9	Telodrin (P)
335104-84-2	Tembotrione (P)
3383-96-8	Temephos (P)
149979-41-9	Tepraloxydim (P)
13071-79-9	Terbufos (P)
56070-16-7	Terbufos-Sulfone (P)

10548-10-4	Terbufos-Sulfoxide (P)
961-11-5	Tetrachloorvinphos (P)
116-29-0	Tetradifon (P)
7696-12-0	Tetramethrin (P)
31895-21-3	Thiocyclam (P)
59669-26-0	Thiodicarb (P)
39196-18-4	Thiofanox (P)
640-15-3	Thiometon (P)
85-40-5	Thpi (P)
731-27-1	Tolylfluanid (P)
210631-68-8	Topramezone (P)
5103-74-2	Trans-Chloordaan (P)
18708-86-6	Trans-Chloorfenvinphos (P)
297-99-4	Trans-Fosfamidon (P)
28044-83-9	Trans-Heptachloorepoxide (P)
61949-77-7	Trans-Permethrin (P)
43121-43-3	Triadimefon (P)
2303-17-5	Tri-Allaat (P)
24017-47-8	Triazofos (P)
72459-58-6	Triazoxide (P)
101200-48-0	Tribenuron-Methyl (P)
327-98-0	Trichloronat (P)
55335-06-3	Triclopyr (P)
41814-78-2	Tricyclazole (P)
1912-26-1	Tri-Etazine (P)
141517-21-7	Trifloxystrobin (P)
64628-44-0	Triflumuron (P)
1582-09-8	Trifluralin (P)
26644-46-2	Triforine (P)
2275-23-2	Vamidothion (P)
50471-44-8	Vinclozolin (P)
156052-68-5	Zoxamide (P)

Attachment II

Pesticides present in drinking water and in ground- and surface water >0.1 µg/L (Figures 2-4 to 2-7)

Pesticides detected in drinking water above the detection limit.

Pesticides	Median conc.	Max. conc.	Detected >0.1 ug/L	Detected >0.01 ug/L	Detected locations (out of 178)	Detections >dl	Nr of measurements	% >DL
dikegulac-sodium	0.12	0.76	127	229	96	232	2420	9.6
metolachloor-s-metaboliet	0.11	0.11	1	1	1	1	1	100.0
n,n-dimethylsulfamide (DMS)	0.1	0.22	15	52	34	52	173	30.1
oxamyl	0.075	0.14	1	1	2	2	2202	0.1
piperonyl-butoxide	0.075	0.1	0	2	2	2	488	0.4
metsulfuron-methyl	0.07	0.09	0	2	2	2	263	0.8
tritosulfuron	0.07	0.07	0	1	1	1	607	0.2
aminomethylfosfonzuur	0.06	0.38	55	196	85	196	1325	14.8
bam	0.06	0.19	59	471	120	480	1341	35.8
bromacil	0.06	0.22	2	54	34	59	2774	2.1
dimethomorf	0.06	0.13	2	13	4	13	321	4.0
desfenylchloridazon	0.05	0.25	4	26	15	26	57	45.6
glyfosaat	0.035	0.42	3	14	12	14	2551	0.5
beta-hexachloorcyclohexaan	0.03	0.03	0	1	1	1	887	0.1
methyl-desfenylchloridazon	0.03	0.06	0	9	9	9	1663	0.5
glufosinaat-ammonium	0.03	0.29	1	19	17	19	2161	0.9
thiophanate-methyl	0.025	0.03	0	2	2	2	170	1.2
atrazine	0.02	0.03	0	2	2	3	2771	0.1
bentazon	0.02	0.14	2	358	123	548	3511	15.6
carbetamide	0.02	0.03	0	1	2	2	237	0.8
endrin	0.02	0.03	0	4	5	6	846	0.7
isoproturon	0.02	0.04	0	2	2	4	2413	0.2
dieldrin	0.015	0.02	0	1	2	2	852	0.2
thiabendazool	0.015	0.05	0	2	3	4	237	1.7
nicosulfuron	0.012	0.012	0	1	1	1	2269	0.0
aldicarb-sulfon	0.01	0.05	0	1	2	3	2088	0.1
carbendazim	0.01	0.01	0	0	2	2	2423	0.1
diethyltoluamide	0.01	0.02	0	1	4	4	1969	0.2
diuron	0.01	0.03	0	1	7	7	1154	0.6

flonicamid	0.01	0.01	0	0	4	4	1676	0.2
p,p'-dde	0.01	0.01	0	0	1	1	511	0.2
barban	0.01	0.01	0	0	1	1	42	2.4

Pesticides detected in groundwater above the threshold of 0.1µg/L.

Pesticides	Median conc.	Max. conc.	Detected >0.1 ug/L	Detected >0.01 ug/L	Detected locations (out of 178)	Detec-tions >dl	Nr of measure-ments	% >DL
n,n-dimethylaminosulfanilide	5.9	5.9	1	1	1	1	2658	0.04
glyfosaat	0.895	2.3	30	44	8	44	2452	1.79
desfenylchloridazon	0.495	21	216	254	42	254	511	49.71
dimethoaat	0.31	0.31	2	2	2	2	390	0.51
thiabendazool	0.22	0.22	1	1	1	1	977	0.10
propoxur	0.18	1.3	4	5	2	5	837	0.60
mcpa	0.17	0.25	1	2	2	2	4620	0.04
n,n-dimethyl-n'-tolylsulfonyldiamide	0.16	0.16	1	1	1	1	2658	0.04
dikegulac-sodium	0.15	0.82	83	134	64	138	3326	4.15
2,4-db	0.15	0.15	1	1	1	1	3629	0.03
n,n-dimethylsulfamide	0.105	0.48	25	50	37	50	139	35.97
metolachloor-s-metaboliet	0.105	0.16	2	4	4	4	5	80.00
bam	0.1	13	608	1302	130	1303	2866	45.46
methyl-desfenylchloridazon	0.1	3.8	59	122	18	122	2481	4.92
tetrahydrothiofeen	0.1	1.4	6	16	12	16	623	2.57
monuron	0.095	0.32	2	2	3	4	3785	0.11
bromacil	0.08	5	65	142	81	149	3705	4.02
ethofumesaat	0.08	0.11	1	6	1	6	691	0.87
mecoprop	0.075	1.1	62	149	31	156	1883	8.28
desisopropylatrazine	0.06	0.13	2	11	8	11	3480	0.32
bentazon	0.05	0.86	205	1081	126	1245	4618	26.96
aminomethylfosfonzuur	0.05	0.7	14	47	33	47	2611	1.80
dichlobenil	0.05	0.36	2	8	8	8	1937	0.41
oxamyl	0.04	0.17	1	11	4	11	2527	0.44
diuron	0.03	23	13	49	26	58	1328	4.37
metalaxyl	0.03	0.12	1	2	3	3	2499	0.12
diethyltoluamide	0.02	6.3	5	49	46	72	2559	2.81
chloridazon	0.02	0.21	4	26	22	37	3118	1.19
simazine	0.02	0.2	2	13	16	23	3891	0.59
atrazine	0.02	1.3	2	9	14	15	3301	0.45

Pesticides detected in surface water above the threshold of 0.1 µg/L.

Pesticides	Median conc.	Max. conc.	Detected >0.1 ug/L	Detected >0.01 ug/L	Detected locations (out of 178)	Detections >dl	Nr of measurements	% >DL
dinoseb	0.5	0.5	1	1	1	1	472	0.2
dcfu	0.5	0.5	1	1	1	1	305	0.3
aminomethylfosfonzuur	0.42	4.2	873	991	96	991	1418	69.9
flumioxazin	0.26	0.26	1	1	1	1	125	0.8
fenamidone	0.2	0.23	3	5	2	5	132	3.8
desfenylchloridazon	0.19	0.7	115	147	34	147	148	99.3
methoxychloor	0.15	0.15	1	1	1	1	317	0.3
aldicarb-sulfoxide	0.145	0.27	4	5	4	6	676	0.9
cis-chloorfenvinfos	0.13	0.13	1	1	1	1	294	0.3
n,n-dimethylsulfamide	0.1	0.94	54	135	37	135	241	56.0
metolachloor-s-metaboliet	0.09	0.28	22	48	4	51	59	86.4
n,n-dimethylaminosulfanilide	0.08	0.11	1	21	5	21	628	3.3
sulcotrione	0.075	0.12	1	2	2	2	289	0.7
glyfosaat	0.07	1.1	118	490	68	490	1232	39.8
metazachloor-s-metaboliet	0.07	0.22	15	50	4	51	54	94.4
dimethomorf	0.07	4.8	14	41	5	45	324	13.9
etridiazool	0.065	0.17	2	16	5	16	144	11.1
metoxuron	0.065	0.11	1	2	1	2	1474	0.1
metolachloor-c-metaboliet	0.06	0.17	11	43	3	46	58	79.3
metazachloor-c-metaboliet	0.05	0.2	4	47	4	51	54	94.4
fenpropimorf	0.05	0.13	1	3	3	3	903	0.3
s-metolachloor	0.05	0.19	1	5	2	5	45	11.1
mcpa	0.04	0.4	23	211	14	216	1116	19.4
dimethenamide-p	0.04	0.31	2	32	3	39	442	8.8
mecoprop	0.035	0.24	11	67	5	80	475	16.8
2,4-d	0.035	0.11	1	16	8	16	975	1.6
terbutylazine	0.03	0.22	13	239	34	276	1597	17.3
metolachloor	0.03	0.27	8	132	23	142	1222	11.6
chloortoluron	0.03	0.11	1	110	12	129	1762	7.3
ethofumesaat	0.03	0.11	1	37	9	37	455	8.1
diethyltoluamide	0.025	0.44	4	264	29	270	1142	23.6
nicosulfuron	0.021	0.6	2	69	12	72	944	7.6
isoproturon	0.02	0.34	24	304	28	431	1769	24.4
bam	0.02	0.3	6	257	45	295	926	31.9
dimethenamide	0.02	0.21	3	73	10	92	617	14.9
bentazon	0.02	0.17	2	131	13	161	1037	15.5
tolclofos-methyl	0.02	0.13	2	32	8	40	705	5.7
2-methyl-4,6-dinitrofenol	0.02	0.14	1	24	3	32	580	5.5
diuron	0.02	0.11	1	236	23	310	1786	17.4
linuron	0.02	0.5	1	73	11	105	1811	5.8

oxamyl	0.02	0.24	1	8	7	9	845	1.1
methiocarb	0.017	0.15	1	11	6	15	208	7.2
butocarboximsulfoxide	0.016	0.3	1	2	2	3	679	0.4
imidacloprid	0.01	0.62	2	16	8	43	740	5.8
atrazine	0.01	0.14	1	14	10	31	2021	1.5
thiabendazool	0.01	0.29	1	20	5	41	537	7.6

Pesticides detected in river bank and dune filtrate >0.1 µg/L

Pesticides	Median conc.	Max. conc.	Detected >0.1 ug/L	Detected >0.01 ug/L	Detected locations (out of 178)	Detections >dl	Nr of measurements	% >DL
dinoseb	0.5	0.5	1	1	1	1	386	0.3
linuron	0.26	0.5	1	2	2	2	852	0.2
desfenylchloridazon	0.13	0.99	25	33	6	33	36	91.7
metazachloor	0.12	0.12	1	1	1	1	336	0.3
tritosulfuron	0.115	0.17	1	2	1	2	73	2.7
glyfosaat	0.1	0.26	12	27	4	27	478	5.6
dikegulac-sodium	0.09	0.68	37	95	8	97	463	21.0
dimethomorf	0.07	0.26	15	74	5	74	293	25.3
2-chlooraniline	0.07	0.22	10	82	10	82	268	30.6
aminomethylfosfonzuur	0.05	4.4	30	132	6	132	505	26.1
n,n-dimethylaminosulfanilide	0.05	0.12	1	3	3	3	500	0.6
thiabendazool	0.05	0.14	1	3	2	3	114	2.6
bentazon	0.04	0.5	83	313	27	365	974	37.5
metolachloor	0.04	0.12	1	5	2	5	445	1.1
bam	0.03	0.11	1	43	11	50	389	12.9
isoproturon	0.02	0.49	2	105	18	144	748	19.3
terbutylazine	0.02	0.13	2	11	6	18	737	2.4
diuron	0.02	0.68	1	95	20	155	634	24.4
glufosinaat-ammonium	0.02	0.13	1	18	3	18	444	4.1
imazalil	0.02	0.21	1	2	3	3	114	2.6
carbendazim	0.011	0.5	1	86	13	165	560	29.5

Presence in drinking water and source water compared

	n>detection limit	n>0.1 ug/L		n>0.01 ug/L	
	Drinking water	Groundwater	surface water	Groundwater	surface water
bentazon	548	14	951	1068	483
bam	480	608	7	1302	421

dikegulac-sodium	232	25	55	134	95
aminomethylfosfonzuur	196	203	89	47	1171
bromacil	59	0	1	142	6
n,n-dimethylsulfamide	52	216	134	50	175
desfenylchloridazon	26	83	37	254	171
glufosinaat-ammonium	19	1	4	2	53
glyfosaat	14	65	0	44	535
dimethomorf	13	0	53	0	151
methyl-desfenylchloridazon	9	30	138	122	22
diuron	7	0	18	49	353
endrin	6	2	22	1	2
isoproturon	4	59	0	3	403
flonicamid	4	0	26	1	88
diethyltoluamide	4	5	5	49	295
thiabendazool	4	0	0	1	26
atrazine	3	0	3	9	15
aldicarb-sulfon	3	0	0	4	1
thiophanate-methyl	2	0	0	0	10
carbetamide	2	0	4	0	5
oxamyl	2	1	2	11	16
carbendazim	2	0	0	3	783
piperonyl-butoxide	2	0	0	0	7
metsulfuron-methyl	2	0	0	0	5
dieldrin	2	0	1	0	1
metolachloor-s-metaboliet	1	13	2	4	48
nicosulfuron	1	2	1	0	81

beta-hexachloorcyclohexaan	1	0	0	1	0
tritosulfuron	1	0	22	0	2
p,p'-dde	1	0	0	0	0
barban	1	0	0	0	0
mecoprop	0	62	11	2	282
mcpa	0	1	43	0	94
tolclofos-methyl	0	0	40	1	62
n,n-dimethylaminosulfanilide	0	1	29	149	67
terbutylazine	0	0	26	2	284
etridiazool	0	0	22	0	46
metolachloor	0	0	15	0	161
thiametoxam	0	0	12	0	82
metalaxyl	0	1	10	2	20
fenamidone	0	0	10	0	26
methiocarb	0	0	9	0	48
methiocarb	0	0	0	0	48
methiocarb	0	0	0	0	48
paclobutrazol	0	0	9	0	38
chloridazon	0	0	9	26	171
linuron	0	0	9	2	92
dimethenamide	0	0	6	0	85
cyprodinil	0	4	4	0	19
tetrahydrothiofeen	0	0	6	16	0
imidacloprid	0	0	6	2	47
propoxur	0	6	0	5	0
ethofumesaat	0	0	5	6	43

metazachloor	0	4	0	0	16
boscalid	0	0	3	0	77
dimethenamide-p	0	1	2	1	32
pymetrozine	0	0	2	0	21
simazine	0	0	2	13	3
dichlobenil	0	0	2	8	1
dimethoaat	0	2	0	2	4
triadimenol	0	0	2	0	5
butocarboximsulfoxide	0	0	2	1	4
monuron	0	2	0	2	2
primicarb	0	2	0	0	4
dinoseb	0	2	0	1	2
chloortoluron	0	0	2	1	114
2-methyl-4,6-dinitrofenol	0	0	1	0	24
2,4-d	0	0	2	1	21
fluopicolide	0	0	1	0	8
s-metolachloor	0	0	1	1	5
imazalil	0	0	1	0	6
sulcotrione	0	0	1	2	2
fenpropimorf	0	0	1	0	3
azoxystrobin	0	0	1	2	1
dalapon	0	1	0	0	3
metoxuron	0	0	1	0	3
folpet	0	0	1	0	2
2,4-db	0	0	1	1	1
cis-chloorfenvinfos	0	0	1	0	2

daminozide	0	0	1	0	1
dcfu	0	0	1	0	1
flumioxazin	0	0	1	0	1
paraoxon-ethyl	0	0	1	0	1
methoxychloor	0	0	1	0	1
r417888	0	0	0	0	51
desethylatrazine	0	0	0	16	26
dinoterb	0	0	0	29	3
propamocarb	0	0	0	0	26
fluroxypyr	0	0	0	1	18
chlorpyrifos	0	0	0	0	15
metribuzine	0	0	0	0	15
metamitron	0	0	1	1	13
hexazinon	0	0	0	0	12
2-chlooraniline	0	0	0	0	10
3,4-dichloorphenylureum	0	0	0	3	5
desmetryn	0	0	0	0	7
prosulfocarb	0	0	0	0	6
propyzamide	0	0	0	0	6
kresoxim-methyl	0	0	0	1	4
parathion-methyl	0	0	0	0	5
pyrimethanil	0	0	0	0	5
dicamba	0	0	0	0	4
pyraclostrobin	0	0	0	0	4
molinaat	0	0	0	0	4
thiofanoxsulfoxide	0	0	0	0	4

thiacloprid	0	0	0	0	3
aldicarb	0	0	0	0	3
flufenacet	0	0	0	0	3
prometryn	0	0	0	0	3
haloxyfop	0	0	0	0	3
glufosinaat	0	0	0	0	3
dichloorvos	0	0	0	0	3
1-(3,4-dichloorfenyl)-3-methylureum	0	0	0	0	2
2,6-dichloorbenzoezuur	0	0	0	0	2
2,4,5-t	0	0	0	2	0
2,4-dp	0	0	0	0	2
terbutryn	0	0	0	0	2
carbofuran	0	0	0	0	2
methabenzthiazuron	0	0	0	0	2
fenhexamid	0	0	0	1	1
fipronil	0	0	0	0	2
6-benzyladenine	0	0	0	0	2
clothianidin	0	0	0	0	2
ethoprofos	0	0	0	0	2
methomyl	0	0	1	0	1
methoxyfenozide	0	0	0	0	1
thiofanoxsulfon	0	0	0	0	1
chloorbromuron	0	0	0	0	1
clomazone	0	0	0	0	1
fonofos	0	0	0	1	0
cyanazine	0	0	0	0	1

4-chloorfenoxyazijnzuur	0	0	0	1	0
lenacil	0	0	0	1	0
azinphos-methyl	0	0	0	0	1
desmethylprimicarb	0	0	0	0	1
p,p'-ddt	0	0	0	0	1
fosthiazate	0	0	0	0	1
joodpropynylcarbamaat	0	0	0	1	0
pcnb	0	0	0	0	1
trichlorfon	0	0	0	0	1
pirimifos-ethyl	0	0	0	0	1
dimethachloor	0	0	0	0	1
asulam	0	0	0	0	1
beta-endosulfan	0	0	0	1	0
chloorthal	0	0	0	0	1
metobromuron	0	0	0	0	1
pyridate	0	0	0	0	1
triflusulfuron-methyl	0	0	0	0	1
fluometuron	0	0	0	1	0
monolinuron	0	0	0	0	1
methyl	0	0	0	0	1
diazinon	0	0	0	0	1
fenuron	0	0	0	1	0
flutolanil	0	0	0	0	1
tebuconazool	0	0	0	0	1

Attachment III

Chemical properties of the recently authorized pesticides

This annex is found in excel file titled ‘Attachment III’

Attachment IV

LC-MS/MS selected reaction monitorings (SRM) parameters

Compound	Precursion	Product ions	Collision energy (eV)	Rt (min)	Window (min)	S-lens	mode
Acetamiprid	223.00	90 / 126	34 / 21	6.83	1.00	78	positive
Amisulbrom	465.90	148.0 / 226.9	46 / 19	13.32	1.00	78	positive
Atrazine-d5	221.13	179.1	19	8.98	1.00	82	positive
Benalaxyl-M	326.10	148.1 / 208.1	21 / 15	12.09	1.00	76	positive
Bentazone-d6	245.90	132.1	28	8.15	1.00	100	negative
Benthiavalicarb-isopropyl	382.09	180.0 / 197.0	32 / 18	10.26	1.00	91	positive
Bixafen	413.90	266.0 / 394.0	23 / 13	11.80	1.00	105	positive
Chlorantraniliprole	481.90	283.8 / 451.0	16 / 17	9.96	1.00	100	positive
Clothianidine	249.90	132.0 / 169.0	17 / 13	6.25	1.00	50	positive
Cyflufenamide	413.10	203.0 / 295.0	40 / 16	13.07	1.00	91	positive
Etoxazool	360.10	141.0 / 304.0	33 / 17	14.24	1.00	106	positive
Fenpyrazamine	332.09	216.1 / 230.1	27 / 18	11.16	1.00	75	positive
Flubendiamide	680.90	254.0 / 274.0	28 / 18	12.07	1.00	148	negative
Flumioxazin	355.04	299.1 / 327.1	30 / 25	10.58	1.00	150	positive
Fluopyram	397.00	173.0 / 208.0	30 / 22	11.26	1.00	112	positive
Fluoxastrobin	459.00	188.0 / 427.0	36 / 16	11.68	1.00	116	positive
Fluxapyroxad	382.03	342.1 / 362.1	21 / 13	11.00	1.00	93	positive
Imazamox	306.10	246.1 / 261.1	23 / 20	6.10	1.00	105	positive
Mandipropamid	412.06	125.0 / 328.1	35 / 14	11.03	1.00	78	positive
Metconazole	320.10	70.0 / 125.0	35 / 39	11.56	1.00	96	positive
Napropamide	272.10	171.1 / 199.1	19 / 12	11.14	1.00	71	positive
Silthiofam	268.10	139.0 / 252.1	19 / 10	11.85	1.00	51	positive
Spirotetramat	374.10	2161 / 330.2	33 / 15	10.56	1.00	84	positive
Thiamethoxam	292.00	181.0 / 211.0	22 / 12	5.70	1.00	59	positive
Triclopyr	255.90	146.0 / 209.9	28 / 16	9.42	1.00	67	positive
Tritosulfuron	446.00	195.0 / 221.0	19 / 19	10.66	1.00	117	positive

Attachment V

Sampling locations

1. Monitoring campaign May/June 2016.

Monster-Nummer	Text-ID	Monster-Datum	Oorsprong	Matrix	Bedrijf
8045	LMC-8058-OW	24/05/2016	Drentse As	OW	WBG
8046	LMC-8059-GW	24/05/2016	PS Gasselte: pp 6 54,0 - 71,13	GW	WMD
8047	LMC-8060-GW	24/05/2016	PS Gasselte: pp 8 48,6 - 69,6	GW	WMD
8048	LMC-8061-GW	24/05/2016	PS Gasselte: pp15 53,6 - 63,2	GW	WMD
8049	LMC-8062-GW	24/05/2016	PS Beilen: pp 6 41,0- 72,0	GW	WMD
8050	LMC-8063-GW	24/05/2016	PS Beilen: pp 7 41,0 - 71,0	GW	WMD
8051	LMC-8064-GW	24/05/2016	PS Beilen: pp 11 50,0 - 69,0	GW	WMD
8052	LMC-8065-GW	24/05/2016	PS Valtherbos: pp 6 28,0 - 50,5	GW	WMD
8053	LMC-8066-GW	24/05/2016	PS Valtherbos: pp 8 25,5 - 47,0	GW	WMD
8054	LMC-8067-GW	24/05/2016	PS Valterbos: pp 10 28,0 - 50,9	GW	WMD
8055	LMC-8068-GW	24/05/2016	PS Noordbargeres: pp 34 50,7 - 60,5	GW	WMD
8056	LMC-8069-GW	24/05/2016	PS Noordbargeres: pp 41 49,9 - 62,73	GW	WMD
8057	LMC-8070-GW	24/05/2016	PS Noordbageres: pp 45 48,0 - 60,0	GW	WMD
8079	LMC-8102-OW	24/05/2016	WPB Lith Ruwwater tak voor PPS: P101 - P105 - P108	GW	BW
8080	LMC-8103-GW	24/05/2016	WPB Lith P101	GW	BW
8081	LMC-8104-GW	24/05/2016	Lith B4513 0305	GW	BW
8082	LMC-8105-OW	23/05/2016	Vessem Ruwwater tak 1: pps 51 - 56 - 60	GW	BW
8083	LMC-8106-GW	23/05/2016	Vessum pp 056	GW	BW
8084	LMC-8107-GW	23/05/2016	Vessum B51C - 0394	GW	BW
8085	LMC-8108-OW	26/05/2016	Waalwijk Ruw water in bedrijf: pp 65-66-67	GW	BW
8086	LMC-8109-GW	26/05/2016	Waalwijk pp 65	GW	BW
8087	LMC-8110-GW	26/05/2016	Waalwijk B44H - 0166	GW	BW
8088	LMC-8111-GW	25/05/2016	Gilze Winning pp 053	GW	BW
8089	LMC-8112-GW	24/05/2016	Gilze B50E - 0366	GW	BW
8090	LMC-8113-GW	24/05/2016	WPB Macharen Ruwwatertak PFG2 pp in bedrijf: pp 101-205-206-207-209-212-213-214-215-216-218-219-220-221-222-223	GW	BW
8091	LMC-8114-GW	24/05/2016	WPB Macharen pp 205	GW	BW
8092	LMC-8115-GW	24/05/2016	Macharen B45E - 0395	GW	BW
8093	LMC-8116-OW	24/05/2016	WPB Nuland Ruwwater tak 2 middeldiep: pps 051-052-053-054-056-057-058-059-060	GW	BW
8094	LMC-8117-GW	24/05/2016	WPB Nuland pp 060	GW	BW

Monster-Nummer	Text-ID	Monster-Datum	Oorsprong	Matrix	Bedrijf
8095	LMC-8118-GW	24/05/2016	Nuland B45B - 0555	GW	BW
8096	LMC-8119-OW	24/05/2016	Evides Ossendrecht Verzameld ruwwater POSS20RUWW	GW	Evides
8097	LMC-8120-GW	24/05/2016	Evides Ossendrecht Pompput A1 P0SS00A1XX	GW	Evides
8098	LMC-8121-GW	24/05/2016	Evides Ossendrecht Waarnemingsfilter 50.053.f1	GW	Evides
8099	LMC-8122-OW	24/05/2016	Evides Ouddorp ruwwater na duinpassage POUD20RUWW	DF	Evides
8100	LMC-8123-OW	24/05/2016	Evides Scheelhoek POUD13INNA	OW	Evides
8101	LMC-8124-OW	24/05/2016	Evides Keizersveer RKEI00MEET	OW	Evides
8129	LMC-8156-GW	18/05/2016	Pb. Vechterweerd, Ruwwater Streng 3: Winputten 11, 12 en 13	RBF	Vitens
8130	LMC-8157-GW	18/05/2016	Pb. Vechterweerd, VEW13P101 filter 2	RBF	Vitens
8131	LMC-8158-GW	18/05/2016	Pb. Vechterweerd, Winput 2014-13	RBF	Vitens
8132	LMC-8159-GW	12/05/2016	Pb. Vorden, PB 34CL0071 5.3m	GW	Vitens
8133	LMC-8160-GW	12/05/2016	Pb. Vorden, Winputgroep 1 winput 01-02, 02-03, 03-04 Tappunt (ruw)	GW	Vitens
8134	LMC-8161-GW	11/05/2016	Pb. Goor gez. Aanvoer VF 11-13 (Ruwwater)	GW	Vitens
8135	LMC-8162-GW	11/05/2016	Pb. Goor Winput 2004-16	GW	Vitens
8136	LMC-8163-GW	11/05/2016	Pb. Goor, GO10P18 4m	GW	Vitens
8137	LMC-8164-GW	10/05/2016	Pb. Wierden, Ruwwater Streng 1	GW	Vitens
8138	LMC-8165-GW	10/05/2016	Pb. Wierden, Winput 2012-54 (electr. Nr. 803) Ypelo	GW	Vitens
8139	LMC-8166-GW	13/05/2016	Pb. Olde Eibergen, Gezamenlijk ruw Tappunt Haarlo	GW	Vitens
8140	LMC-8167-GW	13/05/2016	Pb. Olde Eibergen, Winput 05-09 Haarlo	GW	Vitens
8141	LMC-8168-GW	13/05/2016	Pb. Olde Eibergen, PB HAL 003-001 2.9-3.9 m-mv	GW	Vitens
8142	LMC-8169-GW	24/05/2016	Pb. Groenekan, GR-RUW: PS GROENEKAN RUW VF 1,2,3	GW	Vitens
8143	LMC-8170-GW	24/05/2016	Pb. Groenekan, GRPP014F01: GR POMPPUT 14 WF 1 (80-82 m-mv)	GW	Vitens
8144	LMC-8171-GW	24/05/2016	Pb. Groenekan, GRPP014F01: GR WP 21 FILTER 2 (17-18 m-mv)	GW	Vitens
8145	LMC-8172-GW	23/05/2016	PB. Heumensoord, Gezamenlijk ruw Heumensoord	GW	Vitens
8146	LMC-8173-GW	23/05/2016	PB. Heumensoord, Winput 1995-4E	GW	Vitens
8147	LMC-8174-GW	23/05/2016	PB. Heumensoord, PB 46AP0705 13m	GW	Vitens
8148	LMC-8175-GW	25/05/2016	Pb Velddriel- Ruw	GW	Vitens
8149	LMC-8176-GW	25/05/2016	Pb Velddriel - Winput 2	GW	Vitens
8150	LMC-8177-GW	25/05/2016	Pb Velddiel - PB 45AP0237	GW	Vitens
8151	LMC-8178-GW	25/05/2016	Zs. Rodenhuis - pompput 25	RBF	Oasen
8152	LMC-8179-GW	25/05/2016	Zs. Rodenhuis - Ruw	RBF	Oasen
8153	LMC-8180-GW	25/05/2016	Zs. Rodenhuis - GRHWE39B	RBF	Oasen
8154	LMC-8181-GW	25/05/2016	Zs. Lekkerkerk - pompput 12	RBF	Oasen
8155	LMC-8182-GW	25/05/2016	Zs. Lekkerkerk - Ruw	RBF	Oasen
8185	LMC-8209-GW	23/05/2016	WBE-IP37 Infiltratie plas 37 Berkheide	OW	Dunea
8186	LMC-8210-GW	23/05/2016	WBE-IP25_3 Infiltratie plas 25_3 Berkheide	OW	Dunea
8187	LMC-8211-GW	23/05/2016	PBL-INF inname Lagedrukpompstation Brakel	OW	Dunea

Monster-Nummer	Text-ID	Monster-Datum	Oorsprong	Matrix	Bedrijf
8188	LMC-8212-GW	23/05/2016	PSC-VK-VOW Onttrokken Water pompstation Scheveningen-Verzameld	DF	Dunea
8189	LMC-8213-GW	23/05/2016	IJM-PW? Pompstation Andijk - IJsselmeer	OW	PWN
8190	LMC-8214-GW	24/05/2016	PNG-OW-02 Ruw water inlaat WCB (Lekkanaal)	OW	Waternet
8191	LMC-8215-GW	24/05/2016	ARK Amsterdam-Rijn-kanaal Nieuwersluis	OW	Waternet
8192	LMC-8216-GW	24/05/2016	WBP-TK-001 Wingebied Bethunepolder - Toevoerkanaal na Bethunegemaal	OW	Waternet
8193	LMC-8217-GW	24/05/2016	PLD-SF-INF002 Pompstation Leiduin 2 - Ruw / Influent Snelfilters Pompstation Leiduin 2	DF	Waternet
8194	LMC-8218-GW	25/05/2016	PBL-INF inname Lagedrukpompstation Brakel	OW	Dunea
8195	LMC-8219-GW	25/05/2016	GBR-AVK Gemaal Brakel - Aanvoerkanaal	OW	Dunea
8196	LMC-8220-GW	25/05/2016	PKW-SFGB-VOW Pompstation Katwijk - Snelfiltergebouw B- Verzameld Uit Duin Onttrokken Water	DF	Dunea
9158	LMC-9171-GW	08-Jun-16	PS. Roosteren Ruwwater 3 Westleiding	RBF	WML
9159	LMC-9172-GW	08-Jun-16	PS. Roosteren Gezaemlijk ruwwater 2 Oostleiding	GW	WML
9160	LMC-9173-GW	08-Jun-16	PS. Roosteren Gezamelijk Ruwwater IRadiaalput	RBF	WML
9161	LMC-9174-GW	08-Jun-16	Gez. Effl. Weekmonster happer	OW	WML
9162	LMC-9175-GW	08-Jun-16	Boschmolenplas mp. 2.1.	OW	WML
9163	LMC-9176-GW	08-Jun-16	Gez. Ruw Galgenberg	GW	WML
9164	LMC-9177-GW	08-Jun-16	Gez. Ruw Langven en Reut	GW	WML
9165	LMC-9178-GW	06-Jun-16	PS. De Tombe Gezamelijk Ruwwater	GW	WML
9166	LMC-9179-GW	06-Jun-16	PS. Heer PP 2 Filter 0	GW	WML
9167	LMC-9180-GW	07-Jun-16	OPB IJzeren Kuilen Aanvoer Ruwwater IJZeren Kuilen	GW	WML
9168	LMC-9181-GW	09-Jun-16	Conv-Ruwwater	GW	WML
9169	LMC-9182-GW	06-Jun-16	PS. Beegelen Gezamelijk Ruwwater 2	GW	WML
9170	LMC-9183-GW	07-Jun-16	Spaarbekken mp 5.1	OW	WML
9068	LMC-9108-GW	30 MEI 2016	WPC DIETS-HEUR, 4022-002-F0, RUW GRONDWATER	GW	De Watergroep
9069	LMC-9109-GW	30 MEI 2016	WPC SPELT, BATTERIJ ZEMST SPELT, RUW GRONDWATER	GW	De Watergroep
9070	LMC-9110-OW	01-Jun-16	GRAVERS HYDROGRAFISCH BEKKEN, S24 SCHELDE BOSSUIT te STASEGE, OPPERVLAKTEWATER	OW	De Watergroep
9071	LMC-9111-OW	01-Jun-16	SCHELDE HYDROGRAFISCH BEKKEN, S21 SCHELDE te HELKIJN, OPPERVLAKTEWATER	OW	De Watergroep
9072	LMC-9112-GW	02-Jun-16	WPC HAC, TOEVOER, LD ABDIJ/CADOL RUW GRONDWATER	GW	De Watergroep
9073	LMC-9113-GW	02-Jun-16	WPC HAC, TOEVOER, LD HUISKENS RUW GRONDWATER	GW	De Watergroep
9074	LMC-9114-GW	02-Jun-16	WPC VEEWEYDE, MENGSEL VEEWEYDE, RUW GRONDWATER	GW	De Watergroep
9075	LMC-9115-GW	02-Jun-16	WPC TOMBEEK, MENGSEL VENUSBERG DRAINS, RUW GRONDWATER	GW	De Watergroep

Monster-Nummer	Text-ID	Monster-Datum	Oorsprong	Matrix	Bedrijf
9076	LMC-9116-GW	02-Jun-16	WPC VLIERBEEK, BATTERIJ VLIERBEEK, RUW GRONDWATER	GW	De Watergroep
9077	LMC-9117-GW	02-Jun-16	WPC WAARMAARDE, BATTERIJ MENGSEL CkCwCa, RUW GRONDWATER	GW	De Watergroep
9078	LMC-9118-GW	02-Jun-16	WPC KLEIN-SINAAI, BATTERIJEN, RUW GRONDWATER	GW	De Watergroep
9079	LMC-9119-GW	03-Jun-16	WPC AARSCHOT, BATTERIJ AARSCHOT SCHOONHOVEN, RUW GRONDWATER	GW	De Watergroep
9080	LMC-9120-GW	03-Jun-16	WPC AARSCHOT, MENG SCHOONHOVEN BRUSSELIAAN, RUW GRONDWATER	GW	De Watergroep
9081	LMC-9121-GW	03-Jun-16	WPC WALSHOUTEM, DRAIN, RUW GRONDWATER	GW	De Watergroep
9082	LMC-9122-GW	06-Jun-16	WPC EEGENHOVEN-OOST, BATTERIJ EGENHOVEN-OOST, RUW GRONDWATER	GW	De Watergroep
9083	LMC-9123-GW	06-Jun-16	WPC EEGENHOVEN-WEST, BATTERIJ EGENHOVEN WEST, RUW GRONDWATER	GW	De Watergroep
9084	LMC-9124-OW	06-Jun-16	WPC ZILLEBEKE, INSTALLATIE, OPPERVLAKTEWATER	OW	De Watergroep
9085	LMC-9125-OW	06-Jun-16	IEPER HYDROGRAFISCH BEKKEN, Y2 BOLLAERTBEEK, OPPERVLAKTEWATER	OW	De Watergroep
9086	LMC-9126-OW	06-Jun-16	IEPER HYDROGRAFISCH BEKKEN, Y4, KEMMELBEEK, OPPERVLAkTEWATER	OW	De Watergroep
9087	LMC-9127-GW	06-Jun-16	WPC BEERNEM, BATTERIJEN, RUW GRONDWATER	GW	De Watergroep
9088	LMC-9128-GW	06-Jun-16	WPC EEKLO, BATTERIJ S1 WAAISTRAAT, RUW GRONDWATER	GW	De Watergroep
9089	LMC-9129-GW	06-Jun-16	WPC EEKLO, BATTERIJ S3 AALSTGOED, RUW GRONDWATER	GW	De Watergroep
9090	LMC-9130-OW	06-Jun-16	IJZER HYDROGRAFISCH BEKKEN, B7N IJZER te KNOKKE/WATERVANG, OPPERVLAKTEWATER	OW	De Watergroep
9091	LMC-9131-OW	06-Jun-16	IJZER HYDROGRAFISCH BEKKEN, B13 IJZER te FINTELE, OPPERVLAKTEWATER	OW	De Watergroep
9092	LMC-9132-OW	06-Jun-16	WPC BLANKAART, INSTALLATIE, OPPERVLAKTEWATER	OW	De Watergroep
9093	LMC-9133-GW	07-Jun-16	WPC EISDEN, PUTTEN, RUW GRONDWATER	GW	De Watergroep
9094	LMC-9134-GW	07-Jun-16	WPC LEUT-MEESWIJK, MENGSEL LEUT-MEESWIJK, RUW GRONDWATER	GW	De Watergroep
9095	LMC-9135-GW	07-Jun-16	WPC AS, MENGSEL AS, RUW GRONDWATER	GW	De Watergroep
9096	LMC-9136-GW	07-Jun-16	WPC BOVELINGEN NIEUW, PUTTEN, RUW GRONDWATER	GW	De Watergroep
9097	LMC-9137-GW	07-Jun-16	WPC VOORT, MENGSEL VOORT, RUW GRONDWATER	GW	De Watergroep
9098	LMC-9138-GW	07-Jun-16	WPC VELM/SINT-TRUIDEN, 4015-007-F0, RUW GRONDWATER	GW	De Watergroep
9099	LMC-9139-GW	07-Jun-16	WPC VELM/SINT-TRUIDEN, 4015-008-F0, RUW GRONDWATER	GW	De Watergroep
9100	LMC-9140-GW	07-Jun-16	WPC HERENT, MENGSEL HEREN BIJLOK, RUW GRONDWATER	GW	De Watergroep
9101	LMC-9141-GW	07-Jun-16	WPC KASTANJEBOS, MENG KASTANJEBOS 010, 011, 012, RUW GRONDWATER	GW	De Watergroep
9102	LMC-9142-GW	07-Jun-16	WPC KASTANJEBOS, MENG KASTANJEBOS 013, 014, 015, RUW GRONDWATER	GW	De Watergroep
9103	LMC-9143-GW	07-Jun-16	WPC KOUTERSTRAAT, DRAINS EN PUTTEN, VOOR AKTIEF KOOLFILTER (grondwater)	GW	De Watergroep

Monster-Nummer	Text-ID	Monster-Datum	Oorsprong	Matrix	Bedrijf
9104	LMC-9144-OW	07-Jun-16	WPC DIKKEBUS, INSTALLATIE, OPPERVLAKTEWATER	OW	De Watergroep
9105	LMC-9145-GW	08-Jun-16	WPC LEEFDAAL, BATTERIJ, RUW GRONDWATER	GW	De Watergroep
9106	LMC-9146-GW	08-Jun-16	WPC PUTTEBOS, BATTERIJ PUTTEBOS, RUW GRONDWATER	GW	De Watergroep
9107	LMC-9147-GW	08-Jun-16	WPC VERONICA, BATTERIJ VERONICA, REIN WATER (grondwater)	GW	De Watergroep

2. Monitoring campaign august 2016.

Code	Text-ID	Sampling date	Origin	Matrix	Bedrijf
14428	LMC-14452-OW	19-Aug-16	PS De Punt [OW] Rivierwater Drentsche Aa	OW	WMD
14429	LMC-14453-OW	23-Aug-16	POUD13INNA Scheelhoek	OW	Evides
14430	LMC-14454-OW	23-Aug-16	RKEI00MEET Keizersveer	OW	Evides
14431	LMC-14455-OW	22-Aug-16	WBE-IP37 Berkheide infiltratieplas 37	OW	Dunea
14432	LMC-14456-OW	22-Aug-16	WBE-IP25_3 Berkheide infiltratieplas 25_3	OW	Dunea
14433	LMC-14457-OW	22-Aug-16	PBL-INF inname Lagedrukpompstation Brakel	OW	Dunea
14434	LMC-14458-OW	22-Aug-16	GBR-AVK Gemaal Brakel	OW	Dunea
14435	LMC-14459-OW	22-Aug-16	IJM-PWN Pompstation Andijk - IJsselmeer	OW	PWN
14436	LMC-14460-OW	22-Aug-16	PNG-OW-02 Ruw water inlaat WCB (Lekkanaal)	OW	Waternet
14437	LMC-14461-OW	23-Aug-16	ARK Amsterdam-Rijn-Kanaal Nieuwersluis	OW	Waternet
14438	LMC-14462-OW	23-Aug-16	WBP-TK-001 Wingebied Bethunepolder - Toevoerkanaal na Bethunegemaal	OW	Waternet
14439	LMC-14463-OW	25-Aug-16	S24 Schelde Bossuit te Stasege	OW	De Watergroep
14440	LMC-14464-OW	25-Aug-16	S21 Schelde te Helkijn	OW	De Watergroep
14441	LMC-14465-OW	25-Aug-16	WPC Zillebeke, Installatie	OW	De Watergroep
14442	LMC-14466-OW	25-Aug-16	Y2 Bollaertbeek	OW	De Watergroep
14443	LMC-14467-OW	25-Aug-16	Y4 Kemmelbeek	OW	De Watergroep
14444	LMC-14468-OW	25-Aug-16	B7N IJzer te Knokke	OW	De Watergroep
14445	LMC-14469-OW	25-Aug-16	B13 IJzer te Fintele	OW	De Watergroep
14446	LMC-14470-OW	25-Aug-16	WPC Blankaart, Installatie	OW	De Watergroep
14447	LMC-14471-OW	25-Aug-16	WPC Dikkebus, Installatie	OW	De Watergroep
14711	LMC-14713-OW	30-Aug-16	PS Heel Spaarbekken	OW	WML
14712	LMC-14714-OW	30-Aug-16	PS Heel Gez. Effl. Weekhapper Heel RU0101 (Schepmonster)	OW	WML

Attachment VI

List of compounds in the analytical method

Analytical method 2016

Nr.	CAS number	Pesticides	Application	Detected
1	135410-20-7	Acetamiprid	insecticide	no
2	348635-87-0	Amisulbrom	fungicide	no
3	98243-83-5	Benalaxyl-M	fungicide	no
4	177406-68-7	Benthiavalicarb-isopropyl	fungicide	no
5	**581809-46-3**	**Bixafen**	**fungicide**	**yes**
6	**500008-45-7**	**Chlorantraniliprole**	**insecticide**	**yes**
7	**210880-92-5**	**Clothianidine**	**insecticide**	**yes**
8	180409-60-3	Cyflufenamide	fungicide	no
9	153233-91-1	Etoxazool	acaracide	no
10	473798-59-3	Fenpyrazamine	fungicide	no
11	272451-65-7	Flubendiamide	insecticide	no
12	103361-09-7	Flumioxazin	herbicide	no
13	**658066-35-4**	**Fluopyram**	**fungicide**	**yes**
14	**361377-29-9**	**Fluoxastrobin**	**fungicide**	**yes**
15	**907204-31-3**	**Fluxapyroxad**	**fungicide**	**yes**
16	**114311-32-9**	**Imazamox**	**herbicide**	**yes**
17	**374726-62-2**	**Mandipropamid**	**fungicide**	**yes**
18	**125116-23-6**	**Metconazole**	**fungicide**	**yes**
19	15299-99-7	Napropamide	herbicide	no
20	175217-20-6	Silthiofam	fungicide	no
21	**203313-25-1**	**Spirotetramat**	**insecticide**	**yes**
22	**153719-23-4**	**Thiamethoxam**	**insecticide**	**yes**
23	55335-06-3	Triclopyr	groeiregulator	no
24	**142469-14-5**	**Tritosulfuron**	**herbicide**	**yes**

Analytical method 2007

Nr.	CAS	Pesticide	Application	Detected
1	120923-37-7	Amidosulfuron	herbicide	no
2	120163-55-2	Azimsulfuron	herbicide	no
3	**81777-89-1**	**Clomazone**	**herbicide**	**yes**
4	**66215-27-8**	**Cyromazin**	**insecticide**	**yes**
5	**163515-14-8**	**Dimethenamid-p**	**herbicide**	**yes**
6	126801-58-9	Ethoxysulfuron	herbicide	no
7	145701-23-1	Florasulam	herbicide	no
8	173159-57-4	Foramsulfuron	herbicide	no
9	**98886-44-3**	**Fosthiazaat**	**nematicide**	**yes**
10	**138261-41-3**	**Imidacloprid**	**insecticide**	**yes**
11	144550-36-7	Jodosulfuron-methyl	herbicide	no
12	135590-91-9	Mefenpyr-diethyl	herbicide	no
13	**104206-82-8**	**Mesotrion**	**herbicide**	**yes**
14	**111991-09-4**	**Nicosulfuron**	**herbicide**	**yes**
15	144651-06-9	Oxasulfuron	herbicide	no
16	94125-34-5	Prosulfuron	herbicide	no
17	123312-89-0	Pymetrozine	insecticide	no
18	**175013-18-0**	**Pyraclostrobin**	**fungicide**	**yes**
19	53112-28-0	Pyrimethanil	fungicide	no
20	122931-48-0	Rimsulfuron	herbicide	no
21	**99105-77-8**	**Sulcotrion**	**herbicide**	**yes**
22	141776-32-1	Sulfosulfuron	herbicide	no
23	**335104-84-2**	**Tembotrione**	**herbicide**	**yes**
24	**111988-49-9**	**Thiacloprid**	**insecticide**	**yes**
25	59669-26-0	Thiodicarb	molluscicide	no
26	126535-15-7	Triflusulfuron-methyl	herbicide	no

Attachment VII

Results pesticide analyses: analytical method 2016 and 2007

Below you will find the results of the pesticide screening analyses. The sample locations are referred to with a number, shown in the table.

Sample number	Sample location – reference to table below
1	IJZER HYDROGRAFISCH BEKKEN, B7N IJZER te KNOKKE/WATERVANG, OPPERVLAKTEWATER
2	IJZER HYDROGRAFISCH BEKKEN, B13 IJZER te FINTELE, OPPERVLAKTEWATER
3	WPC DIKKEBUS, INSTALLATIE, OPPERVLAKTEWATER
4	IEPER HYDROGRAFISCH BEKKEN, Y2 BOLLAERTBEEK, OPPERVLAKTEWATER
5	IEPER HYDROGRAFISCH BEKKEN, Y4, KEMMELBEEK, OPPERVLAKTEWATER
6	WPC BLANKAART, INSTALLATIE, OPPERVLAKTEWATER
7	SCHELDE HYDROGRAFISCH BEKKEN, S21 SCHELDE te HELKIJN, OPPERVLAKTEWATER
8	WPC ZILLEBEKE, INSTALLATIE, OPPERVLAKTEWATER
9	GRAVERS HYDROGRAFISCH BEKKEN, S24 SCHELDE BOSSUIT te STASEGE, OPPERVLAKTEWATER
10	WPC HAC, TOEVOER, LD HUISKENS RUW GRONDWATER
11	WPC VELM/SINT-TRUIDEN, 4015-007-F0, RUW GRONDWATER
12	Gilze B50E - 0366
13	PBL-INF
14	PBL-INF
15	WBE-IP37
16	GBR-AVK
17	WBE-IP25_3
18	PSC-VK-VOW
19	PKW-SFGB-VOW
20	POUD13INNA
21	RKEI00MEET
22	IJM-PW?
23	Pb. Vechterweerd
24	ARK
25	PNG-OW-02
26	PLD-SF-INF002
27	Gez. Effl. Weekmonster happer

Screening method 2016

Results june

Drinking Water Company	De Watergroep											BW	Dunea							Evides		PWN	Vitens	Waternet			WML
Water type	Surface water									GW		GW	Surface water							Surface wate		SW	GW	Surface water			SW
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Thiamethoxam	0.07	0.09										0.01	0.41	0.12	0.04	0.02	0.01						0.01				
Fluopyram	0.04	0.02	0.02	0.03	0.01	0.1	0.01	0.05	0.01				0.28	0.05	0.03	0.02	0.02	0.01	0.01	0.02	0.01	0.01		0.02	0.01	0.01	0.01
Clothianidine	0.08	0.05	0.03	0.05	0.02		0.03					0.12	0.02	0.01													0.01
Fluxapyroxad	0.09	0.07	0.06	0.04	0.02	0.02	0.03	0.02																			0.01
Bixafen	0.05	0.05	0.03	0.02	0.01	0.01	0.03		0.01																		0.01
Imazamox	0.03	0.04																									
Metconazool	0.02	0.02	0.01	0.02	0.01	0.01																					
Chlorantraniliprole													0.02							0.01							
Tritosulfuron	0.02	0.01	0.01																								
Fluoxastrobin	0.01	0.01	0.01	0.01	0.01				0.01																		
Mandipropamid				0.01	0.01																						
Spirotetramat													0.01														

empty cell: below detection limit (0.01 ug/L)

Results august

Drinking Water Company	De Watergroep											BW	Dunea							Evides		PWN	Vitens	Waternet			WML
Water type	Surface water									GW		GW	Surface water							Surface wate		SW	GW	Surface water			SW
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Thiamethoxam	0.01	0.02		0.23	0.01					-	-	-	0.03	-	0.01	0.26	0.01		0.01				-				
Fluopyram	0.3	0.14	0.02	0.24	0.03	0.05	0.01	0.07	0.01	-	-	-	0.03	-	0.02	0.13	0.02		0.02	0.01	0.02	0.01	-	0.01	0.01		
Clothianidine			0.01	0.01				0.01		-	-	-		-		0.02							-				
Fluxapyroxad	0.03	0.03	0.13	0.05	0.04	0.03		0.09	0.01	-	-	-		-									-				
Bixafen	0.02	0.02	0.02	0.06	0.02			0.01	0.02	-	-	-		-									-				0.01
Imazamox	0.07	0.03		0.04						-	-	-		-									-				
Metconazool	0.01	0.01	0.01	0.01	0.01					-	-	-		-									-				
Chlorantraniliprole										-	-	-	0.01	-		0.04	0.01						-				
Tritosulfuron	0.01	0.01						0.01		-	-	-		-									-				
Fluoxastrobin		0.01	0.01	0.15	0.01					-	-	-		-									-				
Mandipropamid	0.04	0.03	0.3	0.16	0.07	0.03		0.1	0.01	-	-	-		-									-				
Spirotetramat										-	-	-		-									-				
Acetamiprid	0.01	0.01		1.1						-	-	-		-									-				
Benthiavalicarb-isopropyl	0.02	0.02		0.06						-	-	-		-									-				
Cyflufenamide					0.01					-	-	-		-									-				

empty cell: below detection limit (0.01 ug/L); (-): not measured

Screening method 2007

Results june

Drinking Water Company	De Watergroep											BW	Dunea							Evides		PWN	Vitens	Waternet			WML
Water type	Surface water									GW		GW	Surface water							Surface wate		SW	GW	Surface water			SW
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Dimethenamid-p	0.48	0.27	0.8	0.1	0.26	0.09			0.03	0.18																	0.25
Fosthiazaat	0.14	0.19	0.09		0.03																						
Clomazone	0.17	0.18	0.07	0.06						0.03																	
Mesotrion	0.1	0.14			0.03					0.05																	0.03
Sulcotrion	0.04	0.07																									
Cyromazin											0.05																
Thiacloprid									0.05				0.03														
Imidacloprid	0.04	0.04											0.03														
Nicosulfuron	0.03	0.04																									
Tembotrione	0.03		0.03																								

empty cell: below detection limit (0.03 ug/L)

Results august

Drinking Water Company	De Watergroep											BW	Dunea							Evides		PWN	Vitens	Waternet			WML
Water type	Surface water									GW		GW	Surface water							Surface wate		SW	GW	Surface water			SW
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Dimethenamid-p	0.67	0.62	0.51	1.3	0.08	0.14		0.4	0.04	-	-	-	0.04	-	0.04		0.04						-				
Fosthiazaat										-	-	-		-									-				
Clomazone	0.07	0.06	0.05	0.07		0.03		0.04		-	-	-		-									-				
Mesotrion								0.06		-	-	-		-									-				
Sulcotrion						0.04				-	-	-		-									-				
Cyromazin	0.04									-	-	-		-									-				
Thiacloprid	0.04	0.06		0.05						-	-	-		-									-				
Imidacloprid		0.04								-	-	-		-									-				
Nicosulfuron	0.04	0.03	0.04	0.08				0.08		-	-	-		-									-				
Tembotrione	0.1	0.07	0.07	0.03				0.09		-	-	-		-									-				
Pymetrozine					0.04					-	-	-		-									-				

empty cell: below detection limit (0.03 ug/L); (-): not measured

References

Adriaanse. Development of an assessment methodology to evaluate agricultural use of plant protection products for drinking water production from surface waters. Alterra, 2008.

Appelo CAJ. Geochemistry, groundwater and pollution. Rotterdam: AA Balkema, 1993.

Brinkmann FJJ, den Engelsman G, Wammes JIJ, Willemsen WH. Metingen van de gehalten aan diaceton-keto-gulonzuur (dikegulac) in grensoverschrijdend rivierwater gedurende het tijdvak 1 oktober 1990 tot en met 30 juni 1994. RIVM, De Bilt, 1995, pp. 28.

Ctgb. Evaulation manual for the Authorisation of Plant protection products and Biocides according to Regulation (EC) No 1107/2009. NL part. Plant protection products. chapter 6 Fate and behaviour in the environment: behaviour in surface water and sediment. Version 2.0. , 2014.

Dolan T, Howsam P, Parsons DJ, Whelan MJ. Is the EU drinking water directive standard for pesticides in drinking water consistent with the precautionary principle? Environmental Science and Technology 2013; 47: 4999-5006.

Dolan T, Howsam P, Parsons DJ, Whelan MJ. Impact of European water framework directive article 7 on drinking water directive compliance for pesticides: Challenges of a prevention-led approach. Water Policy 2014; 16: 280-297.

Drinkwaterbesluit. 2011.

Emke E. New pesticides. An anlytical survey. KWR Watercycle Research Institute, Nieuwegein, The Netherlands, 2007, pp. 78.

European Commision. EU Water Framework Directive - integrated river basin management for Europe, 2000/60/EC, Brussels, Belgium, 2000.

European Commission. The Drinking Water Directive, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption Brussels, Belgium, 1998, pp. 32-54.

European Commission. EU Pesticide database. Active substances. Reguation (EC) No 1107/2009, 2016.

FOCUS. FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. In: Scenarios FWGoSW, editor, 2001, pp. 245.

González-Rodríguez RM, Rial-Otero R, Cancho-Grande B, Gonzalez-Barreiro C, Simal-Gándara J. A review on the fate of pesticides during the processes within the food-production Chain. Critical Reviews in Food Science and Nutrition 2011; 51: 99-114.

Heuvelink GBM, Burgers SLGE, Tiktak A, Den Berg FV. Uncertainty and stochastic sensitivity analysis of the GeoPEARL pesticide leaching model. Geoderma 2010; 155: 186-192.

Hopman R, van beek CGEM, janssen HMJ, Puijker LM. Pesticides and the Drinking water Supply in the Netherlands. KIWA, 1990.

Linders JBHJ, Van der Linden AMA, Stienstra YJ. Surface water intended for the abstraction of drinking water after use of plant protection products on hard surfaces – Evaluation of plant production products. With corrigendum by Van der Linden (2012) RIVM, 2010.

Lovley DR, Chapelle FH. Deep subsurface microbial processes. Reviews of Geophysics 1995; 33: 365-381.

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, et al. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment 2014; 473–474: 619-641.

Peters JH. Pesticiden in waterwingebieden. KIWA, 1985.

Reemtsma T, Berger U, Arp HPH, Gallard H, Knepper TP, Neumann M, et al. Mind the Gap: Persistent and Mobile Organic Compounds - Water Contaminants That Slip Through. Environmental Science and Technology 2016; 50: 10308-10315.

RIWA. De kwaliteit van het Maaswater in 2015. RIWA-Maas, 2016a.

RIWA. Jaarpport 2015. De Rijn. RIWA-Rijn, 2016b.

Schreiner VC, Szöcs E, Bhowmik AK, Vijver MG, Schäfer RB. Pesticide mixtures in streams of several European countries and the USA. Science of the Total Environment 2016; 573: 680-689.

Sjerps RMA, ter Laak TL, Zwolsman JJG. Effect van klimaatverandering en vergrijzing op waterkwaliteit en drinkwaterfunctie van Maas en Rijn. Vakblad H2O 2016a: 10.

Sjerps RMA, ter Laak TL, Zwolsman JJG. Ontwikkeling waterkwaliteit bij innamepunten van oppervlaktewater voor de drinkwatervoorziening. KWR Watercycle Research Institute, Nieuwegein, The Netherlands, 2016b, pp. 107.

Stumm W, Morgan JJ. Aquatic chemistry. Third edition. . New York: John Wiley & Sons, Inc., 1996.

Stuyfzand PJ, Lüers F. Gedrag van milieugevaarlijke stoffen bij oeverinfiltratie en kunstmatige infiltratie. Effecten van bodempassage gemeten langs stroombanen. KIWA, VEWIN, 1996.

Swartjes FA, Van Der Linden AMA, van Der Aa NGFM. Bestrijdingsmiddelen in grondwater bij drinkwaterwinningen: huidige belasting en mogelijke maatregelen. RIVM, 2016, pp. 124.

Tiktak A, Boesten JJTI, Van Der Linden AMA, Vanclooster M. Mapping ground water vulnerability to pesticide leaching with a process-based metamodel of EuroPEARL. Journal of Environmental Quality 2006; 35: 1213-1226.

van Eerdt MM, Spruijt J, van der Wal E, van Zeijts H, Tiktak A. Costs and effectiveness of on-farm measures to reduce aquatic risks from pesticides in the Netherlands. Pest Management Science 2014; 70: 1840-1849.

Van Leerdam R, Adriaanse P. Evaluation of agricultural use of plant protection products for drinking water production from surface waters in the Netherlands - User□s manual of DROPLET to calculate concentrations at drinking water abstraction points. , 2009.

van Loon A, Sjerps RMA, Raat KJ. Gewasbeschrmingsmiddelen en hun afbraakproducten in Nederlandse drinkwaterbronnen. KWR, Nieuwegein, 2017, pp. 60.

Vijver MG, Kruijne R, Van 'T Zelfde M, Van Der Linden AM, Tamis WL, De Snoo GR. Similarities and differences between measured and predicted concentrations of pesticides in Dutch surface waters. Communications in agricultural and applied biological sciences 2011; 76: 879-889.