ISPRA
Istituto Superiore per la Protezione
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Sistema Nazionale
per la Protezione
dell'Ambiente

RAPPORTI

Pesticides in water
Italian monitoring 2016

Synthesis Report

289/2018

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1. INTRODUCTION

Pesticides are chemicals used to control weeds, insects and other pests in agricultural areas, and a variety of other land-use settings. Pesticides can be distinguished, from a regulatory point of view, among substances used in plant protection products and in biocidal products, which are used in various fields (disinfectants, wood preservatives, pesticides for non agricultural use, antifouling, etc.). Often, the two types of products use the same active substances. Every year in Italy are used approximately 130,000 tons of pesticides, affecting approximately 70% of the utilized agricultural area, (ca. 13,000,000 hectares) [ISTAT, 2015].

Despite the acknowledged benefits in various fields of application, the use of these substances raises concerns in terms of possible adverse effects on humans health and the environment. Most of them, in fact, are synthetic molecules designed to kill harmful organisms and therefore they are generally hazardous to all living organisms.

Molecular characteristics, management practices, climatic and territorial conditions affect the environmental fate of these substances, that can be found in different compartments (air, soil, water, sediment). Because of their acute and/or long-term impact, pesticides may pose a risk to humans and ecosystems that are exposed to them.

Pesticides monitoring is a quite complex and challenging task because of the diffuse source of pollution, the huge number of substances and the seasonal patterns of the meteoric precipitations which are the main contamination transport route, through runoff and leaching. In order to implement a wide monitoring of pesticides, it is necessary to consider several factors, like substance properties, use patterns, hydrology and hydrogeology of the interested areas.

European regulatory framework covers the risk raising in all life cycle phases of the pesticides: production, use, disposal. According to the Regulation (EC) No 1107/2009, active substances are evaluated before they are put on the market, to demonstrate their safety for human health and the environment. Moreover, Directive 2009/128/EC, on sustainable use of pesticides, aims to improve controls on the distribution and use, reducing the levels of harmful active substances and encouraging the use of good agricultural practices to reduce the risks and impacts of pesticide use.

Despite of the well defined regulatory framework, in general monitoring data from Member States show a diffuse pollution of surface and groundwater in several countries [SOeS, 2015; Stone, 2014; Petersen, 2012]. The national monitoring plan aims to identify issues not adequately foreseen by the regulatory framework.

The Institute for Environmental Protection and Research (ISPRA) is responsible for technical management and assessment of the monitoring. Analytical investigations are carried out by the territorial Agencies and are transmitted to the Institute, in accordance with the provisions of the Directive 2009/128/EC and the relevant National Action Plan (DM 35/2014). Previous reports and technical guidance are available in the ISPRA website [ISPRA, Report].

The present report refers to the national survey in the year 2016. The data are reported as detection frequency and concentration distribution of pesticides in surface and groundwater. The measured concentrations are compared with legal threshold fixed by European and national legislation. The availability of monitoring data, since 2003, allows the trend analysis of contamination.

2. MATERIAL AND METHODS

2.1. Description of Study Area

The criteria for the definition of the monitoring networks and sampling rates are set by the relevant legislation (EU Water Framework Directive 2000/60/EC - WFD; Directive 2006/118/EC on the protection of groundwater against pollution and deterioration), with the purpose to provide a coherent and comprehensive overview of ecological and chemical status within each river basin.

In 2016, the surface water net has an average of 5.4 points per 1000 km^2. The average frequency of sampling is 7.3 samples/year.
In groundwater, the average density of the network is 11.8 points/1000 km^2. The average sampling per year is 2.1.

The monitoring program is not uniform throughout the country, with a more developed and efficient network in the northern part (Padan-venetian valley) compared to the southern region.
The monitoring involved 1554 sites and 11114 samples in surface water; 3129 sites and 6161 samples in groundwater.

A total of 398 substances were investigated: 370 in surface water, 367 in groundwater. Herbicides and their metabolites are the most searched substances (Fig. 1).

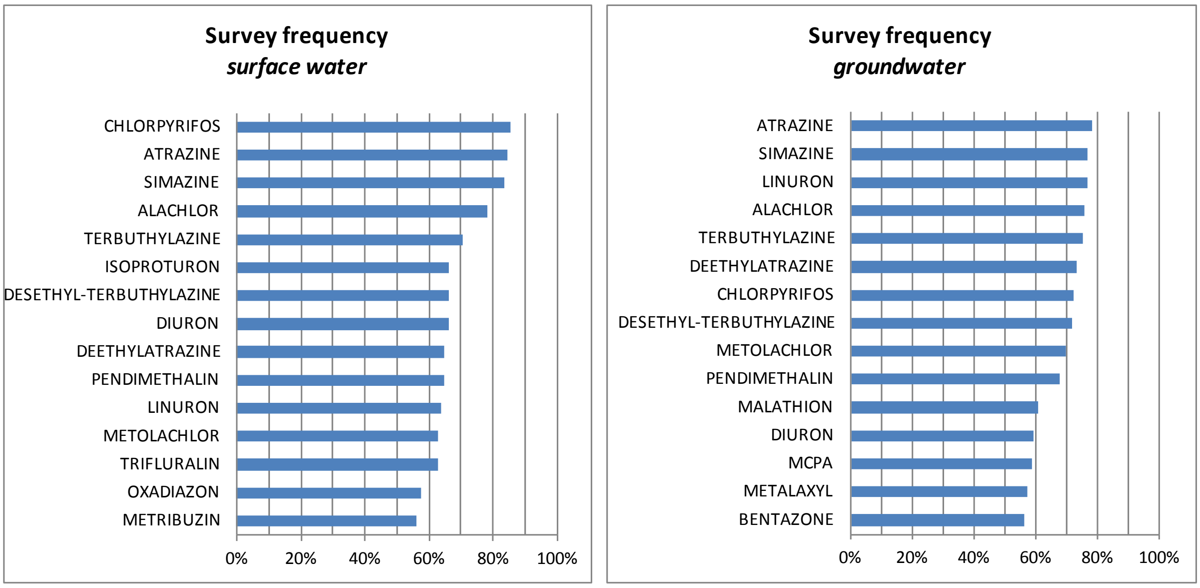

Fig. 1 - *Most investigated substances in surface and groundwater.*

2.2. Methodology used to define the Contamination Level

The levels of contamination are compared with the regulatory limits for surface water and for groundwater. Environmental Quality Standards (EQS), set for surface water in the contest of the WFD, are concentrations of pollutants or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment.

The derivation of EQS is based on the knowledge of the levels of acute and chronic toxicity of the species representative of three trophic levels of the aquatic environment[1].

The European legislation (Directive 2008/105/EC) sets the EQS for a limited number of priority substances (including few pesticides). Moreover the Italian legislation (D.lgs. 172/2015) sets EQS for some other pesticides and fixes for all the other pesticides (including metabolites), not explicitly regulated, the limit of 0.1 µg/L and, for the sum of pesticides, the limit of 1 µg/L.

The Directive 2006/118/EC on the protection of groundwater, sets standards of environmental quality, defined as the concentrations which should not be exceeded in order to protect the human health and the environment. In particular for the pesticides and their degradation products the limits are equal to those for drinking water, equal to 0.1 µg/L and 0.5 µg/L, respectively for the single substance and for the sum of the substances. The state of groundwater quality is determined by comparing the annual average concentrations with those limits.

The provisions in Directive 2009/90/EC, which lay down technical specifications for chemical analysis and monitoring of water status, are taken into account to compare monitored pesticide levels with the EQS. The Directive sets minimum performance criteria for the analytical methods and rules to validate the quality of analytical results. In particular, the minimum performance criteria for methods of analysis should be based on an uncertainty of measurement equal or below to 50% of the relevant EQS and a limit of quantification (LQ) equal or below to 30% of the relevant EQS. The Directive also defines the methods for the calculation of mean values, in particular: where measures are below the LQ, they shall be set to 1/2 of LQ, if a calculated mean value is below the LQ, the value shall be referred to as “less than the LQ”.

The pesticide contamination level in the maps is reported with different colours, in red monitoring points the contamination level is higher than the EQS, in blue points the pollution is within the limits, and in the gray ones the contamination level is not quantifiable. A result is not quantifiable when there isn’t any evidence of contamination, i.e. there are not analytical measurements above the limit of quantification. This could mean that there is not pollution, but it must be aware that, in some cases, either the LQ are too high, or the number of investigated substances is limited and not enough representative of the pesticide uses on the territory.

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[1] algae and/or aquatic plants, *Daphnia* or representative organisms of marine water, fish.

3. RESULTS AND DISCUSSION

3.1. Contamination Levels

Overall 259 substances were detected, more than in previous years, 244 substances in surface water and 200 in groundwater. Herbicides are the most occurring substances, mainly because of the timing of their use in relation to the seasonal rainfall in early spring. However, compared to the past, the presence of fungicides and insecticides has increased significantly, especially in groundwater.

In figure 2 is shown the detection frequency of the substance in samples, grouped for functional categories. The most detected substances in terms of frequency in the samples are shown in figure 3.

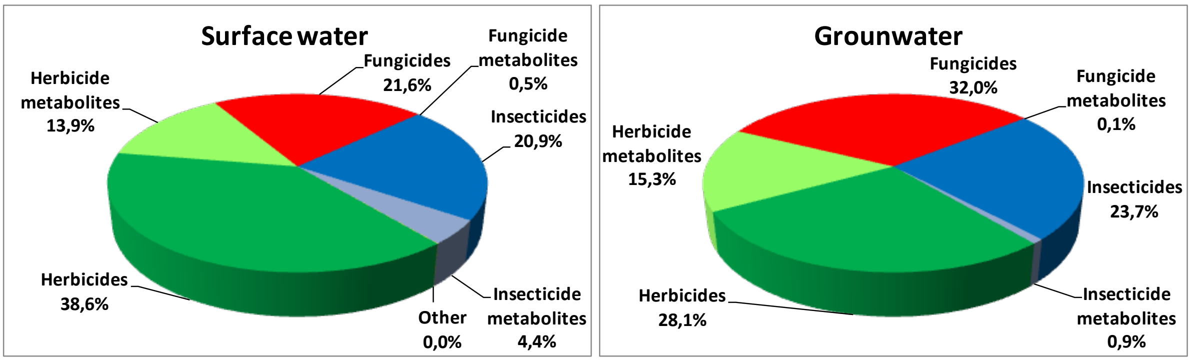


Fig. 2 - *Type of detected pesticides in surface and groundwater.*

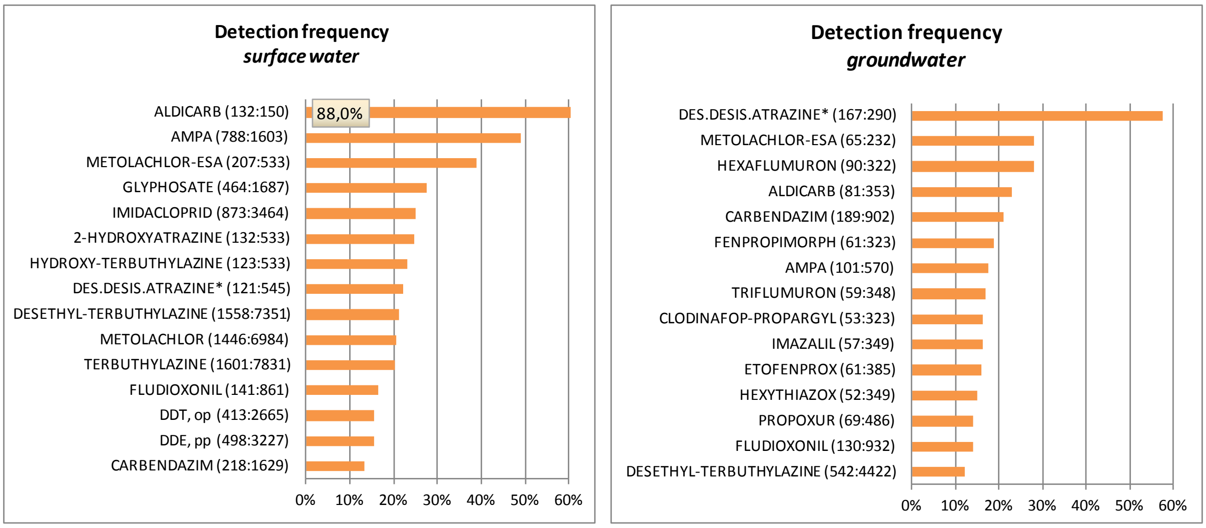
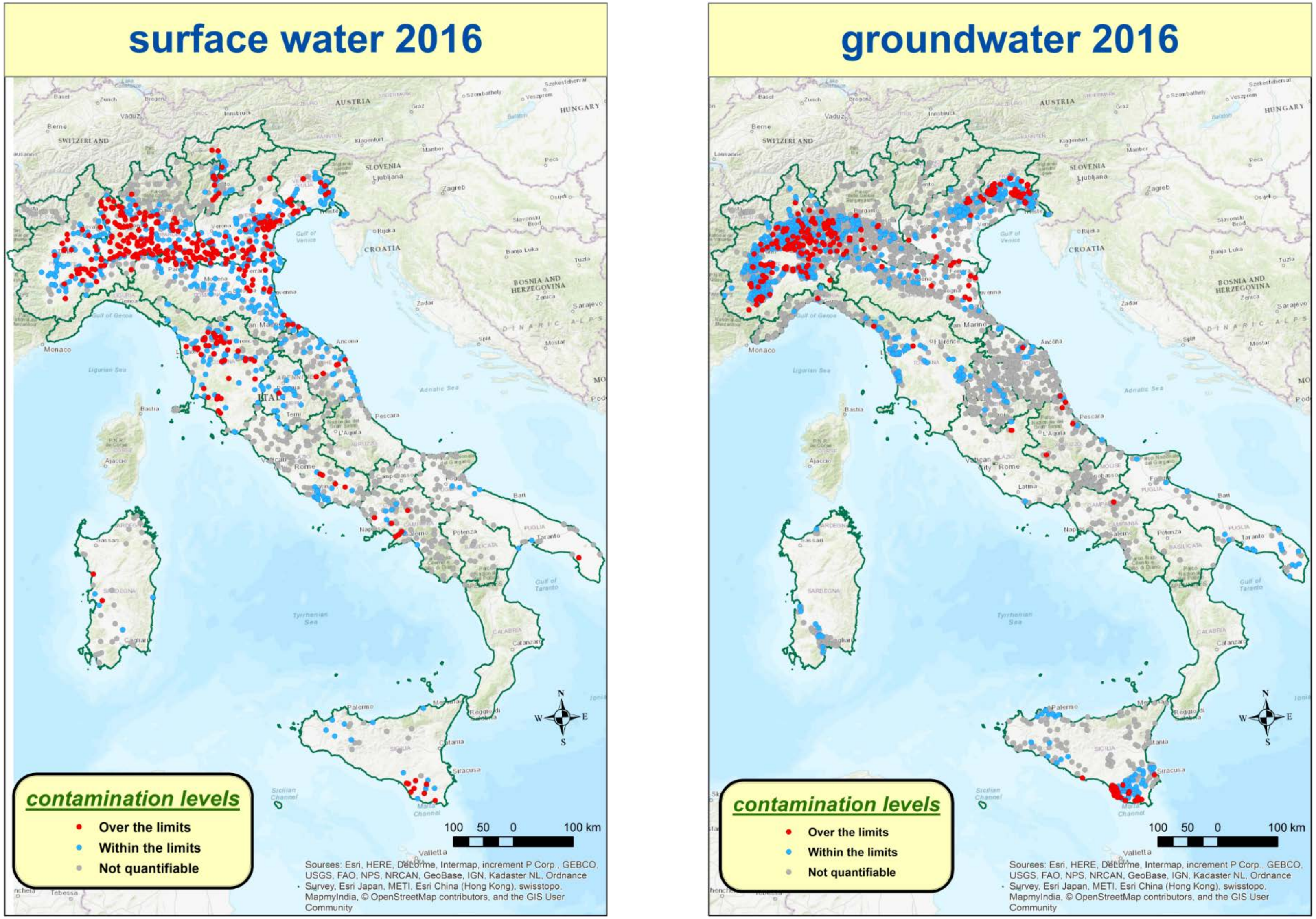


Fig. 3 - *Pesticides detected most frequently in water (No. of positive samples on total samples).*

* Desethyl-desisopropyl-atrazine

Pesticide contamination is significant in the Po river valley. This depends on the hydrological characteristics of the area and on the intense agricultural use, but also by the fact that the investigations are generally more comprehensive and representative in the northern Italy. In south-central Regions information is limited by poor monitoring network, as well as the small number of investigated substances.

The maps of figure 4 show the national monitoring network and the pesticide contamination level.



surface water 2016

groundwater 2016

Sourses: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

Fig. 4 - *Pesticide contamination levels.*

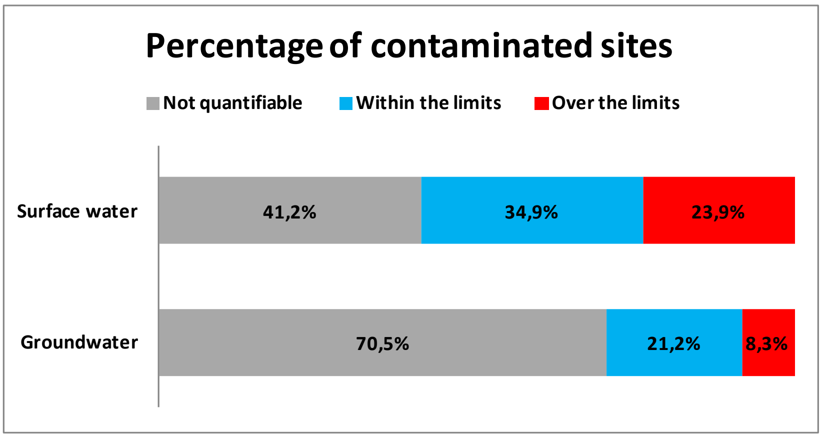


Fig. 5 - *Percentage of contaminated sites.*

The percentage of contaminated sites is shown in figure 5. Pesticides were detected in 58.8% of surface water sites and in 29.5% of groundwater sites. The measured concentrations were often low, nevertheless the overall occurrence in pesticides indicates a widespread contamination, that also affects deep aquifers geologically protected by layers of low permeability.

In 23.9% of surface water sites, pesticide concentrations were above the EQS. The substances that most frequently exceeded the concentration levels were (Fig. 6): glyphosate and its metabolite AMPA, above the EQS respectively in 24.5% and 47.8% of the monitored sites. Of note, the herbicide metolachlor and its metabolite metolachlor-esa above the limits in 7.7% and in 16% of the sites, as well as the herbicide quinclorac higher than the limits in 10.2% of the cases.

As regards groundwater, pesticide concentrations above the limit were detected in 8.3% of sites. The substance most frequently found was atrazine desetil desisopropil, a metabolite of atrazine and terbuthylazine. Its high rate of detection depends on a considerable analytic efficiency. The presence of the other triazine compounds is also confirmed. As for the past few years significant is the presence of glyphosate and AMPA exceeding the limits in 5.8% and 4.8% of the cases, the herbicide bentazone (2.4%) and the insecticide imidacloprid (1.6%).

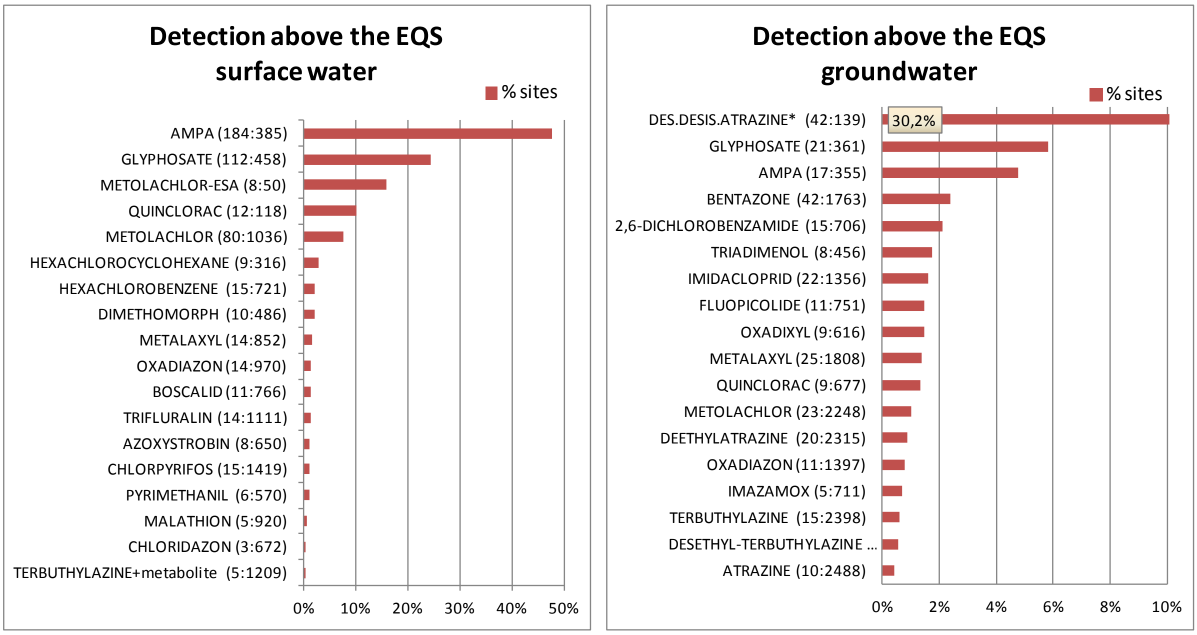


Fig. 6 - *Pesticides detected most frequently above the EQS in surface and ground water.*

* Desethyl-desisopropyl-atrazine

Glyphosate is the most widely used herbicide in the world, with average sales (years 2013-2015) in Italy exceeding 1000 tonnes/year. It is one of the major water contaminants, as widely acknowledged by international data; its use has also increased rapidly as a result of the development of genetically modified crops resistant to the substance. It is used on arboreal and herbaceous crops but is also used on areas not intended for agricultural crops, such as industrial, civil, riverbank and roadside areas.

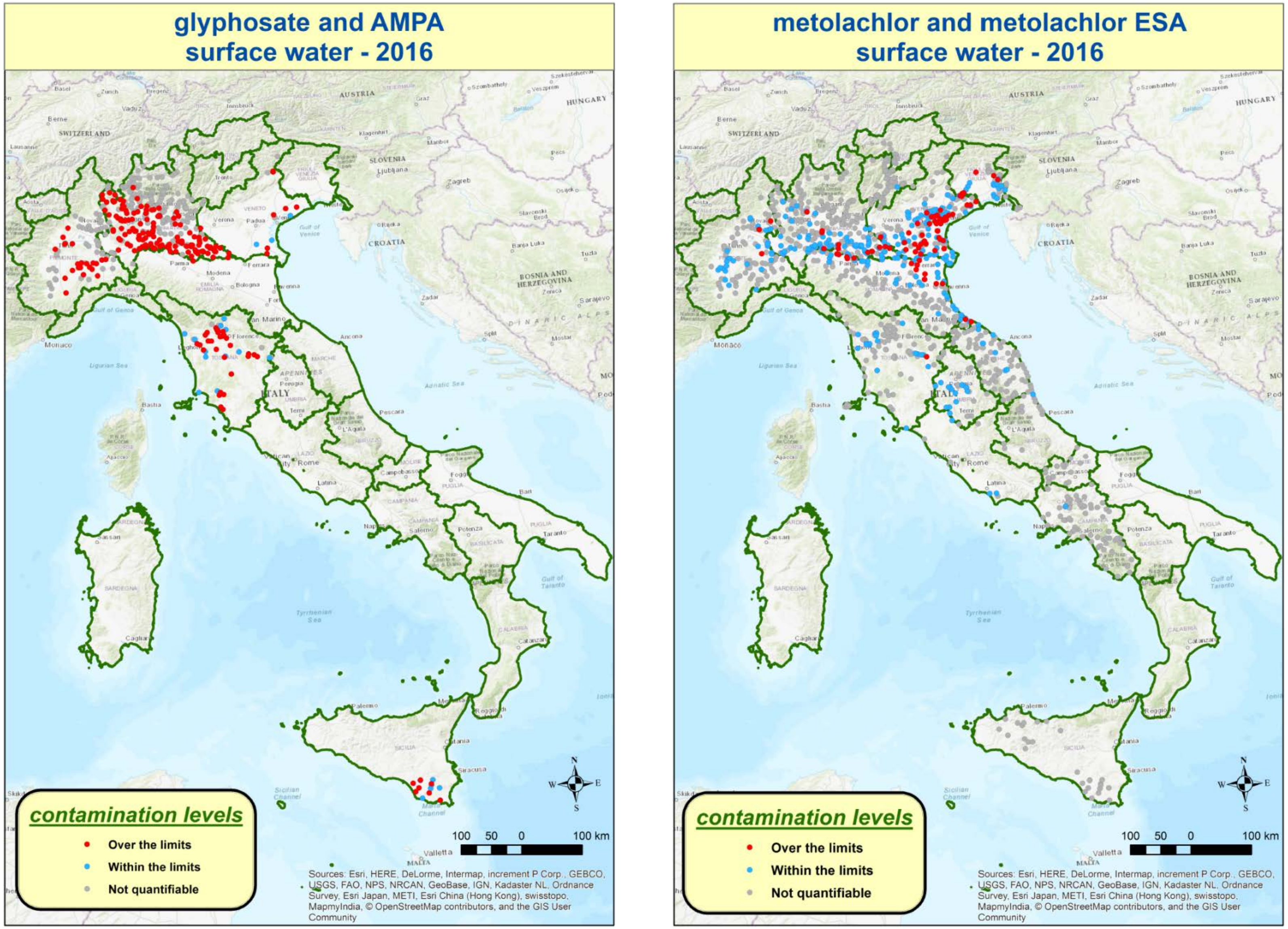
The substance was recently classified as toxic to aquatic life with long lasting effects and causes serious eye damage. In 2016 the conditions of approval of glyphosate were restricted by the European Commission, in particular with respect to the protection of the groundwater in vulnerable areas (Reg. Impl. (EU) 2016/1313).

The substance monitoring is poorly representative compared to the wide use in the territory. A significant increase of detection is expected with its inclusion in the monitoring programs.

The triazine herbicides: atrazine, simazine, terbuthylazine and the metabolites deethylatrazine, desethyl-desisopropyl-atrazine and desethyl-terbuthylazine, are among the substances most frequently detected in waters. With the exception of terbuthylazine, all other substances are no longer authorized in Europe, therefore the monitoring highlights the residue of a historical contamination, due to the widespread use in the past and to the environmental persistence of these substances.

Imidacloprid is the insecticide most frequently found in groundwater. It is a systemic insecticide belonging to the Neonicotinoid substance group, and it is used to control sucking and soil insects. The insecticide is approved for use in the EU with certain restrictions for flowering crops, as it is known to be highly toxic to birds and honeybees.

The maps of a few relevant pesticides are reported, showing the contamination levels at the monitored sites (Fig. 7).

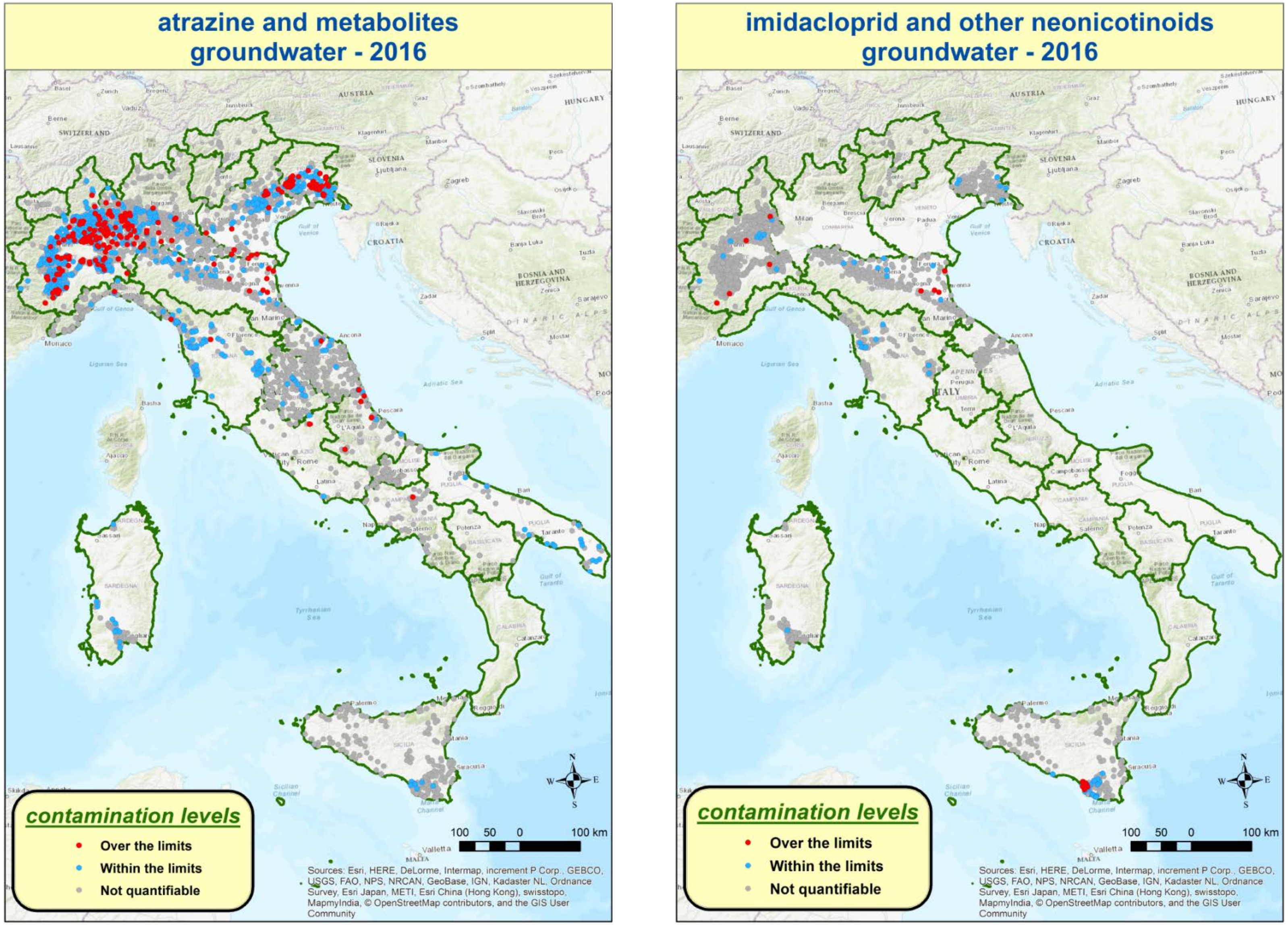


glyphosate and AMPA surface water - 2016

metolachlor and metolachlor ESA surface water - 2016

Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

Fig. 7a - *Contamination levels of specific pesticides in surface water.*


atrazine and metabolites
groundwater - 2016

imidacloprid and other neonicotinoids
groundwater - 2016

contamination levels
- 🟥 Over the limits
- 🟦 Within the limits
- ● Not quantifiable

Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

Fig. 7b - *Contamination levels of specific pesticides in groundwater.*

3.2. *Trend of the Contamination Analysis*

The study of the evolution of the water contamination is essential in order to foresee the effects and reverse any negative trends. For this purpose, the National Action Plan (NAP), according to the Directive 2009/128/EC on the sustainable use of pesticides, defines a series of indicators, among which some specific for the protection of the aquatic environment. An indicator identifies the pesticide occurrence over the time.
The frequency of detection is however still strongly connected with the efficiency of monitoring and does not directly represents the pesticide use. Therefore, the trend of detection frequency is compared to the sampling and the number of investigated substances (Fig. 8, 9).

In surface water the frequency of detection of pesticides at monitoring points increases almost constantly throughout the observation period, and reaches the maximum value (67.0%) in 2016. The trend is closely related to the extension of the network, a raise in frequency is expected with the increase of territorial coverage.

The frequency in the samples increases significantly in the early years, from 2010 the frequency drops below 30% and then gradually rises to the maximum value in 2016 (42.1% of samples). The interpretation of the data is not easy and should take into account the use of different limits of analytical detection, the lack of harmonization of the monitoring programs, mainly as territorial coverage and number of monitored substances. This has probably led to a fall in frequency from 2009 to 2012. The subsequent increase is clearly related to the increase in effectiveness of the monitoring that has been taking place in recent years, especially in terms of substances.

Fig. 8 - *Trend of detection frequency in surface water. The numbers are normalized based on the data at the beginning of the trend, corresponding to 670 sites 5,136 samples and 157 substances.*

The frequency in the monitoring points in groundwater, even with fluctuations, increases during the observation period and reaches a maximum value in 2013 (34.7%). The trend is correlated with the number of monitoring points, which in 2016 correspond to 3,129.

The frequency trend in groundwater samples is similar to that of surface waters, and the data interpretation is similar. The overall frequency grows significantly until 2009, after that, even if the monitoring extent increases, the frequency of pesticides tends to decrease, until 2011, subsequently it grows gradually up to a maximum of 28% in 2015.

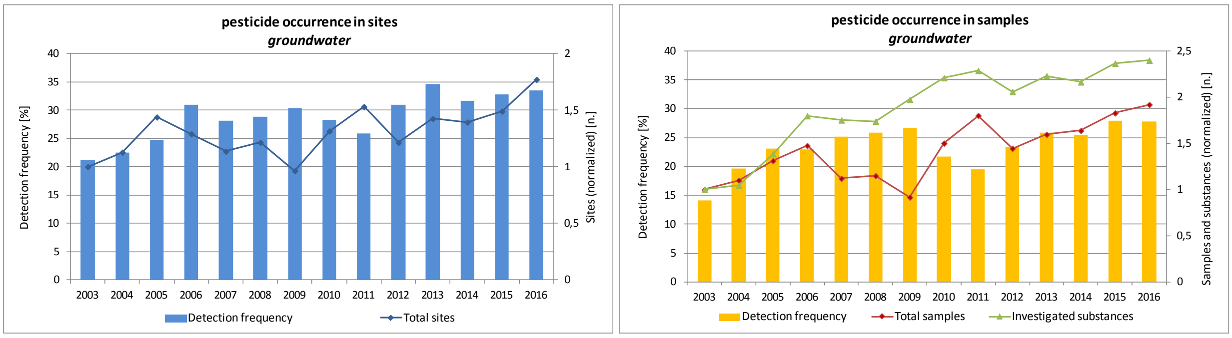


Fig. 9 - *Trend of detection frequency in groundwater The numbers are normalized based on the data at the beginning of the trend, corresponding to 1,766 sites 3,210 samples and 153 substances.*

The trends of some individual substances, considered relevant for the extent of contamination, were also analyzed. The histogram represents the frequency of detection in the samples, while the curve represents the percentage of analyzed samples for the specific substance on the total samples.

The atrazine and metabolite rate is decreasing over time (Fig. 10), in line with the fact that the substance has been banned in the late '80s due to a widespread contamination of groundwater in the Po river basin. Therefore, what is found is the trace of historical contamination due to the environmental persistence of the substance. The fact that the metabolite is more frequent than the active substance is a further confirmation that there is no longer a new entry into the environment of the substance. In recent years there is an increase in frequency. It depends on the fact that locally the substances have been investigated more in depth, operating with LQ lower than the national average. The substance and the metabolite are still among the major water contaminants, in terms of detection frequency as well as for the exceeding of the concentration limits.

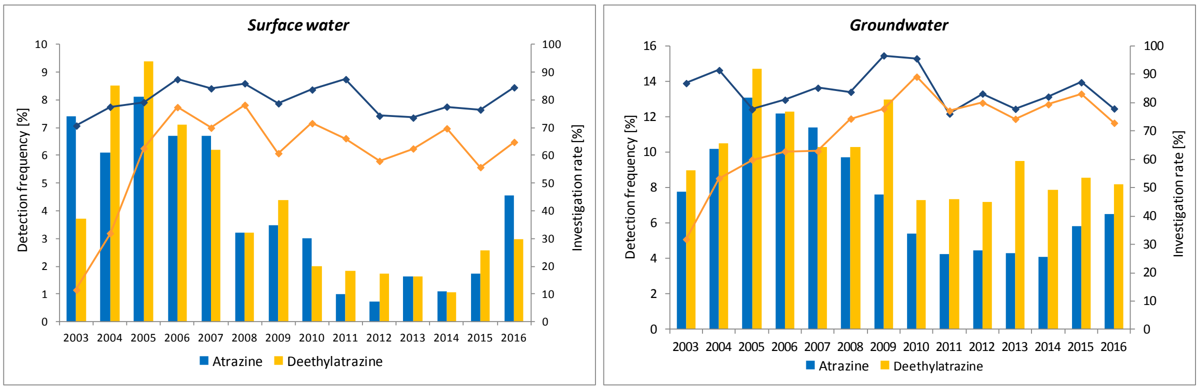


Fig. 10 - *Trend of detection frequency of atrazine and deethylatrazine* (*the histogram represents the frequency of detection in the samples; the curve represents the percentage of analyzed samples*).

Glyphosate and AMPA, until 2013 monitored only in Lombardy, are now investigated in five regions. (Fig. 11). The substance is mostly present in surface waters, but the increase in frequency in groundwater is significant. Territorial representativeness is still limited and does not allow to highlight trends at national level.

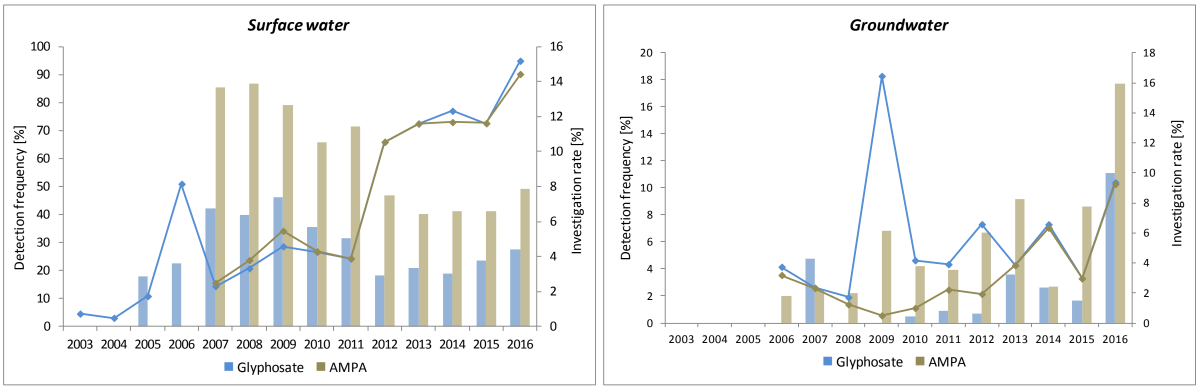


Fig. 11 - *Trend of detection frequency of glyphosate and AMPA (the histogram represents the frequency of detection in the samples; the curve represents the percentage of analyzed samples).*

The occurrance of the insecticide imidacloprid both in surface and groundwater is relatively recent (Fig. 12). The rate of investigation is significantly increasing over the years, but still largely incomplete, considering that the substance is used throughout the country and determines the highest number of exceedances of the EQSs.

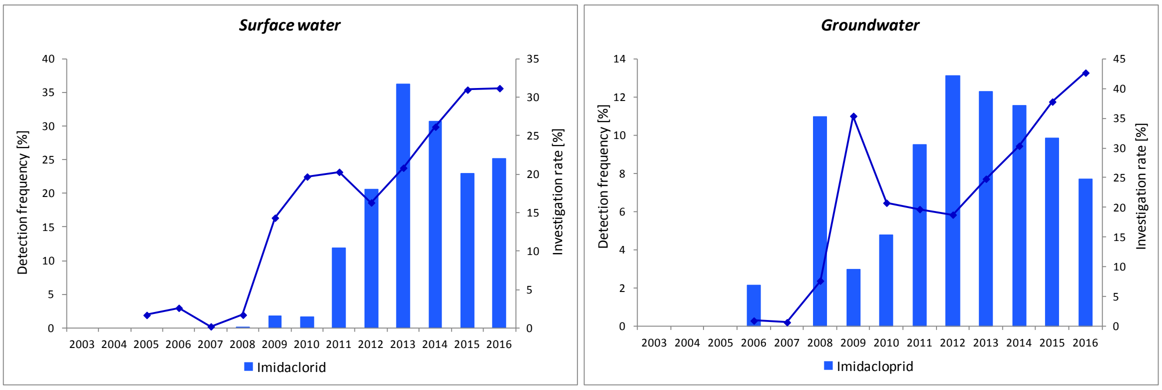


Fig. 12 - *Trend of detection frequency of imidacloprid (the histogram represents the frequency of detection in the samples;the curve represents the percentage of analyzed samples).*

3.3. Mixtures of Pesticides

The monitoring shows the presence of several substances in the samples. This means that aquatic organisms, but also other organisms, including humans (for example via the food chain), are often exposed to mixtures of pesticides. There are gaps in knowledge about the effects of chemical mixtures and, consequently, it is difficult to achieve a correct toxicological evaluation in the case of simultaneous exposure to different substances [Backhaus, 2010].

The possible risks from chemical combined exposures arouse a growing concern both in scientific and regulatory context, as the toxicological evaluation in risk assessment procedure doesn't take account of the mixture, but it is based on the effects of the single substance. The European Commission [EC, 2011] recognizes that it is scientifically proved that the simultaneous exposure to different chemical substances can, under certain conditions, give rise to combined effects that may be additive, as well as synergistic, with an overall toxicity higher than the individual substance toxicity. The Commission, moreover, underlines the limited knowledge about the ways in which substances exert their toxic effects on organisms.

Generally, mixtures of pesticides belonging to the same chemical class and sharing very similar mode of action, show an additive toxicological effect, where the overall toxicity is the result of the sum of the concentrations of the individual components normalized for the respective doses of effect (EC50, concentration at which 50 % of tested organisms show sub-lethal effects).
On the other hand, mixtures of pesticides show independent action when the mode of action are different and a substance does not affect the toxicity of the other.
When the mode of action is unknown, it is preferable to decide for the precautionary additive toxicological effect [EC, 2012]. It is known, on the base of available data, that the synergistic effect is infrequent and it must be treated on a case by case basis.

To date, however, European legislation does not provide for a complete and integrated assessment of the cumulative effects of the various components of a mixture in relation also to the different routes of exposure [Tørsløv, 2011]. Moreover, concerns arise in relation to the multiplicity of mixtures of unknown composition found in the environment.

The monitoring data reveal the presence of mixtures of pesticides in the samples. By analyzing the frequency of mixtures in the samples (Fig. 13), in surface water, the presence of at least two substances in 31.4% of the samples is detected, with a maximum of 55 substances in a single sample and an average of 4.7 substances. In groundwater, in 17.5 % of the samples there are at least two substances, the maximum of substances in a sample is 54, and the average is 4.8 substances.

The largest number of substances found in a single sample, as well as the average values, are in line with the significant improvement in monitoring effort and effectiveness over the years.

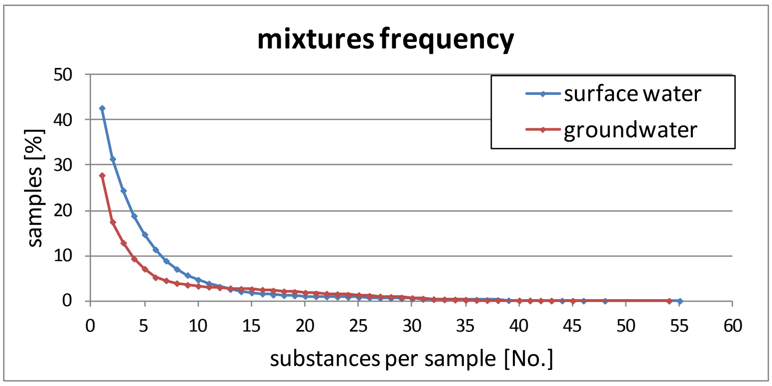


Fig. 13 - *Mixtures of pesticides in samples.*

The most common substances in mixtures (Fig. 14) are herbicides, with a significant presence in groundwater of fungicides and insecticides. The most frequently revealed components in mixtures, as well as in the past, are the triazine herbicides and some of their metabolites (terbuthylazine, desethyl-terbuthylazine, atrazine, deethylatrazine) and metolachlor. It is also relevant the presence in surface water of the herbicides oxadiazon, bentazone, glyphosate and its metabolite AMPA and diuron. The insecticide imidacloprid is found in both surface water and groundwater. Remarkable even the presence of the insecticide DDT and its metabolites. In groundwater is important the presence of fungicides such as metalaxyl, carbendazim, oxadixyl, dimethomorph, triadimenol e azoxistrobin.

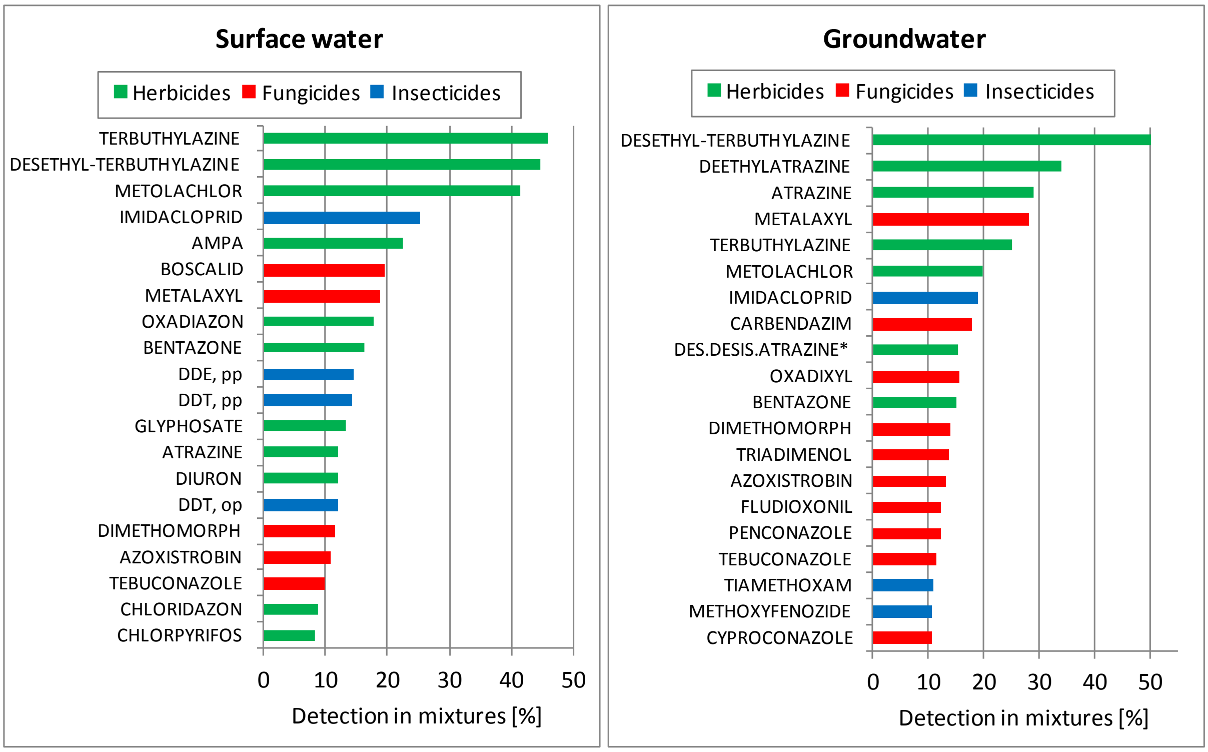


Fig. 14 - *Main components of the mixtures.*

The risk assessment should, therefore, take into account that humans and other organisms are often subjected to a simultaneous exposure to different chemicals, and that the normally used evaluation scheme is not precautionary about the risks of combined exposures.

To increase the level of knowledge, it may be useful to carry out a retrospective evaluation of the risk from multi-exposure, starting from the existing monitoring data.

4. THE MONITORING SUMMARY TABLES

NATIONAL DATA SURFACE WATER 2016			DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES	LQ (µg/L)	Sites	Detection	% detection	Samples	Detection	% detection	> 0,1 µg/L	% > 0,1 µg/L	25-th	50- th	75- th	90- th	95- th	Max
5915-41-3	terbuthylazine	0,010	1208	549	45,4	7831	1601	20,4	227	2,9	<LQ	0,010	0,013	0,028	0,060	2,750
30125-63-4	desethyl-terbuthylazine	0,010	1084	465	42,9	7351	1558	21,2	127	1,7	<LQ	0,010	0,018	0,025	0,043	1,130
51218-45-2	metolachlor	0,010	1036	532	51,4	6984	1446	20,7	291	4,2	<LQ	0,010	0,020	0,040	0,080	10,180
105827-78-9	imidacloprid	0,010	473	243	51,4	3464	873	25,2	42	1,2	<LQ	<LQ	0,010	0,020	0,038	0,690
1066-51-9	AMPA	0,100	385	264	68,6	1603	788	49,2	652	40,7	<LQ	<LQ	0,310	1,610	3,497	66,000
188425-85-6	boscalid	0,010	766	233	30,4	5107	676	13,2	67	1,3	<LQ	<LQ	0,010	0,025	0,035	21,000
57837-19-1	metalaxyl	0,010	852	254	29,8	5679	644	11,3	70	1,2	<LQ	<LQ	0,010	0,025	0,025	2,700
19666-30-9	oxadiazon	0,010	970	229	23,6	6365	625	9,8	98	1,5	<LQ	<LQ	0,010	0,025	0,025	1,985
25057-89-0	bentazone	0,050	987	202	20,5	6184	567	9,2	236	3,8	<LQ	<LQ	<LQ	<LQ	0,080	13,000
72-55-9	DDE, pp	0,010	473	51	10,8	3227	498	15,4	0	0,0	<LQ	<LQ	<LQ	0,025*	0,025*	0,009
50-29-3	DDT, pp	0,010	825	63	7,6	5426	493	9,1	2	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,750
1071-83-6	glyphosate	0,100	458	217	47,4	1687	464	27,5	308	18,3	<LQ	<LQ	<LQ	0,230	0,527	26,000
1912-24-9	atrazine	0,010	1401	162	11,6	9388	426	4,5	3	0,0	<LQ	<LQ	0,010	0,025	0,030	0,280
330-54-1	DIURON	0,010	1159	151	13,0	7348	422	5,7	11	0,1	<LQ	0,010	0,025	0,025	0,045	2,100
789-02-6	DDT, op	0,010	435	50	11,5	2665	413	15,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,004
110488-70-5	dimethomorph	0,020	486	157	32,3	3019	393	13,0	39	1,3	<LQ	<LQ	<LQ	0,025	0,030	12,295
131860-33-8	azoxystrobin	0,010	650	137	21,1	4321	373	8,6	51	1,2	<LQ	<LQ	0,010	0,025	0,025	1,900
107534-96-3	tebuconazole	0,005	520	144	27,7	3158	331	10,5	21	0,7	<LQ	0,010	0,015	0,025	0,025	2,510
1698-60-8	chloridazon	0,010	672	125	18,6	4602	312	6,8	21	0,5	<LQ	<LQ	0,015	0,015	0,015	0,870
2921-88-2	chlorpyrifos	0,010	1419	133	9,4	9506	290	3,1	15	0,2	<LQ	<LQ	0,010	0,015	0,025	2,290
161050-58-4	methoxyfenozide	0,010	454	104	22,9	2947	279	9,5	3	0,1	<LQ	<LQ	<LQ	0,015	0,020	0,560
94-74-6	MCPA	0,050	987	132	13,4	6189	244	3,9	48	0,8	<LQ	<LQ	<LQ	0,050	0,050	0,660
10605-21-7	carbendazim	0,005	229	58	25,3	1629	218	13,4	13	0,8	<LQ	0,005	0,005	0,020	0,030	1,850
6190-65-4	deethylatrazine	0,010	1090	81	7,4	7200	214	3,0	2	0,0	<LQ	<LQ	0,013	0,025	0,025	0,200
171118-09-5	metolachlor ESA	0,010	50	32	64,0	533	207	38,8	51	9,6	<LQ	<LQ	0,040	0,100	0,154	2,120
72-54-8	DDD, pp	0,010	504	50	9,9	3322	206	6,2	0	0,0	<LQ	<LQ	<LQ	0,025*	0,025*	0,010
500008-45-7	chlorantraniliprole	0,010	305	68	22,3	2144	199	9,3	13	0,6	<LQ	<LQ	<LQ	<LQ	0,013	0,440
66246-88-6	penconazole	0,010	644	80	12,4	4533	185	4,1	3	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,200
239110-15-7	fluopicolide	0,005	321	83	25,9	1994	185	9,3	15	0,8	<LQ	0,010	0,025	0,025	0,025	0,274
91-20-3	naphthalene	0,100	394	41	10,4	3008	177	5,9	46	1,5	<LQ	<LQ	<LQ	0,100	0,250	1,000
70630-17-0	metalaxyl-M	0,005	297	84	28,3	1371	177	12,9	18	1,3	<LQ	0,005	0,013	0,015	0,030	1,050
3424-82-6	DDE, op	0,010	313	49	15,7	2069	173	8,4	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,005
94-75-7	2,4-D	0,050	848	66	7,8	5461	159	2,9	13	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	3,805
153719-23-4	thiamethoxam	0,010	371	69	18,6	2713	158	5,8	4	0,1	<LQ	<LQ	<LQ	<LQ	0,010	9,800
330-55-2	linuron	0,010	1149	67	5,8	7108	152	2,1	25	0,4	<LQ	<LQ	0,015	0,025	0,025	1,760
21087-64-9	metribuzin	0,010	947	112	11,8	6243	150	2,4	38	0,6	<LQ	<LQ	0,015	0,025	0,025	1,300
60-51-5	dimethoate	0,010	883	90	10,2	5699	146	2,6	10	0,2	<LQ	<LQ	0,015	0,025	0,025	3,100
131341-86-1	fludioxonil	0,050	107	25	23,4	861	141	16,4	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,110
2163-68-0	2-hydroxyatrazine	0,010	50	33	66,0	533	132	24,8	5	0,9	<LQ	<LQ	<LQ	0,020	0,040	0,250
116-06-3	aldicarb	0,020	16	14	87,5	150	132	88,0	0	0,0	0,020	0,020	0,020	0,020	0,020	0,020
23950-58-5	propyzamide	0,010	741	69	9,3	4951	131	2,6	11	0,2	<LQ	<LQ	<LQ	0,025	0,025	0,630
66753-07-9	hydroxy-terbuthylazine	0,010	50	25	50,0	533	123	23,1	12	2,3	<LQ	<LQ	<LQ	0,040	0,060	0,310
3397-62-4	desethyl-desisopropyl-atrazine	0,010	52	18	34,6	545	121	22,2	0	0,0	<LQ	<LQ	<LQ	0,030	0,040	0,100
40487-42-1	pendimethalin	0,010	1067	79	7,4	7185	120	1,7	10	0,1	<LQ	<LQ	0,010	0,013	0,025	1,110
60207-90-1	propiconazole	0,010	530	72	13,6	3756	120	3,2	6	0,2	<LQ	<LQ	0,010	0,025	0,025	0,930
608-93-5	pentachlorobenzene	0,010	497	24	4,8	3598	119	3,3	2	0,1	<LQ	<LQ	0,010	0,050	0,25*	0,130
112281-77-3	tetraconazole	0,010	376	50	13,3	2776	114	4,1	3	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,340
53-19-0	DDD, op	0,010	342	49	14,3	2307	109	4,7	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,010
135410-20-7	acetamiprid	0,010	511	38	7,4	3876	103	2,7	2	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,360
53112-28-0	pyrimethanil	0,010	570	58	10,2	4212	102	2,4	15	0,4	<LQ	<LQ	0,010	0,025	0,025	1,700
2164-08-1	lenacil	0,010	570	55	9,6	4048	98	2,4	4	0,1	<LQ	<LQ	<LQ	0,010	0,010	0,400
886-50-0	terbutryn	0,010	401	62	15,5	2906	98	3,4	2	0,1	<LQ	<LQ	0,010	0,025	0,025	0,350
84087-01-4	quinclorac	0,030	118	36	30,5	811	98	12,1	49	6,0	<LQ	<LQ	<LQ	0,039	0,140	4,897
142459-58-3	flufenacet	0,010	717	81	11,3	4810	97	2,0	5	0,1	<LQ	<LQ	0,010	0,010	0,010	0,260
7085-19-0	mecoprop	0,050	534	53	9,9	3439	97	2,8	16	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	1,200
111991-09-4	nicosulfuron	0,010	494	55	11,1	3259	96	2,9	22	0,7	<LQ	<LQ	0,010	0,015	0,015	0,390
87392-12-9	S-metolachlor	0,005	164	38	23,2	951	90	9,5	4	0,4	<LQ	<LQ	0,005	0,005	0,014	0,679
23103-98-2	pirimicarb	0,010	518	39	7,5	3822	85	2,2	2	0,1	<LQ	<LQ	<LQ	0,025	0,025	6,500
55219-65-3	triadimenol	0,050	128	16	12,5	976	85	8,7	5	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	1,300
2008-58-4	2,6-dichlorobenzamide	0,020	344	34	9,9	2209	80	3,6	6	0,3	<LQ	<LQ	0,025	0,025	0,025	0,240

NATIONAL DATA SURFACE WATER 2016			DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES	LQ (µg/L)	Sites	Detection	% detection	Samples	Detection	% detection	> 0,1 µg/L	% > 0,1 µg/L	25-th	50- th	75- th	90- th	95- th	Max
122-34-9	simazine	0,010	1401	58	4,1	9278	79	0,9	4	0,0	<LQ	<LQ	0,025	0,025	0,050	3,500
121552-61-2	cyprodinil	0,020	518	34	6,6	3511	75	2,1	8	0,2	<LQ	<LQ	<LQ	0,025	0,025	0,550
24579-73-5	propamocarb	0,005	187	25	13,4	973	75	7,7	3	0,3	<LQ	<LQ	<LQ	0,010	0,020	0,308
81777-89-1	clomazone	0,020	222	44	19,8	1484	74	5,0	7	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	0,180
114-26-1	propoxur	0,050	69	15	21,7	630	74	11,7	3	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	0,450
83055-99-6	bensulfuron-methyl	0,010	407	46	11,3	2795	71	2,5	3	0,1	<LQ	<LQ	0,010	0,015	0,015	0,338
1582-09-8	trifluralin	0,010	1111	19	1,7	6973	71	1,0	1	0,0	<LQ	<LQ	<LQ	0,010	0,025	0,110
41394-05-2	metamitron	0,030	797	47	5,9	4871	69	1,4	8	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	0,900
126833-17-8	fenhexamid	0,010	443	30	6,8	3380	69	2,0	2	0,1	<LQ	<LQ	<LQ	0,025	0,025	16,900
140923-17-7	iprovalicarb	0,010	538	44	8,2	4074	68	1,7	6	0,1	<LQ	<LQ	0,010	0,025	0,025	0,920
1007-28-9	6-deisopropyl atrazine	0,010	727	41	5,6	5090	63	1,2	6	0,1	<LQ	<LQ	0,025	0,025	0,025	0,490
2212-67-1	molinate	0,010	853	23	2,7	5499	57	1,0	11	0,2	<LQ	<LQ	0,010	0,013	0,015	0,320
111988-49-9	thiacloprid	0,010	472	22	4,7	3454	56	1,6	2	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,470
118-74-1	hexachlorobenzene	0,010	721	37	5,1	4999	55	1,1	0	0,0	<LQ	<LQ	<LQ	0,010	0,025	0,100
22224-92-6	fenamiphos	0,020	22	9	40,9	183	53	29,0	0	0,0	<LQ	<LQ	0,020	0,020	0,030	0,060
34123-59-6	isoproturon	0,010	1163	23	2,0	7361	52	0,7	2	0,0	<LQ	<LQ	0,015	0,025	0,050	0,240
35554-44-0	imazalil	0,010	30	12	40,0	297	51	17,2	0	0,0	<LQ	<LQ	0,010	0,020	0,030	0,090
112410-23-8	tebufenozide	0,010	305	24	7,9	2144	49	2,3	13	0,6	<LQ	<LQ	<LQ	<LQ	<LQ	0,496
118134-30-8	spiroxamine	0,010	500	24	4,8	3451	45	1,3	1	0,0	<LQ	<LQ	0,010	0,025	0,025	0,110
7287-19-6	prometryn	0,010	249	22	8,8	1935	45	2,3	0	0,0	<LQ	<LQ	0,020	0,025	0,025	0,030
94361-06-5	cyproconazole	0,005	282	12	4,3	1556	44	2,8	0	0,0	<LQ	<LQ	0,010	0,010	0,010	0,089
67306-03-0	fenpropimorph	0,020	14	12	85,7	140	44	31,4	1	0,7	<LQ	<LQ	0,020	0,020	0,020	0,170
36734-19-7	iprodione	0,005	403	13	3,2	2782	42	1,5	0	0,0	<LQ	0,005	0,010	0,025	0,025	0,073
77732-09-3	oxadixyl	0,005	345	17	4,9	1955	41	2,1	2	0,1	<LQ	0,005	0,010	0,013	0,013	0,180
26225-79-6	ethofumesate	0,010	569	33	5,8	3535	39	1,1	4	0,1	<LQ	<LQ	0,010	0,010	0,010	0,390
78587-05-0	hexythiazox	0,010	30	12	40,0	297	38	12,8	0	0,0	<LQ	<LQ	0,010	0,020	0,020	0,050
98886-44-3	fosthiazate	0,020	14	10	71,4	140	38	27,1	0	0,0	<LQ	<LQ	0,020	0,020	0,020	0,030
106700-29-2	pethoxamid	0,010	339	32	9,4	2520	37	1,5	4	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	1,490
67129-08-2	metazachlor	0,010	318	26	8,2	2213	36	1,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,099
15545-48-9	chlorotoluron	0,010	437	17	3,9	3123	35	1,1	2	0,1	<LQ	<LQ	<LQ	0,010	0,010	1,151
86479-06-3	hexaflumuron	0,020	14	13	92,9	140	35	25,0	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,030
2032-65-7	methiocarb	0,010	288	17	5,9	2339	34	1,5	1	0,0	<LQ	<LQ	0,010	0,025	0,025	0,210
153233-91-1	etoxazole	0,050	81	12	14,8	764	34	4,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
42874-03-3	oxyfluorfen	0,005	259	17	6,6	1791	33	1,8	4	0,2	<LQ	<LQ	0,025	0,025	0,025	0,577
16752-77-5	methomyl	0,020	123	17	13,8	895	32	3,6	2	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	0,790
79241-46-6	fluazifop-P-butyl	0,010	34	13	38,2	313	32	10,2	0	0,0	<LQ	<LQ	0,010	0,019	0,020	0,030
608-73-1	HCH	0,010	316	13	4,1	2201	31	1,4	1	0,0	<LQ	<LQ	<LQ	0,010	0,025	0,118
80844-07-1	etofenprox	0,050	96	10	10,4	824	31	3,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
163515-14-8	dimethenamid-P	0,010	149	25	16,8	1230	30	2,4	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,350
88671-89-0	myclobutanil	0,020	267	30	11,2	1890	30	1,6	2	0,1	<LQ	<LQ	0,025	0,025	0,025	0,290
1918-00-9	dicamba	0,005	525	25	4,8	2898	28	1,0	10	0,3	<LQ	0,015	0,025	0,050	0,050	0,540
319-85-7	HCH, beta	0,010	476	12	2,5	2908	26	0,9	2	0,1	<LQ	<LQ	<LQ	<LQ	0,025	0,270
101200-48-0	tribenuron-methyl	0,020	14	13	92,9	140	26	18,6	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,050
55335-06-3	triclopyr	0,020	121	11	9,1	739	25	3,4	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
95465-99-9	cadusafos	0,001	14	12	85,7	140	24	17,1	0	0,0	<LQ	<LQ	<LQ	0,010	0,020	0,080
124495-18-7	quinoxyfen	0,010	249	13	5,2	2026	24	1,2	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,030
23564-05-8	thiophanate-methyl	0,020	161	17	10,6	1199	24	2,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,100
148-79-8	thiabendazole	0,005	61	9	14,8	642	24	3,7	0	0,0	<LQ	<LQ	0,005	0,010	0,010	0,030
15972-60-8	alachlor	0,010	1301	20	1,5	8683	23	0,3	3	0,0	<LQ	<LQ	0,010	0,025	0,025	1,510
470-90-6	chlorfenvinphos	0,010	917	10	1,1	6147	23	0,4	0	0,0	<LQ	<LQ	<LQ	0,01*	0,025*	0,008
319-84-6	HCH, alpha	0,010	528	15	2,8	3376	23	0,7	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,030
731-27-1	tolylfluanid	0,001	17	9	52,9	149	23	15,4	0	0,0	<LQ	<LQ	<LQ	0,010	0,020	0,050
120928-09-8	fenazaquin	0,010	30	11	36,7	297	22	7,4	0	0,0	<LQ	<LQ	<LQ	<LQ	0,010	0,033
67747-09-5	prochloraz	0,010	365	14	3,8	2130	22	1,0	1	0,0	<LQ	<LQ	<LQ	<LQ	0,010	0,200
99105-77-8	sulcotrione	0,050	338	15	4,4	1917	22	1,1	11	0,6	<LQ	<LQ	<LQ	<LQ	<LQ	0,415
161326-34-7	fenamidone	0,010	319	17	5,3	2284	21	0,9	1	0,0	<LQ	<LQ	<LQ	<LQ	0,010	0,220
175013-18-0	pyraclostrobin	0,010	378	9	2,4	2787	21	0,8	1	0,0	<LQ	<LQ	<LQ	0,025	0,025	4,100
333-41-5	diazinon	0,020	618	17	2,8	4336	20	0,5	1	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,170
95-76-1	3,4-dichloroaniline	0,010	95	10	10,5	603	20	3,3	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,053
319-86-8	HCH, delta	0,010	437	19	4,3	2610	20	0,8	0	0,0	<LQ	<LQ	<LQ	<LQ	0,015	0,051

The percentile values marked with * are greater than the maximum value because of the high limit of quantification used by some regional laboratories

NATIONAL DATA GROUNDWATER 2016			DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES	LQ (µg/L)	Sites	Detection	% detection	Samples	Detection	% detection	> 0,1 µg/L	% > 0,1 µg/L	25-th	50- th	75- th	90- th	95- th	Max
30125-63-4	desethyl-terbuthylazine	0,020	2261	343	15,2	4422	542	12,3	26	0,6	<LQ	<LQ	<LQ	0,025	0,040	0,570
6190-65-4	deethylatrazine	0,020	2315	242	10,5	4490	367	8,2	31	0,7	<LQ	<LQ	<LQ	0,025	0,030	0,320
1912-24-9	Atrazine	0,020	2488	205	8,2	4801	312	6,5	24	0,5	<LQ	<LQ	<LQ	0,025	0,040	6,560
57837-19-1	metalaxyl	0,020	1808	151	8,4	3528	301	8,5	76	2,2	<LQ	<LQ	<LQ	<LQ	0,020	12,000
5915-41-3	terbuthylazine	0,020	2398	184	7,7	4614	272	5,9	24	0,5	<LQ	<LQ	<LQ	0,025	0,040	0,960
51218-45-2	metolachlor	0,020	2248	154	6,9	4272	215	5,0	39	0,9	<LQ	<LQ	<LQ	<LQ	0,025	10,900
105827-78-9	imidacloprid	0,020	1356	111	8,2	2628	202	7,7	44	1,7	<LQ	<LQ	<LQ	<LQ	0,025	1,670
10605-21-7	carbendazim	0,005	409	88	21,5	902	189	21,0	1	0,1	<LQ	0,005	0,010	0,020	0,020	3,790
3397-62-4	Desethyl-desisopropyl-atrazine	0,010	139	93	66,9	290	167	57,6	75	25,9	<LQ	0,040	0,120	0,200	0,266	0,650
77732-09-3	oxadixyl	0,005	616	66	10,7	1535	167	10,9	34	2,2	<LQ	0,010	0,015	0,025	0,030	1,870
25057-89-0	bentazone	0,020	1763	129	7,3	3453	162	4,7	69	2,0	<LQ	<LQ	0,025	0,025	0,250	1319,0
110488-70-5	dimethomorph	0,020	1189	64	5,4	2554	146	5,7	7	0,3	<LQ	<LQ	<LQ	0,020	0,025	0,280
55219-65-3	triadimenol	0,050	456	64	14,0	1210	145	12,0	22	1,8	<LQ	<LQ	<LQ	<LQ	<LQ	4,230
131860-33-8	azoxystrobin	0,020	1424	64	4,5	2773	137	4,9	16	0,6	<LQ	<LQ	<LQ	<LQ	0,025	4,900
66246-88-6	penconazole	0,010	1213	70	5,8	2192	130	5,9	2	0,1	<LQ	<LQ	0,010	0,020	0,025	7,800
131341-86-1	fludioxonil	0,020	390	66	16,9	932	130	13,9	1	0,1	<LQ	<LQ	0,020	0,025	0,025	0,120
107534-96-3	tebuconazole	0,020	1292	58	4,5	2084	120	5,8	11	0,5	<LQ	<LQ	<LQ	0,020	0,025	0,540
153719-23-4	thiamethoxam	0,010	760	44	5,8	1617	113	7,0	2	0,1	<LQ	<LQ	0,010	0,015	0,020	0,180
161050-58-4	methoxyfenozide	0,010	703	69	9,8	1381	112	8,1	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,070
94361-06-5	cyproconazole	0,020	911	50	5,5	1513	110	7,3	7	0,5	<LQ	<LQ	<LQ	<LQ	0,020	1,440
112281-77-3	tetraconazole	0,010	641	50	7,8	1347	105	7,8	11	0,8	<LQ	<LQ	0,010	0,015	0,025	0,410
1066-51-9	AMPA	0,100	355	82	23,1	570	101	17,7	21	3,7	<LQ	<LQ	<LQ	<LQ	<LQ	5,250
188425-85-6	boscalid	0,020	1613	49	3,0	3273	99	3,0	12	0,4	<LQ	<LQ	<LQ	0,024	0,028	1,630
86479-06-3	hexaflumuron	0,020	104	65	62,5	322	90	28,0	0	0,0	<LQ	<LQ	0,020	0,020	0,020	0,030
53112-28-0	pyrimethanil	0,020	1394	43	3,1	2830	90	3,2	7	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	1,350
23103-98-2	pirimicarb	0,005	899	51	5,7	1705	87	5,1	0	0,0	<LQ	0,005	0,010	0,015	0,020	0,050
2008-58-4	2,6-dichlorobenzamide	0,020	706	55	7,8	1373	86	6,3	27	2,0	<LQ	<LQ	<LQ	0,025	0,030	1,12
84087-01-4	quinclorac	0,020	677	82	12,1	1321	84	6,4	13	1,0	<LQ	<LQ	<LQ	<LQ	0,039	4,960
330-54-1	diuron	0,020	1866	46	2,5	3645	83	2,3	1	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,130
122-34-9	Simazine	0,020	2445	59	2,4	4722	82	1,7	3	0,1	<LQ	<LQ	<LQ	0,025	0,150	0,180
87674-68-8	dimethenamid	0,020	877	79	9,0	1693	81	4,8	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	7,500
116-06-3	aldicarb	0,020	110	59	53,6	353	81	22,9	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,020
330-55-2	linuron	0,020	2393	53	2,2	4703	74	1,6	4	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,310
16752-77-5	methomyl	0,020	775	36	4,6	1651	74	4,5	8	0,5	<LQ	<LQ	<LQ	<LQ	0,020	1,210
94-74-6	MCPA	0,020	1847	57	3,1	3620	71	2,0	1	0,0	<LQ	<LQ	<LQ	0,025	0,050	0,130
19666-30-9	oxadiazon	0,020	1397	54	3,9	2760	71	2,6	17	0,6	<LQ	<LQ	<LQ	<LQ	0,025	0,560
114-26-1	propoxur	0,020	185	50	27,0	486	69	14,2	0	0,0	<LQ	<LQ	<LQ	0,020	0,025	0,030
171118-09-5	metolachlor-ESA	0,010	129	39	30,2	232	65	28,0	2	0,9	<LQ	<LQ	0,010	0,020	0,034	0,210
7287-19-6	prometryn	0,025	768	51	6,6	1524	65	4,3	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,080
81777-89-1	clomazone	0,020	850	51	6,0	1772	64	3,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
1071-83-6	glyphosate	0,100	361	54	15,0	577	64	11,1	37	6,4	<LQ	<LQ	<LQ	<LQ	0,142	3,400
7085-19-0	mecoprop	0,020	1178	46	3,9	2368	61	2,6	1	0,0	<LQ	<LQ	0,025	0,025	0,075	0,500
80844-07-1	etofenprox	0,020	143	41	28,7	385	61	15,8	0	0,0	<LQ	<LQ	<LQ	0,020	0,025	0,030
67306-03-0	fenpropimorph	0,020	104	46	44,2	323	61	18,9	5	1,5	<LQ	<LQ	<LQ	0,020	0,020	0,720
135410-20-7	acetamiprid	0,010	781	45	5,8	1562	59	3,8	1	0,1	<LQ	<LQ	0,010	0,025	0,025	0,290
64628-44-0	triflumuron	0,020	118	48	40,7	348	59	17,0	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,030
99-30-9	dicloran	0,020	686	28	4,1	1467	58	4,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
239110-15-7	fluopicolide	0,020	751	57	7,6	986	57	5,8	12	1,2	<LQ	<LQ	<LQ	<LQ	0,025	0,730
35554-44-0	imazalil	0,020	118	39	33,1	349	57	16,3	1	0,3	<LQ	<LQ	<LQ	0,020	0,020	0,170
94-75-7	2,4-D	0,050	1075	47	4,4	2118	56	2,6	1	0,0	<LQ	<LQ	<LQ	<LQ	0,075	0,210
79241-46-6	fluazifop-P-butyl	0,020	151	43	28,5	470	55	11,7	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,060
2032-65-7	methiocarb	0,020	653	38	5,8	1264	54	4,3	1	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,120
105512-06-9	clodinafop-propargyl	0,020	104	40	38,5	323	53	16,4	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,040
78587-05-0	hexythiazox	0,020	118	34	28,8	349	52	14,9	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,050
24579-73-5	propamocarb	0,005	302	36	11,9	752	51	6,8	0	0,0	<LQ	0,010	0,010	0,015	0,020	0,040
121552-61-2	cyprodinil	0,020	1274	33	2,6	2063	50	2,4	1	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,310
1746-81-2	monolinuron	0,020	276	39	14,1	640	47	7,3	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
111988-49-9	thiacloprid	0,010	799	38	4,8	1594	47	2,9	1	0,1	<LQ	<LQ	0,010	0,025	0,025	0,200
1007-28-9	6-deisopropyl atrazine	0,010	921	31	3,4	1475	45	3,1	3	0,2	<LQ	<LQ	<LQ	0,025	0,025	0,190
314-40-9	bromacil	0,010	271	23	8,5	507	43	8,5	2	0,4	<LQ	0,010	0,025	0,025	0,030	0,270
83121-18-0	teflubenzuron	0,020	121	42	34,7	366	43	11,7	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,040
95465-99-9	cadusafos	0,020	104	35	33,7	323	41	12,7	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,050
22224-92-6	fenamiphos	0,020	122	32	26,2	403	41	10,2	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,050

NATIONAL DATA GROUNDWATER 2016			DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES	LQ (µg/L)	Sites	Detection	% detection	Samples	Detection	% detection	> 0,1 µg/L	% > 0,1 µg/L	25-th	50- th	75- th	90- th	95- th	Max
36734-19-7	iprodione	0,020	1337	29	2,2	2431	40	1,6	3	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,966
98886-44-3	fosthiazate	0,020	104	27	26,0	323	39	12,1	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,060
1689-83-4	ioxynil	0,020	104	36	34,6	322	37	11,5	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,030
153233-91-1	etoxazole	0,020	130	31	23,8	372	36	9,7	0	0,0	<LQ	<LQ	<LQ	0,020	0,025	0,030
23950-58-5	propyzamide	0,010	1502	28	1,9	2839	34	1,2	2	0,1	<LQ	<LQ	0,010	0,015	0,025	0,661
1698-60-8	chloridazon	0,020	1270	27	2,1	2333	33	1,4	2	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,120
107-06-2	ethylene dichloride	0,010	1078	27	2,5	2111	33	1,6	4	0,2	<LQ	0,050	0,150	0,250	0,500	1,800
110235-47-7	mepanipyrim	0,010	603	24	4,0	1315	33	2,5	0	0,0	<LQ	<LQ	0,010	0,015	0,015	0,050
2921-88-2	chlorpyrifos	0,010	2386	24	1,0	4453	31	0,7	4	0,1	<LQ	<LQ	0,010	0,013	0,013	0,800
35367-38-5	diflubenzuron	0,020	203	29	14,3	516	31	6,0	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
148-79-8	thiabendazole	0,020	417	25	6,0	731	31	4,2	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,030
1646-87-3	aldicarb sulfoxide	0,020	104	20	19,2	323	29	9,0	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
1593-77-7	dodemorph	0,020	104	24	23,1	323	29	9,0	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,070
88671-89-0	myclobutanil	0,020	1144	22	1,9	1868	29	1,6	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,340
175013-18-0	pyraclostrobin	0,010	537	22	4,1	1061	29	2,7	2	0,2	<LQ	<LQ	0,010	0,010	0,010	0,120
101007-06-1	acrinathrin	0,020	185	26	14,1	474	28	5,9	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
1646-88-4	aldoxycarb	0,020	104	20	19,2	323	28	8,7	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
2163-68-0	2-hydroxyatrazine	0,010	132	19	14,4	231	28	12,1	0	0,0	<LQ	<LQ	<LQ	0,010	0,023	0,080
55335-06-3	triclopyr	0,020	681	27	4,0	1364	28	2,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
126833-17-8	fenhexamid	0,010	764	24	3,1	1475	27	1,8	0	0,0	<LQ	<LQ	0,010	0,010	0,010	0,020
124495-18-7	quinoxyfen	0,010	385	24	6,2	728	27	3,7	0	0,0	<LQ	<LQ	0,010	0,010	0,020	0,040
134098-61-6	fenpyroximate	0,020	118	23	19,5	349	25	7,2	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,050
101200-48-0	tribenuron-methyl	0,020	104	22	21,2	323	23	7,1	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,100
140923-17-7	iprovalicarb	0,020	1329	18	1,4	2627	21	0,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,070
40487-42-1	pendimethalin	0,020	2116	17	0,8	4168	19	0,5	2	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,225
51235-04-2	hexazinone	0,020	737	17	2,3	1427	19	1,3	5	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	4,090
60168-88-9	fenarimol	0,005	529	10	1,9	1101	19	1,7	2	0,2	<LQ	<LQ	0,013	0,013	0,013	1,120
81334-34-1	imazapyr	0,020	104	17	16,3	323	19	5,9	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,050
60207-90-1	propiconazole	0,005	1376	18	1,3	1996	19	1,0	0	0,0	<LQ	0,005	0,010	0,010	0,010	0,080
1563-66-2	carbofuran	0,020	1024	18	1,8	2096	18	0,9	1	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,220
57966-95-7	cymoxanil	0,020	1256	15	1,2	2084	17	0,8	1	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,150
120928-09-8	fenazaquin	0,020	118	15	12,7	349	17	4,9	1	0,3	<LQ	<LQ	<LQ	<LQ	<LQ	0,310
23135-22-0	oxamyl	0,020	151	14	9,3	470	16	3,4	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,020
32809-16-8	procymidone	0,005	985	13	1,3	1979	16	0,8	4	0,2	<LQ	<LQ	0,005	0,013	0,013	1,900
60-57-1	dieldrin	0,010	1347	14	1,0	2747	15	0,5	0	0,0	<LQ	<LQ	<LQ	0,010	0,025*	0,015
55179-31-2	bitertanol	0,020	118	13	11,0	349	15	4,3	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
7786-34-7	mevinphos	0,020	427	15	3,5	769	15	2,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
118134-30-8	spiroxamine	0,020	1201	15	1,2	2357	15	0,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
2312-35-8	propargite	0,020	151	15	9,9	470	15	3,2	2	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	0,530
114311-32-9	imazamox	0,020	711	14	2,0	1361	14	1,0	8	0,6	<LQ	<LQ	<LQ	<LQ	<LQ	0,720
2212-67-1	molinate	0,020	1802	8	0,4	3219	13	0,4	5	0,2	<LQ	<LQ	<LQ	<LQ	0,025	0,430
141112-29-0	isoxaflutole	0,020	829	12	1,4	1516	13	0,9	7	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	2,810
470-90-6	chlorfenvinphos	0,010	1116	12	1,1	2119	12	0,6	0	0,0	<LQ	<LQ	<LQ	0,010	0,015*	0,010
4891-54-7	demeton-sulfone	0,020	104	8	7,7	323	12	3,7	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
34123-59-6	isoproturon	0,010	1345	12	0,9	2675	12	0,4	0	0,0	<LQ	0,010	0,015	0,025*	0,025*	0,020
309-00-2	aldrin	0,010	1284	11	0,9	2549	11	0,4	0	0,0	<LQ	<LQ	<LQ	0,01*	0,025*	0,006
959-98-8	alpha-endosulfan	0,002	529	7	1,3	1386	11	0,8	3	0,2	<LQ	0,002	0,003	0,005	0,010	0,467
500008-45-7	chlorantraniliprole	0,010	421	8	1,9	715	11	1,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,024
731-27-1	tolylfluanid	0,020	187	11	5,9	525	11	2,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
1918-00-9	dicamba	0,020	465	10	2,2	1024	10	1,0	0	0,0	<LQ	<LQ	0,025*	0,025*	0,05*	0,020
29232-93-7	pirimiphos-methyl	0,020	481	10	2,1	812	10	1,2	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
33213-65-9	beta-endosulfan	0,002	560	6	1,1	1459	9	0,6	3	0,2	<LQ	<LQ	0,003	0,005	0,005	0,860
82097-50-5	triasulfuron	0,020	917	6	0,7	2014	9	0,4	0	0,0	<LQ	<LQ	<LQ	<LQ	0,025*	0,020
87392-12-9	S-metolachlor	0,005	172	9	5,2	328	9	2,7	0	0,0	<LQ	<LQ	<LQ	0,005	0,005	0,053
69327-76-0	buprofezin	0,010	499	6	1,2	984	8	0,8	2	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	0,600
66753-07-9	hydroxy-terbuthylazine	0,010	132	8	6,1	232	8	3,4	1	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	0,200
56-38-2	parathion	0,010	1043	6	0,6	2009	8	0,4	3	0,1	<LQ	<LQ	<LQ	0,013	0,013	0,560

The percentile values marked with * are greater than the maximum value because of the high limit of quantification used by some regional laboratories

5. CONCLUSIONS

Pesticide pollution is widespread concerning 67.0% of the sampling sites in surface water and 33.5 % of groundwater. The contamination is over the regulatory threshold values in 23.9% of the sites in surface water and in 8.3% in groundwater.

259 pesticides have been detected in surface and groundwater, a number that is considerably higher than in previous years. Herbicides are the most frequent substances, however, compared to the past, the presence of fungicides and insecticides has been considerably increased.
The substances most frequently detected in concentrations above the thresholds are: triazinic herbicides, glyphosate, metolachlor and bentazone, insecticide imidacloprid, fungicides triadimenol, oxadixil and metalaxyl.

The pollution is more widespread in the Po river basin. As already pointed out in the past, this largely depends on the fact that surveys are generally more representative in the northern regions, where are concentrated about 50% of the monitoring sites of the entire national network.

The overall frequency of pesticides referred to the monitoring points indicates a progressive increase in the spread of contamination, in the period 2003-2016, with a direct correlation to the extension of the network and the number of investigated substances. In surface water, the percentage of contaminated points has increased by about 20%, in groundwater by around 10%.

Even more than in the past mixtures have been found in water, with an average number of 5 substances and up to 55 substances in a single sample. Predicting contamination by pesticides is complex, both for the large number of substances used and for the multiplicity of pathways that can follow in the environment. Humans and other organisms are often exposed to mixtures of chemicals, of which the composition is not known beforehand, moreover the evaluation scheme based on the single substance is not adequate. A more cautious approach in pesticide authorization process is necessary, as required globally.

An increase in the coverage and representativeness of surveys occurred over the years 2003-2016. However, there is still a lack of homogeneity between the regions of the north and those of the south-central Italy, where monitoring is still generally less representative, both in terms of the network and in terms of number of monitored substances.

An overall update of monitoring programs is necessary in order to take into account the new substances placed on the market. Some of these are classified as hazardous, in particular are hazardous to aquatic environment.
Furthermore, it is necessary to investigate more extensively those substances that are responsible for the most cases of non-conformities, such as glyphosate and AMPA, but also, for example, imidacloprid, metolachlor-ESA, triadimenol, oxadixil.

It is still necessary to harmonize the performance of the laboratories, given the differences still present between the various regions. The analytical limits should, in particular, be adequate to allow comparison with the EQSs, which are often significantly lower.

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Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Water Framework Directive.

Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides.

Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status.

Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC.

Commission Implementing Regulation (EU) 2016/1313 of 1 August 2016 amending Implementation Regulation (EU) No 540/2011 as regards the conditions of approval of the active substance glyphosate.

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