



## Occurrence of pesticides in Dutch drinking water sources

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### HIGHLIGHTS

- 15 out of 24 recently authorized pesticides were detected, including neonicotinoids.
- Of 408 pesticides and 52 metabolites, 63 pesticides and 6 metabolites were prioritized.
- In the majority of drinking water sources, pesticides and/or metabolites were detected.
- Some prioritized pesticides were not earlier detected in large monitoring studies.

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### ABSTRACT

We determined pesticide occurrence in groundwater and surface water sources used for drinking water production in The Netherlands, using both routine monitoring data from Dutch drinking water companies and by studying the presence of newly authorized pesticides in drinking water sources.

An analytical LC-MS/MS method was developed for 24 recently authorized pesticides, selected based on their mobility and persistence, and applied in a Dutch/Belgian ground- and surface water monitoring campaign. 15 of these pesticides were detected, including seven in concentrations above the water quality standard from the Water Framework Directive. Two neonicotinoids were detected in highest concentrations: acetamiprid (1.1 µg/L) and thiamethoxam (0.4 µg/L).

The routine monitoring data was collected over 2010–2014 in The Netherlands, covering 408 pesticides and 52 metabolites. 63 pesticides and 6 metabolites were prioritized according to their presence in groundwater, surface water and drinking water. The vast majority of the pesticides in routine monitoring has not been detected or only in low concentrations.

Overall, the study shows that pesticides are of major concern in drinking water sources across the Netherlands. In two third of the abstraction areas pesticides and/or metabolites have been detected. In one third of the abstraction areas pesticide and/or metabolites concentration exceeded water quality standards according to the Water Framework Directive. The results emphasize that monitoring should focus on priority pesticides, since the vast majority of the pesticides has a low priority. The occurrence of recently authorized pesticides in drinking water sources demonstrates the importance to keep routine monitoring methods up to date.

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### 1. Introduction

Pesticides are used widely in agriculture to protect crops from e.g. pathogens, fungi, insects and weeds. The global production and use of pesticides strongly grows in time (Bernhardt et al., 2017).

Pesticides contain one or more active substances, that can enter surface waters by drift or agriculture runoff, or leach into groundwater (González-Rodríguez et al., 2011; Heuvelink et al., 2010; van Eerd et al., 2014). These emissions may form a risk for ecosystem or human health (Kim et al., 2017; Munz et al., 2017; Nienstedt et al., 2012; Shelton et al., 2014; Stehle and Schulz, 2015). Pesticides are regularly monitored in surface water, groundwater and drinking water in the Netherlands (Hopman et al., 1990; Peters, 1985; RIWA, 2016a; RIWA, 2016b; Schipper et al., 2008; Schreiner et al., 2016; Stuyfzand and Lüers, 1996; Vijver et al., 2011; Vijver et al., 2008)

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and in Europe (Åkesson et al., 2015; Amalric et al., 2013; Köck-Schulmeyer et al., 2014; Loos et al., 2009, 2010; McManus et al., 2014; Schreiner et al., 2016; Stuart et al., 2012; Guillon et al., 2019).

Active ingredients used change in time, as they can be banned or identified as candidate for substitution and new substances are allowed. In Europe, pesticides are regulated and authorized according to the Plant Protection Products Regulation 1107/2009. Active substances can have access on the market if a safe use is possible (European Commission, 2016). Further authorization of pesticide products takes place per climatic zone and per type of use. National authorities evaluate the risks for humans and the environment, based on experimental data supplied by pesticide producers and standard scenarios in modelling studies (Tiktak et al., 2012).

When available, monitoring data are incorporated in the risk assessment. Drinking water companies regularly monitor drinking-, surface- and groundwater quality for the occurrence of pesticides and their metabolites, using routine target chemical analysis. Proactive monitoring, including newly authorized pesticides, can signal potential risks (Dolan et al., 2013, 2014). Several factors influence the potential risks of a pesticide for drinking water production. A large scale of use are often coupled to crops that are cultivated on large areas such as potatoes or corn, or to active ingredients that are used for many different purposes. Another factor is the vulnerability of the soil for leaching of the pesticides to groundwater. Also chemical specific properties such as the persistence, mobility and toxicity are relevant drivers of the risk (Stuart et al., 2012). Persistent and mobile organic compounds or PMOCs can more easily pass wastewater treatment, environmental removal processes and drinking water treatment, and thus pose risks for drinking water production (Reemtsma et al., 2016). For these PMOCs gaps exist in terms of analysis, monitoring, water treatment and regulation. Part of the (newly authorized) pesticides and their transformation products can be classified as PMOCs. During dry periods, which are expected to occur more frequently and prolonged under climate change, the dilution of these substances in surface water is reduced (Sjerps et al., 2017).

The EU Drinking Water Directive sets general drinking water quality standards for the active substances within pesticide products (hereafter referred to as pesticides) and their human toxicological relevant metabolites at 0.1 µg/L, and for non-relevant metabolites at 1 µg/L. The drinking water quality standard for summed concentrations of pesticides and their metabolites is 0.5 µg/L. The EU Water Framework Directive sets water quality standards for a good chemical status of ground- and surface water, amongst which the quality standard of 0.1 µg/L for groundwater. Furthermore, conservative safe concentrations for organic chemicals have been established for drinking water based on the approach of the Threshold of Toxicological Concern (Kroes et al., 2004). The TTC-based target value for individual genotoxic and steroid endocrine chemicals is 0.01 µg/L and for all other organic chemicals 0.1 µg/L. The target value for the total sum of genotoxic chemicals, the total sum of steroid hormones and the total sum of all other organic chemicals are 0.01, 0.01 and 1.0 µg/L, respectively (Mons et al., 2013).

Here, we assess the occurrence of pesticides in ground- and surface water used as drinking water sources. Recently authorized pesticides are evaluated and selected based on their mobility and persistence. An analytical LC-MS/MS method for the simultaneous detection and sensitive quantification for relevant recently authorized pesticides is developed and applied in a Dutch/Belgian ground- and surface water monitoring campaign. Existing pesticide routine monitoring data collected in 2010–2014 are evaluated and prioritized according to their occurrence in groundwater, surface water and drinking water. A list of drinking water relevant

pesticides is proposed for monitoring of drinking water sources. Finally a national overview is presented of the occurrence of pesticides in drinking water sources.

## 2. Material and methods

### 2.1. Selecting relevant recently authorized pesticides

Pesticides authorized on the Dutch market from 2005 to 2015 are selected based on their persistence and mobility, i.e., a half-life in soil (DT50) > 7 days (Zarfl et al., 2011) and a mobility as expressed by the octanol-water partition coefficient ( $\log K_{ow}$ ) < 4 (U.S. EPA, 2016). The DT50 and  $\log K_{ow}$  values are adopted from publicly available authorization reports by the Dutch Board for the Authorization of Plant Protection Products and Biocides (CTGB), shown in S.I.1. The variation in DT50 values may be large for different types and conditions of studies, e.g. lab or field, and aerobic or anaerobic. The normalized geometric mean DT50 under aerobic conditions in soil, which is also used in the model calculations (PEARL and FOCUS) by the CTGB, is used here.

### 2.2. Analytical methods

For several of the selected recently authorized pesticides, no routine analytical method used by drinking water laboratories is available. For 24 compounds a LC-MS/MS method is developed and validated.

All solvents used are of analytical grade with minimal purity of 96%. Acetonitrile (ultra gradient HPLC grade) is obtained from Avantor Performance Materials B.V. (Deventer, the Netherlands). Acetic acid (HPLC quality) is purchased from Sigma Aldrich (Steinheim, Germany). Pesticides are purchased from Sigma Aldrich (Zwijndrecht, the Netherlands) and Toronto Research Chemicals (Toronto, Canada). The isotope labelled internal standard atrazine- $d_5$  is purchased from CDN Isotopes (Nieuwegein, the Netherlands) and bentazone- $d_6$  from Sigma Aldrich (Zwijndrecht, the Netherlands). Ultrapure water is obtained from a Veolia ELGA PURELAB Chorus system (Ede, the Netherlands).

For sample treatment, 50 µL of an internal standard solution at a concentration of 0.50 mg/L is added to 45 mL of water sample and homogenized. The samples are filtered with a 0.20 µm filter and transferred into an auto sampler vial.

A Thermo Fischer Accela UHPLC system equipped with a Hypersil GOLD C18 (100 mm × 2.1 mm, 1.9 µm) column is used for the chromatographic separation. Mobile phase A is composed of 0.05% (v/v) acetic acid in water and mobile phase B is composed of 0.05% (v/v) acetic acid in acetonitrile. The column temperature is kept at 25 °C and flow rate is 300 µL/min. The gradient conditions are 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 is kept at 15 °C, and 100 µL is injected into the LC-MS/MS system.

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

determine retention time and peak shape. For validation, the pesticides are spiked at concentration of 0.01, 0.10 and 1.0  $\mu\text{g/L}$  to drinking- and surface water to determine relative standard deviation and recovery and the limit of quantification.

### 2.3. Monitoring campaign for recently authorized pesticides

Water samples are taken at 127 locations in The Netherlands and Flanders. The samples include 23 surface waters used for drinking water production, 4 dune filtrates, 10 river bank filtrates, and 90 groundwaters used as drinking water source. The surface water samples include 5 large river systems as the Rhine and Meuse, 10 small river systems, 4 reservoir systems, 2 infiltration ponds and 2 seepage waters. The samples from dune- and river bank filtrates and groundwater originate from mixed raw waters, pumping wells and observation wells. All locations were sampled in May and June 2016. Due to potential seasonal differences surface waters were sampled a second time end of august 2016. The developed analytical method for the recently authorized pesticides as described above, was applied in these samples.

### 2.4. Evaluating routine monitoring data 2010–2014

All ten water companies in the Netherlands provided their routine monitoring data over the years 2010–2014, the composite dataset includes 408 pesticides and 52 metabolites in 29,766 individual records. The largest part of the dataset contains samples from groundwater (50%), including raw water (28%), pumping wells (48%) and observation wells (25%). The dataset contains 109 (semi-) phreatic groundwater wells and 77 non-phreatic wells. 33% of the dataset includes samples from drinking water. The remaining part of the samples include surface water from eight intake water point (8% of the samples), river bank filtrate (4%), dune filtrate (2%), water from surface water reservoirs (2%) and seepage water (1%). Data on main constituents, trace elements, and depth of sampling points are also provided.

Pesticides are prioritized according to their occurrence in drinking water, and their concentrations in groundwater or surface water (Table 1). Pesticides are attributed a (high) priority which are detected in produced drinking water or which have concentrations in source water (90 percentile concentration of all available data > LOQ) that exceed the water quality standard of 0,1  $\mu\text{g/L}$  according to the EU Water Framework Directive, Groundwater Directive and Drinking Water Directive (Table 1). The human toxicological non-relevant metabolites are assessed using the water quality standard of 1  $\mu\text{g/L}$ . Occurrence of pesticides and metabolites in drinking water sources in concentrations exceeding 10% of the water quality standard are classified as a potential priority, as future concentrations could raise by increased use or low river discharges. For pesticides with less than 10 positive detections, the maximum concentration was assessed. In addition, an overview is made of locations where priority pesticides have been detected.

## 3. Results and discussion

### 3.1. Selecting relevant recently authorized pesticides

Since 2005, 66 active substances are newly authorized on the Dutch market (Table 2). Eight of these were not further evaluated, as they are either only applied in closed systems without possible emissions to water (1-methylcyclopropene, ethylene, nonanoic acid, sulfuryl fluoride) or as have a low inherent toxicity (three feromones, laminarin). 28 of the evaluated newly authorized pesticides are classified as relevant as they are both persistent ( $\text{DT}_{50} > 7\text{d}$ ) and mobile ( $\log K_{ow} < 4$ ), 26 pesticides are either mobile or persistent and therefore classified as potentially relevant (Table 2). These 54 relevant and potentially relevant pesticides are candidates for implementation in a measurement method.

### 3.2. Analytical method for relevant recently authorized pesticides

For the largest part of the 54 prioritized substances (32 compounds) an analytical method was already implemented at one of the Dutch water laboratories. For the 22 pesticides without an analytical method available plus 10 extra substances a novel LC-MS/MS method for the simultaneous detection and sensitive quantification for the relevant or potentially relevant newly authorized pesticides on the market was developed and validated in drinking- and surface water, underlined in Table 2. From these 32 compounds, eight pesticides could not be included in the method for several reasons (Table 2, in italics). For benfluralin no useable products ions are visible. The polar compounds aminopyralid, mepiquatchlorid and tefluthrin showed no retention on the C18 column. During the validation emamectin benzoate, lufenuron, pyridalyl and spiromesifen showed a decrease in response of the standards up to 75%.

For the remaining 24 pesticides, satisfactory LOD and LOQ results were obtained for drinking- and surface water (see SI, Table 1). The LOQ for most pesticides is in the range of 0.01–0.05  $\mu\text{g/L}$ , for flubendiamide and flumioxazin higher LOQs of respectively 1.0 and 0.50  $\mu\text{g/L}$  were obtained. The recoveries in drinking- and surface water are between 87.7 and 124.9%. The repeatability for all pesticides is below 12% (see S.I. Table 1).

### 3.3. Monitoring campaign for relevant recently authorized pesticides

15 out of the 24 recently authorized pesticides included in the novel LC-MS/MS method are encountered in the monitored drinking water relevant surface waters, including seven pesticides in concentrations above the water quality standard (Fig. 1, Table 3). More than half of the measured pesticides were detected, independent of their mobile and persistent properties (Fig. 2). The pesticides that were not detected, often had low sales data (Fig. 2). Largest sales in 2012 (Nefyto. Afzetzgegevens gewasbeschermingsmiddelen, 2013) were accounted to the fungicide mandapropamid (45,000 kg) followed by another fungicide

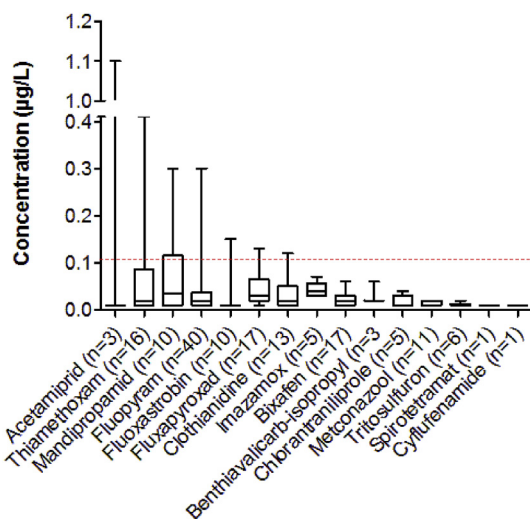
**Table 1**  
Method for risk classification of pesticides.

Priority class	Criteria
High priority	Pesticides or relevant metabolites present in produced drinking water
Priority	Pesticides or relevant metabolites present in drinking water sources >0.1 $\mu\text{g/L}$ (for 90th % of all data > LOQ) Non-relevant metabolites present in drinking water sources > 1 $\mu\text{g/L}$ (for 90th % of all data > LOQ)
Potential priority	Pesticides or relevant metabolites present drinking water sources > 0.1 < 0.1 $\mu\text{g/L}$ (for 90th % of all data > LOQ) Non-relevant metabolites present in drinking water sources > 0.1 < 1 $\mu\text{g/L}$ (for 90th % of all data > LOQ)
Low priority	Not detected pesticides and or relevant metabolites and pesticides or relevant metabolites present drinking water sources do not exceed 0.01 $\mu\text{g/L}$

**Table 2**

Newly authorized pesticides on the Dutch market after 2005 per pesticide use type, and their selection as relevant (r) or potentially relevant (pr). Underlined pesticides are included in the analytical LC-MS/MS method, whereas the pesticides in italics are not.

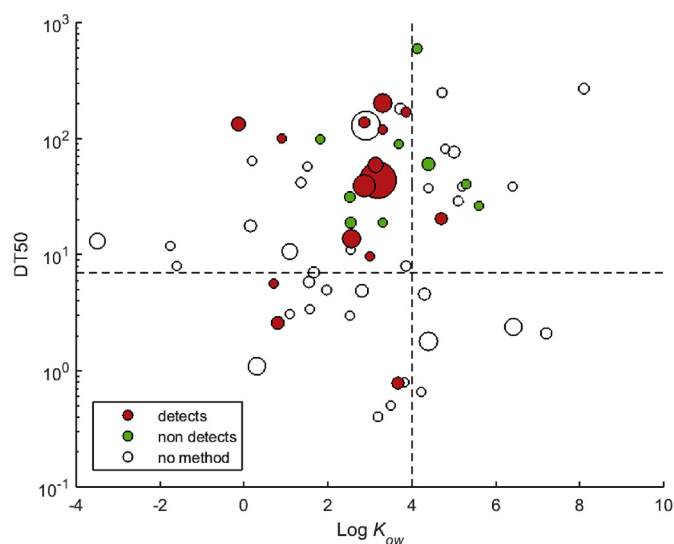
Cas number	Herbicides	374726-62-2	Mandipropamid (r)
150114-71-9	<i>Aminopyralid (r)</i>	125116-23-6	<u>Metconazole (r)</u>
1861-40-1	<i>Benfluralin (pr)</i>	220899-03-6	Metrafenon (pr)
3861-41-4	Bromoxynil butyrate (r)	178928-70-6	Prothioconazol (pr)
99129-21-2	Clethodim	175217-20-6	<u>Silthiofam (pr)</u>
103361-09-7	<u>Flumioxazin (r)</u>	68694-11-1	<u>Triflumizool (pr)</u>
114311-32-9	<u>Imazomox (pr)</u>	<b>Cas number</b>	<b>Insecticides</b>
3861-47-0	loxynil octanoate	135410-20-7	<u>Acetamiprid (pr)</u>
144550-36-7	Iodosulfuron-methyl-natrium (pr)	500008-45-7	<u>Chlorantraniliprole (r)</u>
208465-21-8	Mesosulfuron-methyl (r)	210880-92-5	<u>Clothianidine (r)</u>
15299-99-7	<u>Napropamide (r)</u>	155569-91-8	<i>Emamectin benzoate (pr)</i>
112-05-0	Nonanoic acid	158062-67-0	Flonicamid (pr)
243973-20-8	Pinoxaden (pr)	272451-65-7	<u>Flubendiamide (pr)</u>
92125-34-5	Prosulfuron (r)	103055-07-8	<i>Lufenuron (pr)</i>
129630-19-9	Pyraflufen-ethyl (pr)	161050-58-4	Methoxyfenozide (r)
422556-08-9	Pyroxsulam (pr)	179101-81-6	<i>Pyridalyl (pr)</i>
2797-51-5	Quinoclamine (pr)	283594-90-1	<i>Spiromesifen (r)</i>
99105-77-8	Sulcotrione (r)	203313-25-1	<u>Spirotetramat (pr)</u>
335104-84-2	Tembotrione (r)	2699-79-8	Sulfurylfluoride
79277-27-3	Thifensulfuron-methyl (pr)	79538-32-2	<i>Tefluthrin (pr)</i>
210631-68-8	Topramezone (r)	153719-23-4	<u>Thiamethoxam (r)</u>
101200-48-0	Tribenuron-methyl (r)	<b>Cas number</b>	<b>Acaricides</b>
142469-14-5	<u>Tritosulfuron (r)</u>	57960-19-7	Acequinocyl
<b>Cas number</b>	<b>Fungicides</b>	180409-60-3	Cyflumetofen
865318-97-4	Ametoctradin	153233-91-1	<u>Etoazol (pr)</u>
348635-87-0	<u>Amisulbrom (pr)</u>	<b>Cas number</b>	<b>Growth regulators</b>
98243-83-5	<u>Benalaxyl-M (r)</u>	3100-04-7	1-methylcyclopropene
177406-68-7	<u>Benthiavalicarb-isopropyl (r)</u>	127277-53-6	<i>Mepiquatchloride (r)</i>
581809-46-3	<u>Bixafen (r)</u>	55335-06-3	<u>Triclopyr (r)</u>
400882-07-7	<u>Cyflufenamide (pr)</u>	<b>Cas number</b>	<b>Feromones</b>
161326-34-7	Fenamidone (pr)	16725-53-4	(Z)-9-tetradecen-1-yl acetate
473798-59-3	<u>Fenpyrazamine (r)</u>	112-53-8	1-dodecanol
239110-15-7	Fluopicolide (r)	112-72-1	1-tetradecanol
658066-35-4	<u>Fluopyram (r)</u>	<b>Cas number</b>	<b>Elicitors</b>
361377-29-9	<u>Fluoxastrobin (r)</u>	9008-22-4	Laminarin
907204-31-3	<u>Fluxapyroxad (r)</u>	<b>Cas number</b>	<b>Sprout inhibitors</b>
881685-58-1	Isopyrazam (pr)	74-85-1	Ethylene



**Fig. 1.** Concentration range of 15 recently authorized pesticides detected in surface waters ( $n = 19$ ) and ground waters ( $n = 2$ ). The box represents the 25th, 50th and 75th percentiles, the edges the minimum and maximum values. The number between brackets after the pesticide names on the x-axis represents the number of detections above the reporting limit. The dotted line represents the water quality standard for individual pesticides according to the Water Framework Directive.

fluoxastrobin (27,000 kg); both detected in surface water samples above 0.1 µg/L (Table 3).

In 19 out of 23 surface water samples one or more recently



**Fig. 2.** Scatter of detected recently authorized pesticides according to their mobile (octanol-water partition coefficient  $\text{Log } K_{ow}$ ) and persistent properties (DT50 in soil), retrieved from authorization documents in The Netherlands. Size range according to sales data in Nefyto, 2013.

authorized pesticides are detected. Thiamethoxam, acetamiprid, fluopyram, mandipropamid, fluxapyroxad and fluoxastrobin occur in concentrations above the drinking water standard of



**Table 3**  
Detected newly authorized pesticides and their occurrence in drinking-water related surface waters (SW), dune filtrates (DF), river bank filtrates (RBF) and groundwater (GW).

Recently authorized pesticides	Number of samples with detected pesticides					Number of samples with pesticides >0.1 µg/L				
	Total (n = 150)	SW (n = 46)	DF (n = 4)	RBF (n = 10)	GW (n = 90)	Total (n = 150)	SW (n = 46)	DF (n = 4)	RBF (n = 10)	GW (n = 90)
Fluopyram	41	38	3	0	0	6	6	0	0	0
Thiamethoxam	17	15	0	0	2	4	4	0	0	0
Mandipropamid	10	10	0	0	0	3	3	0	0	0
Fluxapyroxad	17	17	0	0	0	1	1	0	0	0
Clothianidine	14	13	0	0	1	1	0	0	0	1
Fluoxastrobin	10	10	0	0	0	1	1	0	0	0
Acetamiprid	3	3	0	0	0	1	1	0	0	0
Bixafen	17	17	0	0	0	0	0	0	0	0
Metconazole	11	11	0	0	0	0	0	0	0	0
Tritosulfuron	6	6	0	0	0	0	0	0	0	0
Imazamox	5	5	0	0	0	0	0	0	0	0
Chlorantraniliprole	5	5	0	0	0	0	0	0	0	0
Benthiavalicarb-isopropyl	3	3	0	0	0	0	0	0	0	0
Spirotetramat	1	1	0	0	0	0	0	0	0	0
Cyflufenamide	1	1	0	0	0	0	0	0	0	0

0,1 µg/L in surface water. During the drinking water production process, after flocculation and dune filtration concentrations are below 0,05 µg/L.

The neonicotinoids thiamethoxam and acetamiprid were detected the highest concentrations, up to 0.41 µg/L in a dead end of the river Meuse (June) and 1.10 µg/L in a Belgian surface water reservoir (August). Thiamethoxam is very mobile ( $\log K_{ow} = -0.13$ ) and persistent ( $DT_{50} = 134$  days). However, during the authorization it was modelled that the uses of thiamethoxam will not result in exposure of surface water. The source of acetamiprid is expected to be local since the compound is easily metabolized ( $DT_{50} = 2.6$  days).

In only 2 out of the 90 drinking-water relevant groundwaters recently authorized pesticides are detected, which may point to the travelling time of these pesticides to drinking water related groundwaters. The mobile and persistent neonicotinoids clothianidine and thiamethoxam are found in shallow groundwater, up to respectively 0.12 µg/L and 0.01 µg/L. During the authorization of clothianidine and thiamethoxam it was modelled that the uses of these products will not result in exposure in groundwater. No other recently authorized pesticides are retrieved in the groundwaters.

For recently authorized pesticides that occur in drinking-water related surface water or groundwater above a concentration of 0.1 µg/L, a human health evaluation based on EFSA derived ADIs shows at least a factor of 700 difference compared to the drinking water standard of 0,1 µg/L. Thus, although the occurrence of the pesticides is a problem for drinking water utilities to produce drinking water according to the drinking water quality guidelines, no adverse human health effects are to be expected for the individual pesticides.

### 3.4. Evaluating existing routine monitoring data 2010–2014 for pesticides

In 67% of the 226 ground- and surface water sources for drinking water production, pesticides that have been on the market for a longer time and/or their metabolites are detected. In 31% of the abstraction areas, the 90th percentile of data > LOQ exceeds the threshold of 0.1 µg/L (pesticides) and/or 1 µg/L (non-relevant metabolites) (Fig. 3).

Of the 408 pesticides and 52 metabolites that were monitored, the vast majority has a low priority according to the criteria as defined (Table 4, details in S.I. Table 2), while 63 pesticides and 6 metabolites are categorized as (high) priority pesticides. Pesticides with more mobile and persistent properties were likely to be

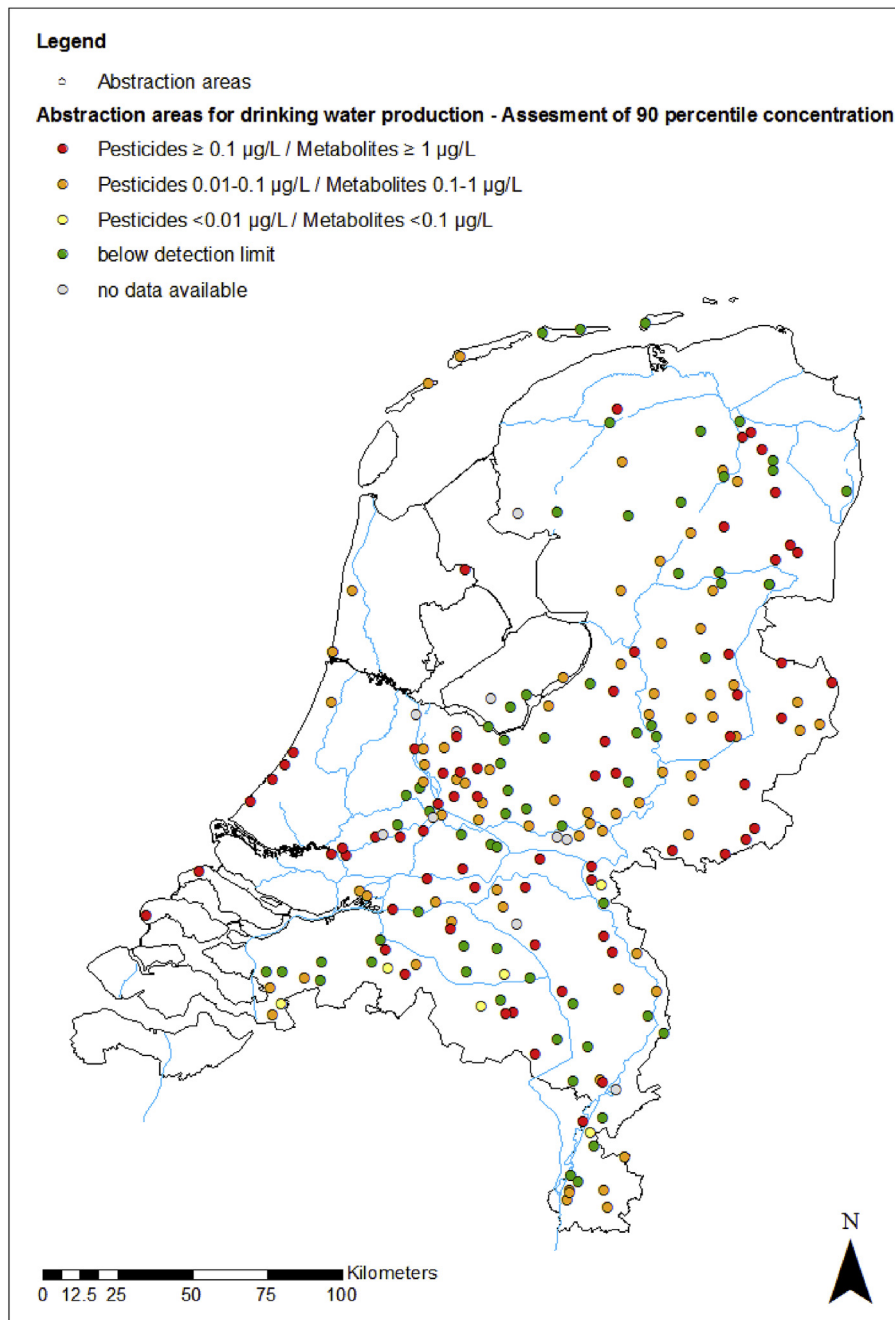
classified as (high) priority pesticides (Fig. 4). Fig. 5 depicts the pesticides and metabolites detected in drinking water, and in drinking water sources that exceed 0.1 µg/L in drinking water sources. In surface water more pesticides are detected above 0.1 µg/L ( $n = 46$  out of 2933 samples), compared to filtrates ( $n = 21$  out of 1977 samples) or groundwater ( $n = 31$  out of 14,778 samples). In groundwater, higher concentrations are found as compared to the other matrices. High concentrations in groundwater are affected by high contamination volumes, short circuiting and the persistent and mobile properties of the pesticides. High pesticide concentrations in groundwater could be a risk for drinking water production, as groundwater is treated with simple treatment steps, such as sand filtration and aeration.

Fig. 6 shows depth plots, which are analysed for 9 frequently occurring pesticides and metabolites. The depths reached by the pesticides are up to 125 m for bentazone. There are distinct differences in maximum depth reached, from deep to shallow bentazone (125 m), dinoterb (100 m), dikegulac sodium (90 m), BAM, chloridazone and desphenyl chloridazone (80 m), mecoprop (70 m), glyphosate (65 m) or DMS (40 m). These great depths can be explained by little or no retardation, hardly any (bio)degradation, and prolonged application. For most pesticides the greatest depths are observed in pumping wells, followed by observation wells and ultimately by the well field. This is explained by the fact that a pumping well pulls down the young polluted groundwater (Aisopou et al., 2015), while an observation well does not. Concentrations in mixed water are regularly below detected concentrations in observation and pumping wells, as different quality groundwater is mixed before treatment.

### 3.5. Occurrence studies in literature

From the 24 analysed recently authorized pesticides clotianidine, triclopyr and napropamide were also detected in low concentrations in German surface- or groundwater (Reemtsma et al., 2013; Schreiner et al., 2016). The neonicotinoid clothianidine and the herbicide triclopyr (not detected in this study) were detected in groundwater in Germany (Reemtsma et al., 2013). The herbicide napropamide, which was not detected in this study was regularly detected in German surface water (Schreiner et al., 2016).

From the 32 high priority compounds, 14 were detected in earlier surface- or groundwater in other studies (S.I. Table 2). Frequent detected pesticides in drinking water sources, such as bentazone, carbendazim, glyphosate and the metabolite AMPA were also detected in Germany and France (Loos et al., 2010;



**Fig. 3.** Pesticides and/or their metabolites occurring in Dutch drinking water sources (surface and ground water).

**Table 4**

Prioritization of routine monitored pesticides and metabolites (more info including occurrence in earlier monitoring studies in S.I. Table 2).

Class	Description	Number of pesticides
High priority	Pesticides and human toxicological relevant metabolites detected in drinking water	26
Priority	Pesticides and human toxicological relevant metabolites detected in sources $P90^a \geq 0.1 \mu\text{g/L}$	37
Potential priority	Pesticides and human toxicological relevant metabolites detected in sources $0.01 \leq P90^a < 0.1 \mu\text{g/L}$	89
Low priority	Not detected pesticides and pesticides and human toxicological relevant metabolites detected in sources $P90^a < 0.01 \mu\text{g/L}$	256
High priority	Human toxicological non-relevant metabolites detected in drinking water	6
Priority	Human toxicological non-relevant metabolites detected in sources $P90^a \geq 1 \mu\text{g/L}$	0
Potential priority	Human toxicological non-relevant metabolites detected in sources $0.1 \leq P90^a < 1 \mu\text{g/L}$	6
Low priority	Not detected metabolites and human toxicological non-relevant metabolites detected in sources water $P90^a < 0.1 \mu\text{g/L}$	40

<sup>a</sup>  $P90 = 90$  percentile concentration of all positive detections. For pesticides and metabolites with less than 10 positive detections the maximum concentration was assessed.

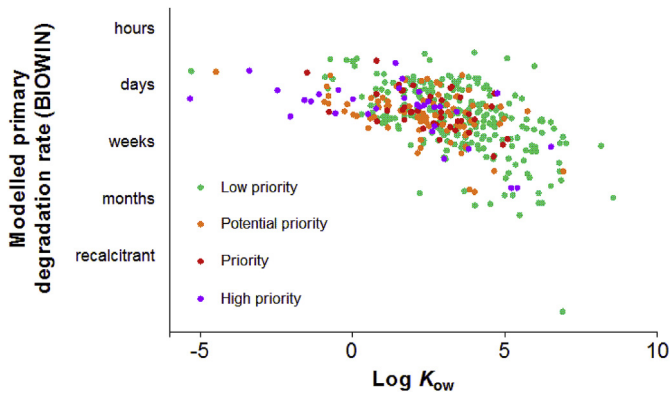


Fig. 4. Scatter of prioritized pesticides and metabolites according to their mobile and persistent properties.

Schreiner et al., 2016), although with a lower frequency. The frequently detected compound BAM (metabolite of the prohibited herbicide dichlobenil and the authorized fluopicolide) was not detected in other countries such as Germany, France or the US (Schreiner et al., 2016).

In groundwater, (high) priority pesticides diuron, mecoprop, MCPA, atrazine, bentazone and (high) priority metabolites (methyl-)desfenylchloridazon en DMS were also detected by Loos et al. (2010).

In surface water, (high) priority pesticides azoxystrobin, bentazone, dimethomorph, flonicamid, glyphosate, mecoprop, MCPA, metalaxyl, metazachlor and primicarb and (high) priority metabolites AMPA were also regularly detected in European surface waters by Schreiner et al. (2016).

Frequent detected pesticides in Spain, such as simazine and

atrazine (Köck-Schulmeyer et al., 2014) were detected in less than 1% of the measurements, since they have been prohibited in The Netherlands. The compounds diuron and isoproturon were also detected much more frequently in Germany and France, compared to the Netherlands.

Pesticide regulation could be further improved to account for 'pestico-vigilance', vigilance concerning pesticide appliance and effects (Milner and Boyd, 2017). Such a system would promote genuinely risk-based pesticide use that would make trade-offs between the environmental costs and food production.

#### 4. Conclusions

In this study the occurrence of pesticides in The Netherlands in groundwater and surface water used as drinking water sources was assessed.

Recently authorized pesticides not yet included in routine monitoring programs are evaluated and selected based on their mobility and persistence, for the development of an analytical LC-MS/MS method which is applied in a non-routine Dutch/Belgian ground- and surface water monitoring campaign. 15 out of the 24 pesticides were detected, including seven pesticides in concentrations above the water quality standard. These recently authorized pesticides are relevant for uptake in routine monitoring programs. Two neonicotinoids, known for their environmental impact, were detected in highest concentrations: acetamiprid (1.1  $\mu\text{g/L}$ ) and thiamethoxam (0.4  $\mu\text{g/L}$ ). The occurrence in drinking water sources of pesticides that haven been authorized within 10 years emphasises the importance to keep routine monitoring methods up to date.

From collected routine pesticide monitoring data over 2010–2014 in The Netherlands, covering 408 pesticides and 52 metabolites, 63 pesticides and 6 metabolites were prioritized according to their occurrence in groundwater, surface water and

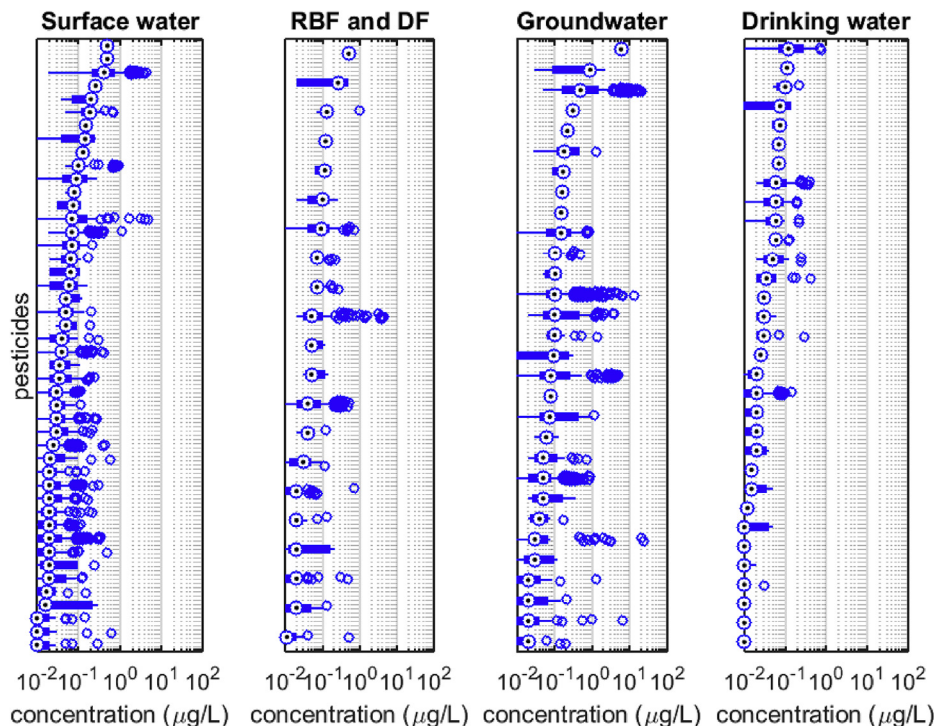
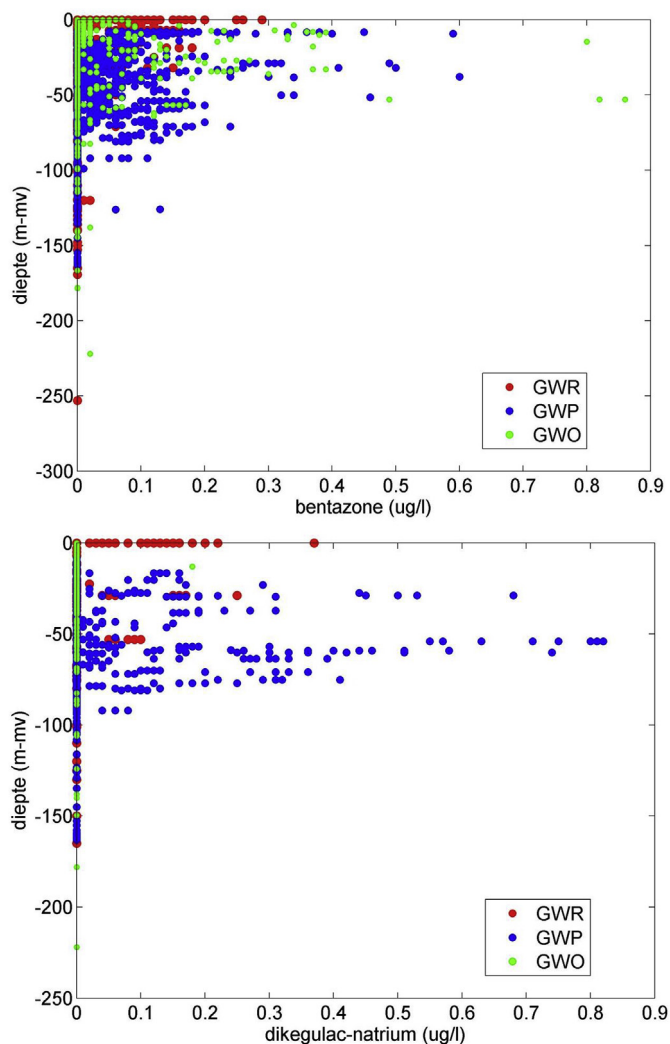


Fig. 5. Pesticides and metabolites from routine monitoring dataset detected in surface water, river bank (RBF) and dune filtrate (DF) and in groundwater above the threshold of 0.1  $\mu\text{g/L}$  and pesticides and metabolites detected in drinking water above LOQ. Central mark is the median, the box represents 25th and 75th percentiles, the whiskers extend to the extreme data points not considered outliers. Outliers are plotted individually.



**Fig. 6.** Bentazone and dikegulac concentration versus depth. Difference between mixed water (GWR), pumping wells (GWP) and observation wells (GWO).

drinking water. This nationwide study points out that source water and drinking water monitoring should focus on priority pesticides, since the vast majority of the pesticides has a low priority. This national overview of pesticide occurrence in water sources emphasises that pesticide pollution is of major concern in drinking water sources in the Netherlands. In two thirds of the Dutch water abstraction areas (226) covering groundwater- and surface water bodies in the Netherlands, pesticides and/or metabolites have been detected. In one third of the abstraction areas pesticide and/or metabolite concentration exceeded water quality standards according to the Water Framework Directive.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.06.207>.

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