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RAPPORTI

Pesticides in surface and groundwater Italian monitoring 2012

Synthesis Report

241 / 2016

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e la Ricerca Ambientale

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The original report is based on information provided by regions and autonomous provinces, that through regional and provincial agencies for environmental protection carry out the surveys on the territory and laboratory analysis. Special thanks to all the experts and institutions, that have contributed to its realisation.

The report is prepared by the Hazardous Substances Sector, Technological Risk Service, Department of Technological and Industrial and Nuclear Risk - ISPRA

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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. In the European Union, from a regulatory point of view, it can be distinguished among substances used in plant protection products and biocidal products, which are used in various fields (disinfectants, wood preservatives, pesticides for non agricultural use, antifouling, etc.). 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).

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 behaviour in the environment of the substance, that can be found in different compartments (air, soil, water, sediment), and may pose a risk to humans and ecosystems, because of acute and long-term impact.
The risk of a chemical depends on its intrinsic properties and its capacity to produce adverse effects on living organisms, that are exposed to the substance. The level of exposure depends on the amount of the substance released to the environment and on the environmental fate.

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, monitoring data show a diffuse pollution of surface and groundwater. The national monitoring plan aims to identify issues not adequately foreseen by the regulatory framework.
Pesticides monitoring is a quite complex and challenging task because of the diffuse source of pollution, the huge number of substances involved and the strong seasonal patterns of the meteoric precipitations which are the main contamination transport route through runoff and leaching. In order to implement a national wide monitoring of pesticides, it’s necessary to consider several factors, like substance properties, use patterns, hydrology and hydrogeology of the interested areas.

The Institute for Environmental Protection and Research (ISPRA) is responsible for technical management and assessment of the monitoring plan, providing guidelines for its implementation. In particular the Institute performs a regular review of the priority substances on which to focus monitoring. The active substances used annually in Italy are about 400, present with different formulations in some thousands of commercial products, used in agriculture and in other non-agricultural fields.
The substance selection is based on the sold amounts, on a preliminary assessment of the potential to contaminate surface and groundwater, and on hazardous properties of substances.

The present paper refers to the national survey in the years 2012. The resulting report [1] is the outcome of a complex activity involving Regions and Environmental Regional Agencies, carrying out investigations on the territory and transmitting the collected data to ISPRA.
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 (WFD, Dir. 2006/118/EC [2, 3]). The monitoring network of surface water, in particular, must be designed so as to provide a coherent and comprehensive overview of ecological and chemical status within each river basin and allow classification of water bodies. For groundwater, similarly, the network must provide a coherent and comprehensive overview of the chemical status within each river basin and shall allow to detect any long-term human induced upward trend of pollutants.

In 2012, the net surface water have an average of 4.8 points per 1000 km2. The average frequency of sampling is 7.4 samples / year.
In groundwater, the average density of the networks is 9 points / 1,000 km2. The average sampling / year is 2.4.

The monitoring program is quite inhomogeneous throughout the country, with a more developed and efficient network in the northern part (Padan-venetian valley) compared to the southern region.
The 2012 monitoring involved 1355 sites and 9612 samples in surface water; 2145 sites and 4638 samples in groundwater.

The surveys covered 3,500 sampling points and 14,250 samples and a total of 335 substances were searched. Herbicides and their metabolites are the most searched substances (Figure 1).

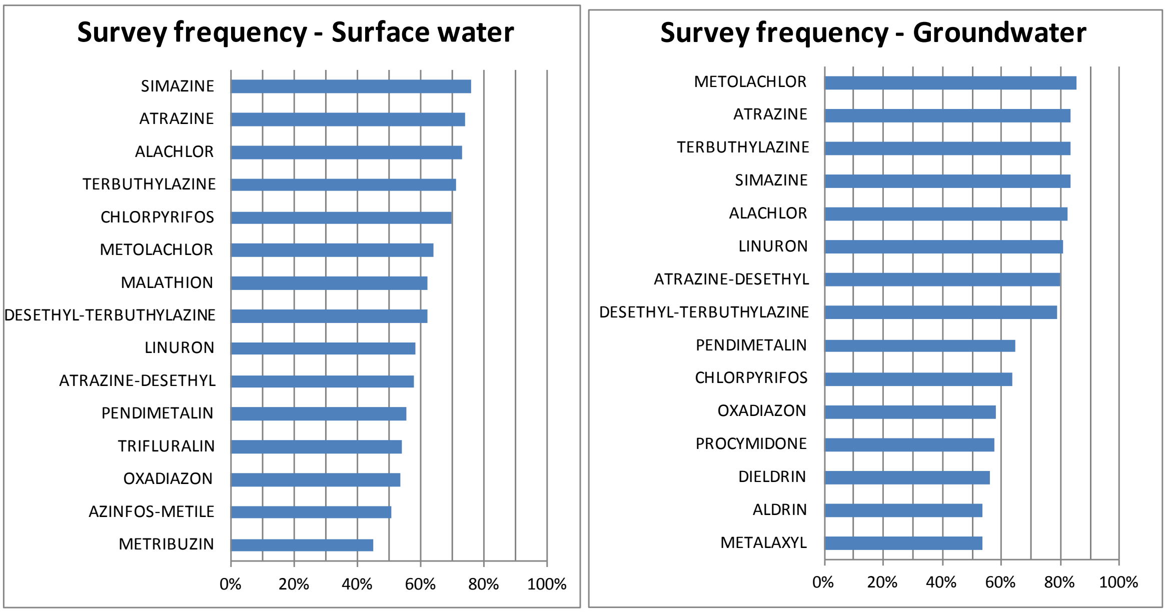


Fig. 1 *Most searched substances in surface and ground water.*

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 .
The European legislation (Directive 2008/105/EC [4]) sets the EQS for a limited number of priority substances (including few pesticides).
Moreover the Italian legislation sets EQS for some other pesticides and fixes for all the other pesticides (including metabolites), not explicitly regulated, it is applied the limit of 0.1 µg/l and for the sum of pesticides the limit of 1 µg/l.

The Directive 2006/118/EC [3] 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 [5], which lays 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, that are:

- where measures are below the LQ, they shall be set to 50% of LQ,
- if 90% of the analytical results are 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 aren’t analytical measurements above the limit of quantification. This could mean that there is not contamination, 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.

3. RESULTS AND DISCUSSION

3.1. Contamination Levels

Altogether, 175 substances were detected, more than in previous years. Herbicides are the most occurring substances, mainly because of the timing of their use in relation to the seasonal rainfall in early spring. These circumstances determine a faster transport of pesticides to surface water bodies and underground. 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.

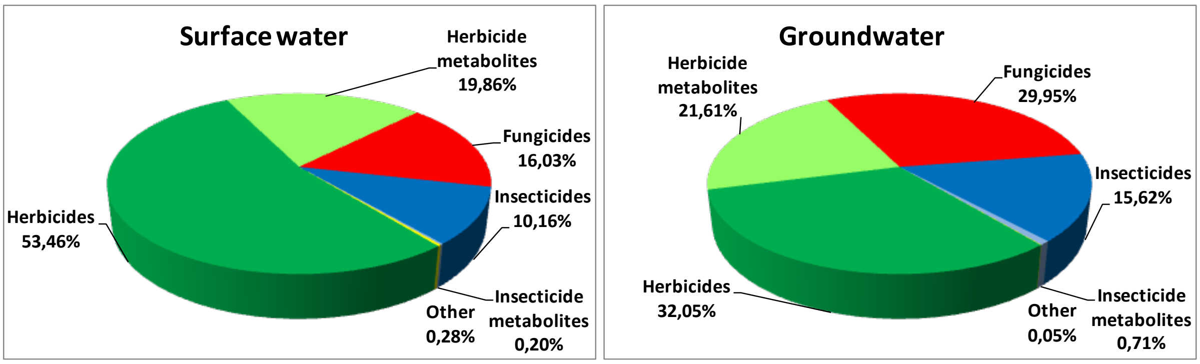


Fig. 2 *Type of detected pesticides in surface and ground water.*

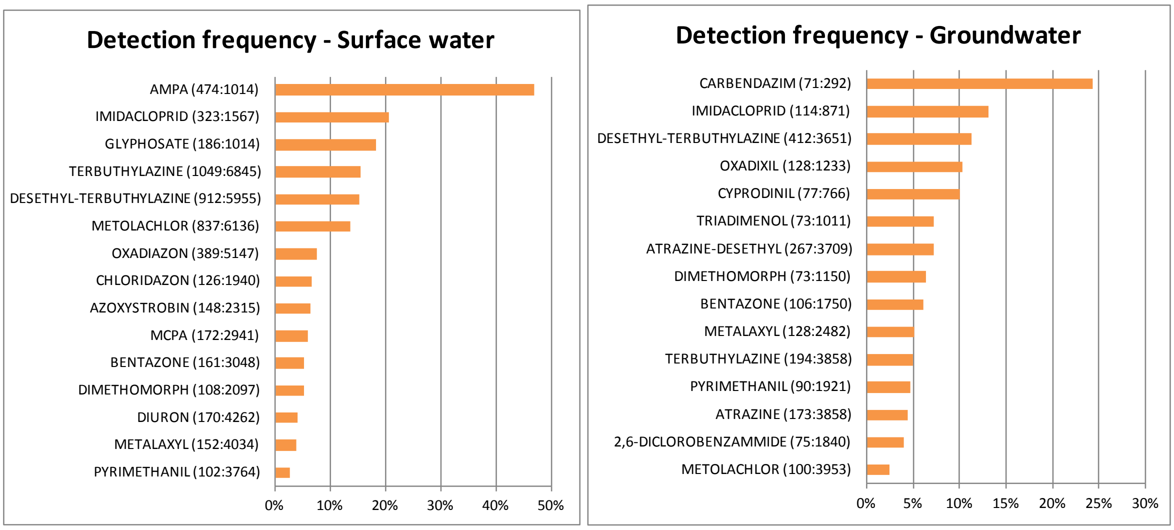


Fig. 3 *Pesticides detected most frequently in water.*

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 searched substances.

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

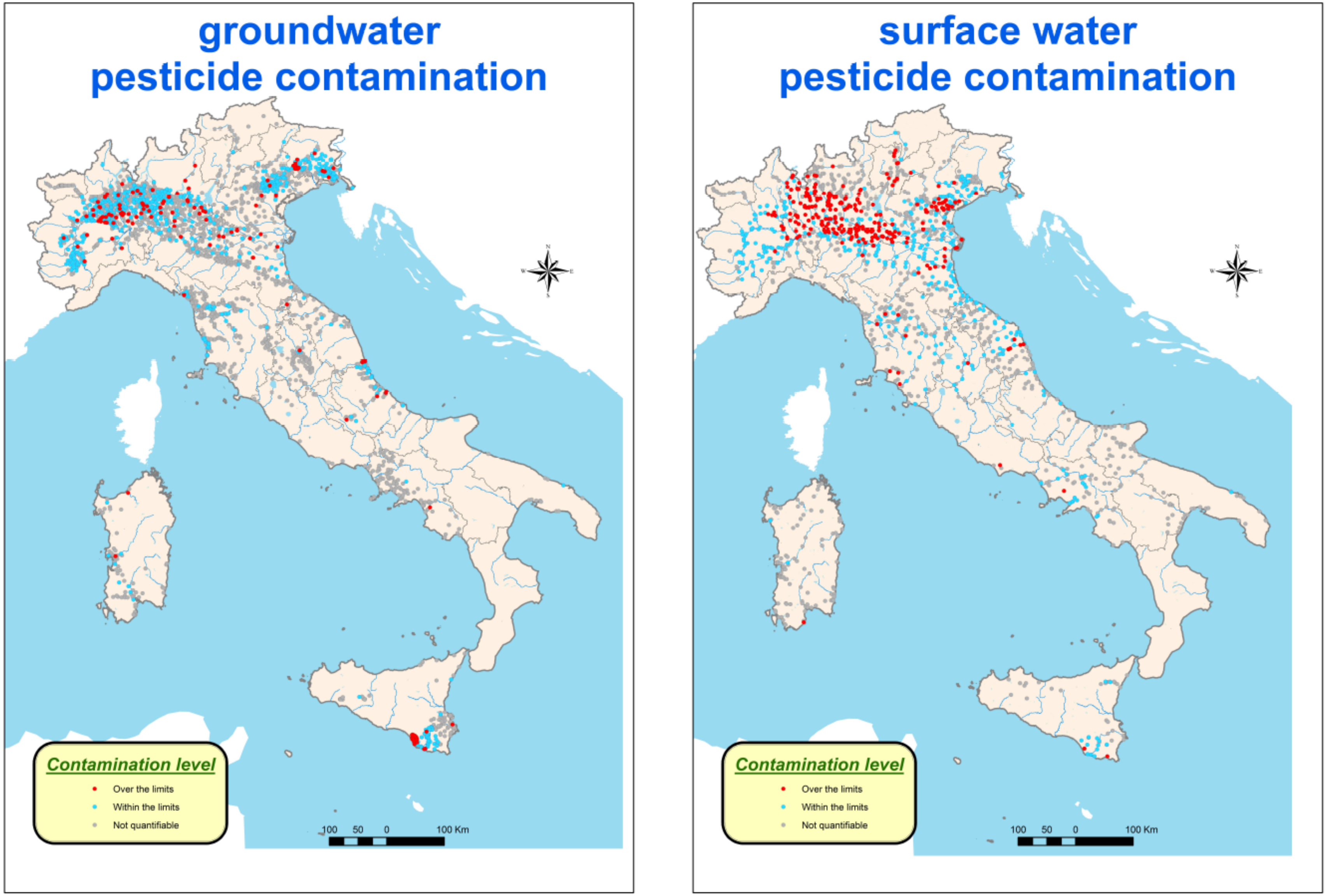


Fig. 4 *Pesticide contamination level.*

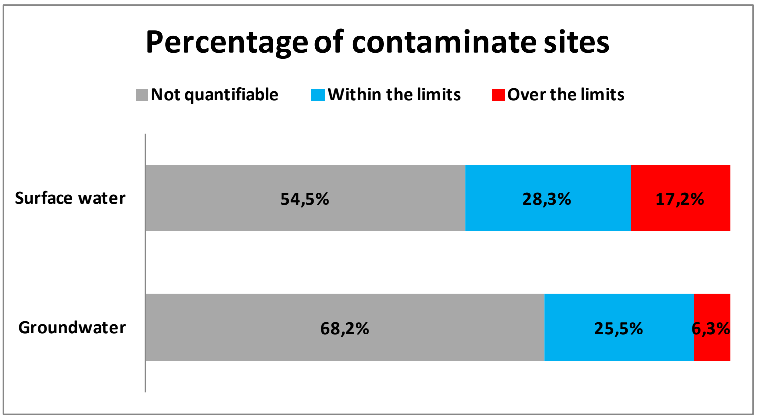
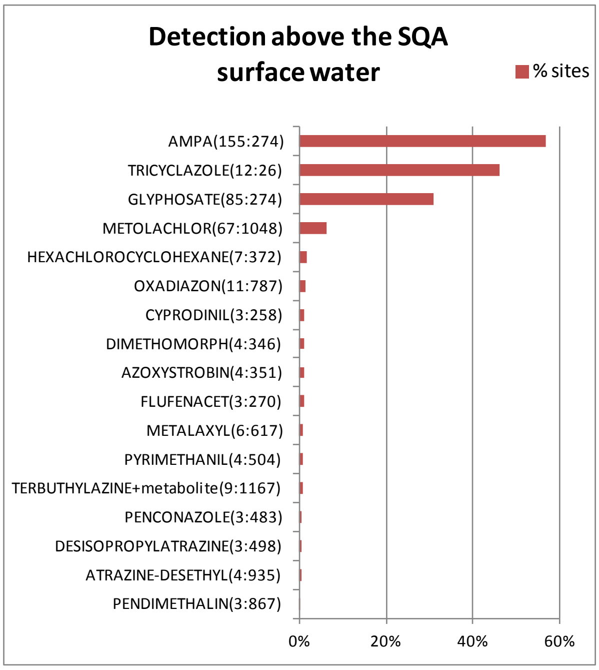


Fig. 5 *Percentage of contaminate sites.*

The percentage of contaminate sites is shown in figure 5. Pesticides were detected in 45.5% of surface water sites and in 31.0% of groundwater sites. The measured concentrations were often low, nevertheless the overall occurrence in pesticides indicates a wide spread of contamination, that also affects deep aquifers geologically protected by layers of low permeability.

In 17.2% 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, metolachlor, tricyclazole, oxadiazon, terbuthylazine and its major metabolite.

As regards groundwater, pesticide concentrations above the limit were detected in 6.3% of sites. The substances most frequently found were: bentazone, metalaxyl, terbuthylazine and desethyl-terbuthylazine, atrazine and atrazine-desethyl, oxadixil, imidacloprid, oxadiazon, bromacile, 2,6-diclorobenzammide, metolachlor.



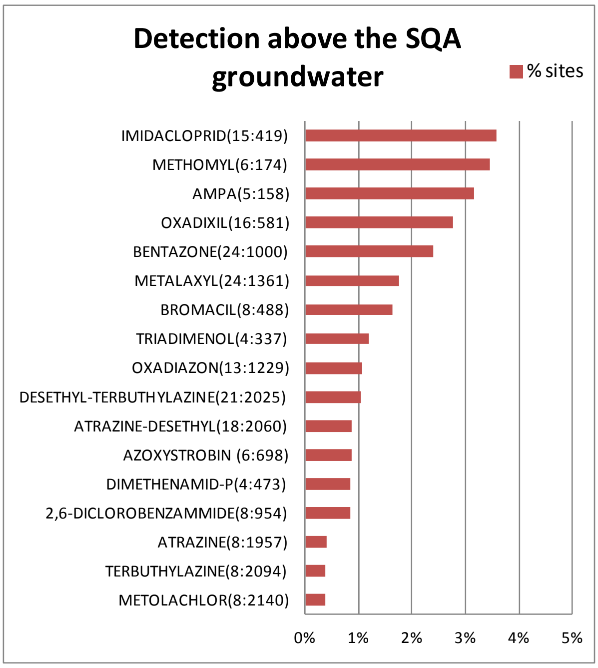


Fig. 6 *Pesticides detected most frequently above the EQS in surface and ground water.*

In figure 6 the frequency of pesticide detection above the EQS is relative to the sites. The herbicide glyphosate and its metabolite AMPA, in spite of their wide use, were monitored only in Lombardy Region in the northern Italy. It's expected a significant increase of detected contamination once these substances will be included in the other Regions' monitoring programs (Fig. 4).

The fungicide tricyclazole is used on rice cultivation, despite its monitoring is limited to restricted areas, the percentage of detection above the EQS is high.

The triazine herbicides: atrazine, simazine, terbuthylazine and the metabolites atrazine–desethyl 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.

The two substances most frequently found in groundwater are insecticides: imidacloprid and methomyl. Imidacloprid is a systemic insecticide approved for use in the EU with certain restrictions for flowering crops. It is used to control sucking and soil insects. It belongs to the Neonicotinoid substance group and 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)

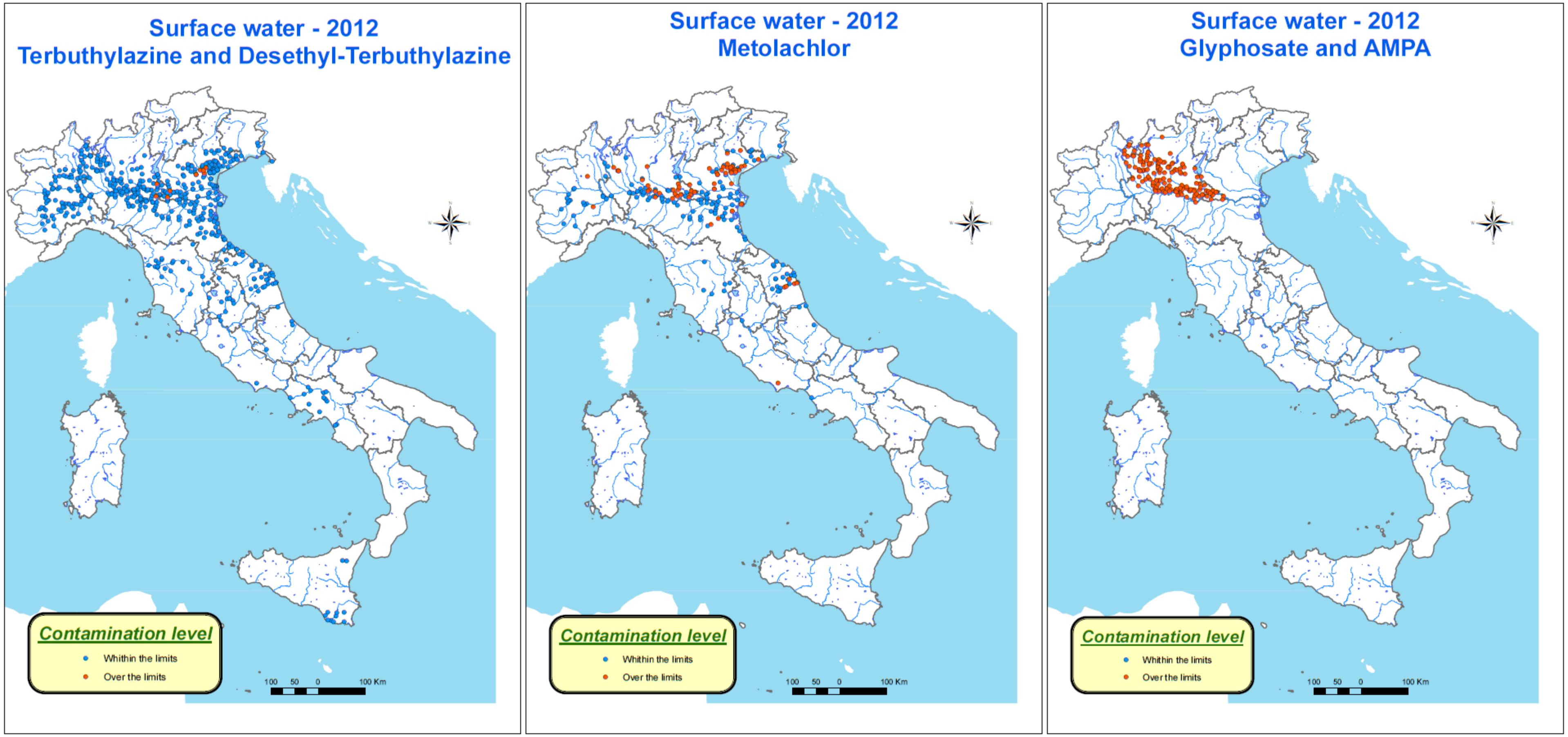


Fig. 7a *Contamination levels of specific pesticides in surface water.*

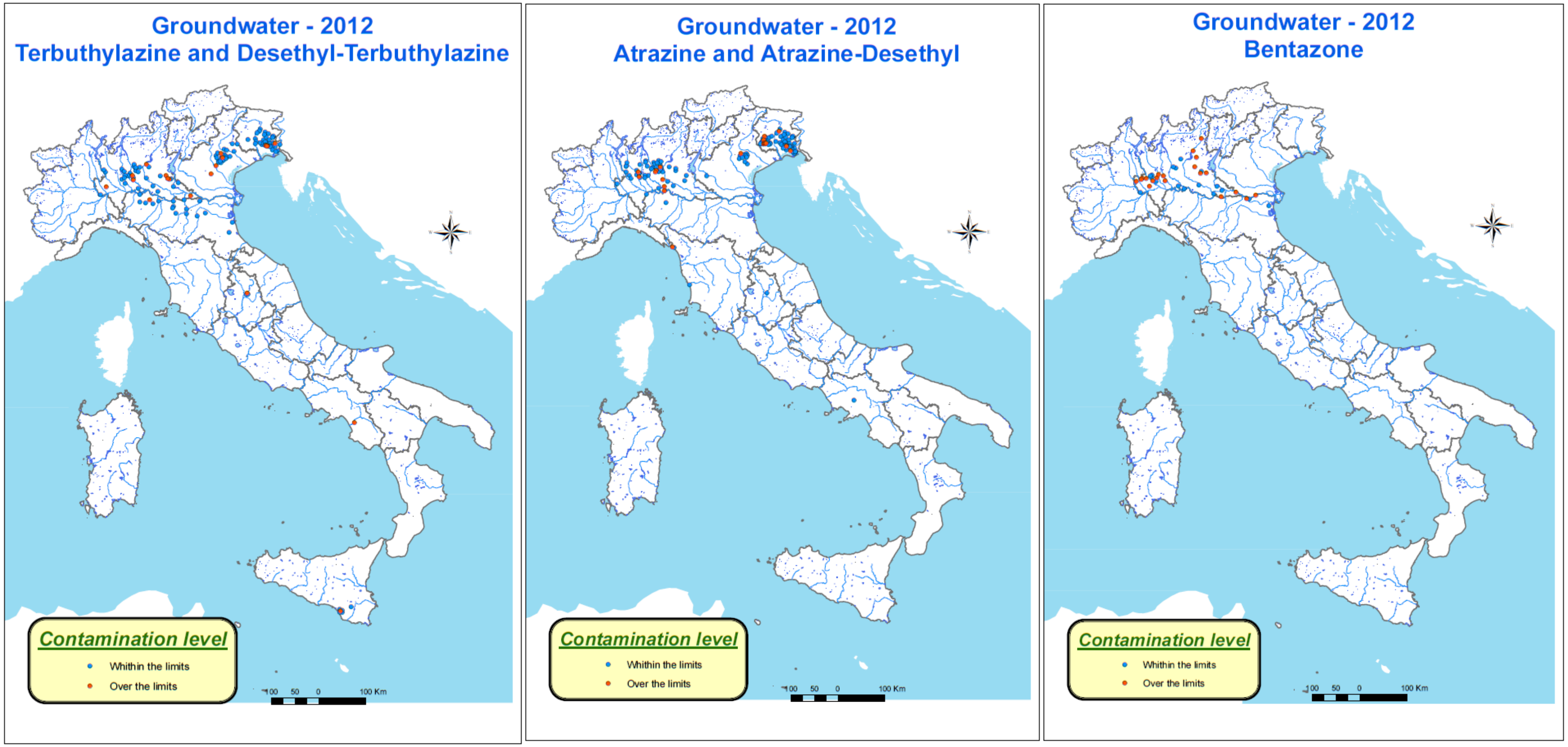


Fig. 7b *Contamination levels of specific pesticides in groundwater.*

3.2. Trend of the Contamination Analysis

The purpose is to follow how the pesticide occurrence in surface and groundwater is changed over the last decade. Compared to previous analyses, the monitoring efficiency is increased.
The results are used to develop indicators relating to the protection of the aquatic environment included in the National Action Plan (PAN), according to the Directive 2009/128/EC on the sustainable use of pesticides [6]. The developed indicator identifies the frequency of detection of active substances in waters at national level. Below, a first application of the indicators is reported (Fig. 8).

The overall trend of monitored substances up to year 2009 shows an increase in the detection frequency of pesticides, both in surface waters and in groundwater. This is correlated to the increase in effectiveness of the monitoring. The trend is an indication of a contamination not fully highlighted because of the inadequacy of this first stage of monitoring. Since 2010, the detection frequency decreases in both compartments. The interpretation of the data is not easy and should take into account, the difference in analytical detection limits through the country, the lack of harmonization of the monitoring programs, mainly in term of territorial coverage and number of monitored substances. It is not possible to assume that the trends indicates a real decrease in the occurrence of pesticides in water. More reasonably it can be concluded that, after an initial widening of investigation, an updating of monitor programs to take into account the new substances put on the market is missing.

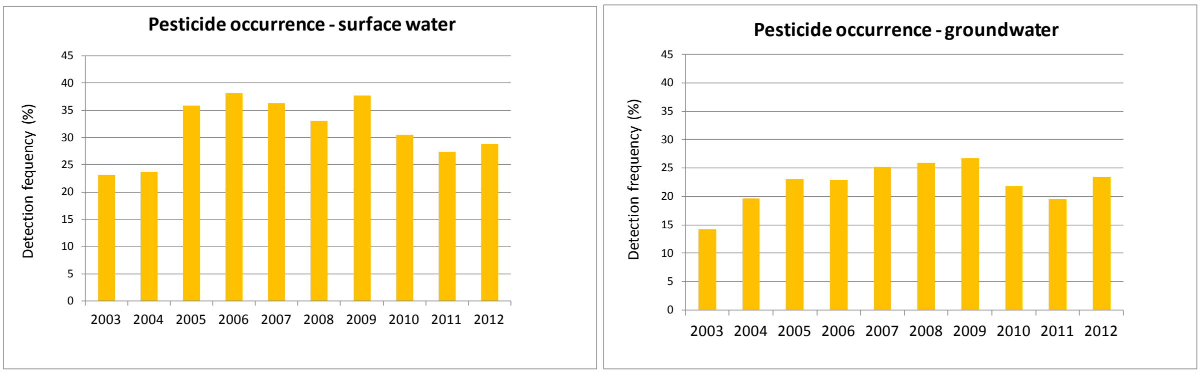


Fig. 8 *Trend of detection frequency in surface and ground water.*

The trend analysis on individual substances in some cases clearly highlights the decline of the detection frequencies, as a consequence of the cease of their use. In Italy atrazine has been banned in the late '80s due to a widespread contamination of groundwater in the Plain Po river basin. The monitoring results show that after 30 years the substance and its major metabolites are among the most frequently detected contaminants both in surface and groundwater (Fig. 9). In this case the frequency shows a decreasing trend almost asymptotic, indicating a long standing contamination due to its high environmental persistency in groundwater.

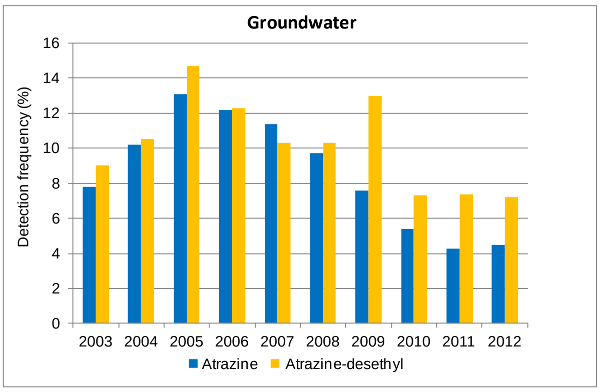


Fig. 9 *Trend of detection frequency of atrazine and atrazine-desethyl in groundwater.*

Simazine, another triazine herbicide, has been banned since 2005 in all European Union. In this case there is a fast decrease of the detection frequency right after the withdrawal, as showed in the figure 10. However the substance is still largely detected in water.

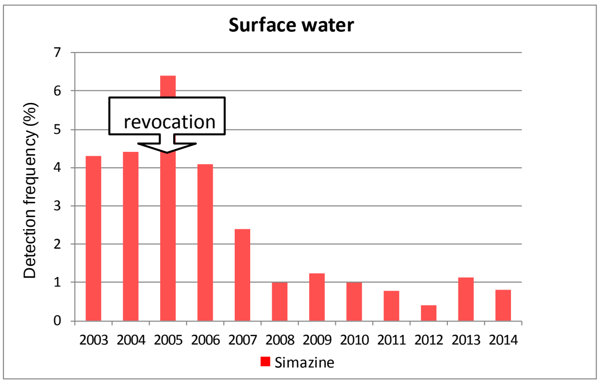


Fig. 10 *Trend of detection frequency of simazine in groundwater.*

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 [7].

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 is based on the effects of the single substance. The European Commission [8] 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 substances 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 [9]. 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.

The monitoring data reveal the presence of mixtures of pesticides in the samples. By analyzing the frequency of mixtures in the samples (Fig. 11), in surface water, it is detected the presence of at least two substances in 17.4% of the samples, with a maximum of 31 substances in a single sample and an average of 2.8 substances. In groundwater, in 13.2 % of the samples there are at least two substances, the maximum of substances in a sample is 36, and the average is 3.4 substances.

The risk assessment must, 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 cautionary about the risks of combined exposures.

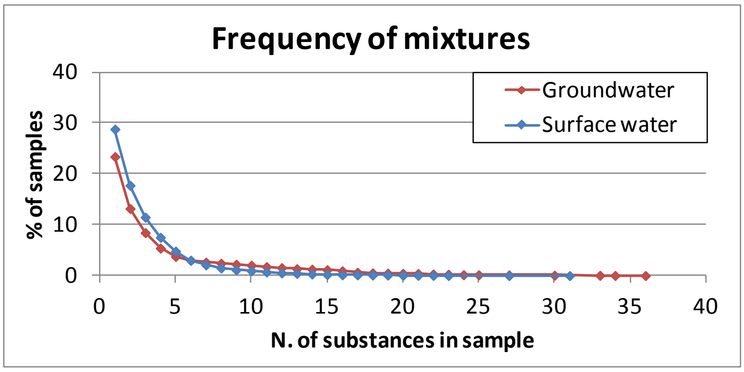


Fig. 11 *Mixtures of pesticides in the samples.*

The most common substances in mixtures (Fig. 12) are herbicides, with a significant presence in groundwater of fungicides and insecticides. This trend was observed in both years of monitoring, either in surface waters or in groundwater. 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, atrazine - desethyl) and metolachlor. It is also relevant the presence of the herbicides oxadiazon, glyphosate and its metabolite AMPA. In groundwater is important the presence of fungicides such as metalaxyl, oxadixil and pyrimethanil. The insecticide imidacloprid is found in both surface water and groundwater.

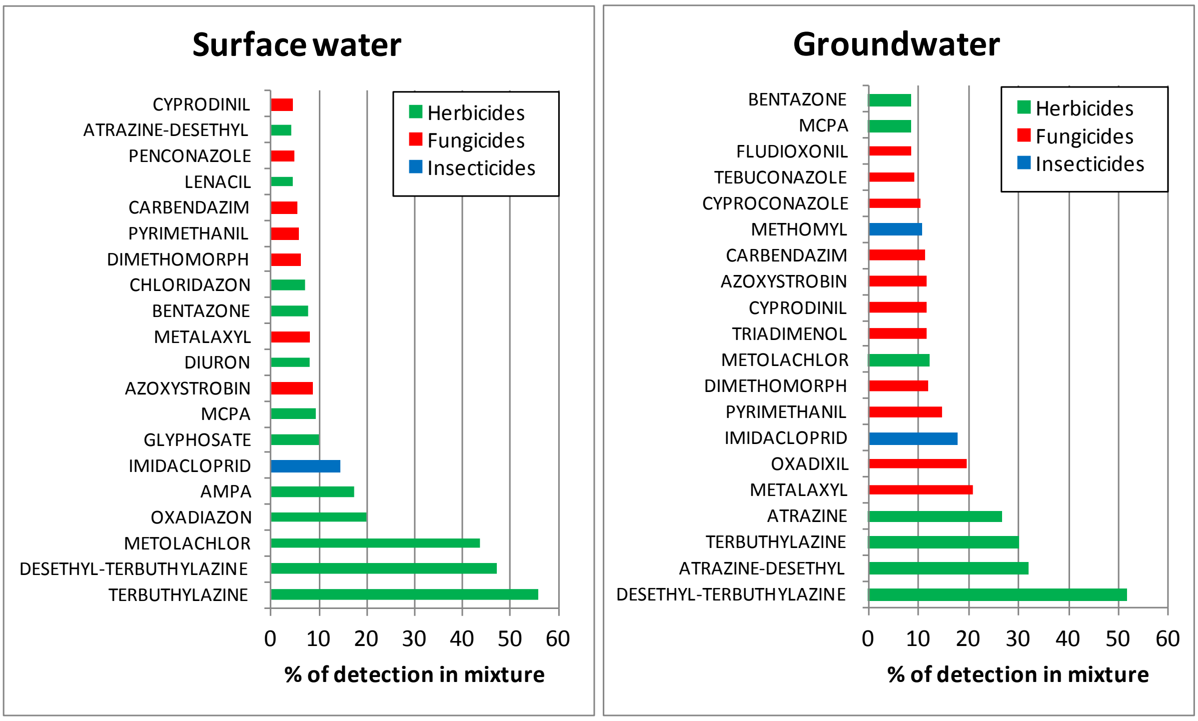


Fig. 12 *Main components of the mixtures.*

4. THE MONITORING SUMMARY TABLES

NATIONAL DATA SURFACE WATER 2012		LQ (µg/L)	DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES		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	TERBUTILAZINA	0,010	1069	458	42,8	6845	1049	15,3	265	3,9	<LQ	0,010	0,025	0,050	0,071	3,000
30125-63-4	TERBUTILAZINA-DESETIL	0,050	921	367	39,8	5954	912	15,3	96	1,6	<LQ	<LQ	<LQ	<LQ	0,050	1,140
51218-45-2	METOLACLOR	0,050	950	386	40,6	6136	837	13,6	215	3,5	<LQ	<LQ	<LQ	<LQ	0,070	64,000
1066-51-9	AMPA	0,100	274	199	72,6	1014	474	46,7	454	44,8	<LQ	<LQ	0,380	1,227	2,638	176,00
19666-30-9	OXADIAZON	0,010	787	131	16,6	5147	389	7,6	74	1,4	<LQ	0,010	0,025	0,025	0,050	2,740
105827-78-9	IMIDACLOPRID	0,010	189	103	54,5	1567	323	20,6	15	1,0	<LQ	<LQ	0,010	0,020	0,030	0,390
1071-83-6	GLIFOSATE	0,100	274	116	42,3	1014	186	18,3	177	17,5	<LQ	<LQ	<LQ	0,237	0,433	4,110
94-74-6	MCPA	0,050	562	109	19,4	2941	172	5,8	32	1,1	<LQ	<LQ	<LQ	<LQ	0,050	2,800
330-54-1	DIURON	0,010	683	80	11,7	4262	170	4,0	9	0,2	<LQ	<LQ	0,025	0,025	0,025	0,630
25057-89-0	BENTAZONE	0,010	663	78	11,8	3048	161	5,3	68	2,2	<LQ	0,025	0,025	0,050	0,050	1,700
57837-19-1	METALAXIL	0,010	538	75	13,9	4034	152	3,8	25	0,6	<LQ	0,010	0,013	0,025	0,025	10,000
131860-33-8	AZOSSISTROBINA	0,020	287	73	25,4	2315	148	6,4	31	1,3	<LQ	<LQ	0,020	0,025	0,025	1,400
1698-60-8	CLORIDAZON	0,010	270	51	18,9	1940	126	6,5	10	0,5	<LQ	<LQ	<LQ	0,010	0,015	3,100
110488-70-5	DIMETOMORF	0,010	346	60	17,3	2097	108	5,2	9	0,4	<LQ	0,010	0,025	0,050	0,050	0,310
53112-28-0	PIRIMETANIL	0,010	504	45	8,9	3764	102	2,7	9	0,2	<LQ	0,010	0,010	0,025	0,025	4,300
188425-85-6	BOSCALID	0,020	198	28	14,1	1709	100	5,9	5	0,3	<LQ	<LQ	0,025	0,025	0,025	0,240
6190-65-4	ATRAZINA-DESETIL	0,050	837	59	7,0	5569	96	1,7	6	0,1	<LQ	<LQ	<LQ	<LQ	0,050	3,230
10605-21-7	CARBENDAZIM	0,020	27	15	55,6	207	96	46,4	6	2,9	<LQ	0,020	0,030	0,044	0,067	0,320
66246-88-6	PENCONAZOLO	0,010	403	50	12,4	3019	86	2,8	4	0,1	<LQ	<LQ	0,025	0,025	0,025	0,230
886-50-0	TERBUTRYN	0,050	264	41	15,5	1522	82	5,4	5	0,3	<LQ	<LQ	<LQ	0,050	0,050	0,710
2164-08-1	LENACIL	0,010	328	45	13,7	2338	80	3,4	5	0,2	<LQ	<LQ	0,010	0,025	0,025	0,390
121552-61-2	CIPRODINIL	0,010	258	26	10,1	2184	74	3,4	4	0,2	<LQ	<LQ	0,025	0,025	0,025	0,490
94-75-7	2,4 D	0,010	501	45	9,0	2612	72	2,8	9	0,3	<LQ	0,010	0,025	0,025	0,050	3,200
140923-17-7	IPROVALICARB	0,050	191	28	14,7	1200	67	5,6	9	0,8	<LQ	<LQ	<LQ	<LQ	<LQ	2,000
2008-58-4	2,6-DICLOROBENZAMMIDE	0,020	335	31	9,3	2087	61	2,9	7	0,3	<LQ	<LQ	0,025	0,025	0,050	0,520
34256-82-1	ACETOCLOR	0,010	163	40	24,5	1369	59	4,3	9	0,7	<LQ	<LQ	<LQ	<LQ	<LQ	0,530
93-65-2	BH (R)-MECOPROP	0,010	291	35	12,0	1690	58	3,4	0	0,0	<LQ	<LQ	0,010	0,025	0,050	0,060
107534-96-3	TEBUCONAZOLO	0,050	216	29	13,4	1308	57	4,4	2	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	3,000
7085-19-0	MECOPROP	0,050	404	46	11,4	1947	54	2,8	4	0,2	<LQ	<LQ	<LQ	<LQ	0,050	0,210
21087-64-9	METRIBUZIN	0,010	595	38	6,4	4324	53	1,2	6	0,1	<LQ	0,010	0,025	0,025	0,025	0,920
1912-24-9	ATRAZINA	0,010	1100	37	3,4	7135	51	0,7	2	0,0	<LQ	0,010	0,025	0,025	0,050	0,550
41814-78-2	TRICICLAZOLO	0,020	26	22	84,6	136	50	36,8	28	20,6	<LQ	<LQ	0,060	0,695	1,305	4,600
26225-79-6	ETOFUMESATE	0,010	559	36	6,4	3825	49	1,3	6	0,2	<LQ	<LQ	0,010	0,025	0,025	1,300
23950-58-5	PROPIZAMIDE	0,010	474	35	7,4	3301	49	1,5	9	0,3	<LQ	<LQ	0,025	0,025	0,025	0,780
142459-58-3	FLUFENACET	0,010	270	36	13,3	1960	44	2,2	13	0,7	<LQ	<LQ	<LQ	0,010	0,015	2,200
60-51-5	DIMETOATO	0,010	637	36	5,7	4309	40	0,9	7	0,2	<LQ	<LQ	0,025	0,025	0,050	1,400
131341-86-1	FLUDIOXONIL	0,050	77	9	11,7	545	40	7,3	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,090
330-55-2	LINURON	0,010	812	28	3,4	5599	39	0,7	1	0,0	<LQ	<LQ	0,013	0,025	0,031	0,160
135410-20-7	ACETAMIPRID	0,010	188	15	8,0	1566	38	2,4	2	0,1	<LQ	<LQ	<LQ	0,010	0,010	0,300
500008-45-7	CLORANTRANILIPROLO	0,010	163	24	14,7	1369	38	2,8	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,110
1918-00-9	DICAMBA	0,010	147	28	19,0	657	36	5,5	3	0,5	<LQ	0,010	0,025	0,025	0,025	0,250
2921-88-2	CLORPIRIFOS	0,010	996	23	2,3	6690	32	0,5	4	0,1	<LQ	0,010	0,015	0,025	0,050	0,410
163515-14-8	DIMETENAMID-P	0,010	163	24	14,7	1369	32	2,3	2	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,180
2385-85-5	MIREX	0,020	67	17	25,4	343	32	9,3	1	0,3	<LQ	<LQ	0,025	0,025	0,040	0,190
41394-05-2	METAMITRON	0,010	272	27	9,9	1917	31	1,6	2	0,1	<LQ	<LQ	<LQ	0,010	0,015	0,210
114-26-1	PROPOXUR	0,020	26	10	38,5	198	31	15,7	0	0,0	<LQ	<LQ	<LQ	0,020	0,020	0,060
40487-42-1	PENDIMETALIN	0,010	796	24	3,0	5311	30	0,6	6	0,1	<LQ	0,010	0,025	0,025	0,025	0,770
120-36-5	DICLORPROP	0,020	42	11	26,2	259	29	11,2	0	0,0	<LQ	<LQ	0,025	0,025	0,025	0,050
122-34-9	SIMAZINA	0,010	1115	24	2,2	7290	29	0,4	3	0,0	<LQ	0,010	0,025	0,025	0,050	0,190
77732-09-3	OXADIXIL	0,005	202	16	7,9	1180	29	2,5	1	0,1	<LQ	0,013	0,025	0,025	0,050	0,230
608-73-1	HEXACHLOROCYCLOHEXANE	0,010	372	15	4,0	2006	27	1,3	7	0,3	<LQ	<LQ	<LQ	0,025	0,050	0,210
118-74-1	HEXACHLOROBENZENE	0,010	399	13	3,3	2366	25	1,1	0	0,0	<LQ	<LQ	0,025*	1,250*	1,250*	0,020
23103-98-2	PIRIMICARB	0,010	250	17	6,8	2017	25	1,2	6	0,3	<LQ	<LQ	0,010	0,025	0,025	1,500
83055-99-6	BENSULFURON-METILE	0,010	189	17	9,0	1564	23	1,5	2	0,1	<LQ	<LQ	<LQ	0,010	0,010	0,260
126833-17-8	FENHEXAMID	0,005	180	11	6,1	1021	23	2,3	4	0,4	<LQ	0,010	0,025	0,025	0,025	48,800
101205-02-1	CICLOXIDIM	0,020	39	11	28,2	236	22	9,3	3	1,3	<LQ	<LQ	<LQ	<LQ	0,030	0,170
87674-68-8	DIMETENAMIDE	0,020	176	13	7,4	1311	19	1,4	7	0,5	<LQ	<LQ	<LQ	<LQ	0,025	0,560
118134-30-8	SPIROXAMINA	0,005	164	11	6,7	960	19	2,0	0	0,0	<LQ	0,010	0,050*	0,050*	0,050*	0,040
1582-09-8	TRIFLURALIN	0,010	834	10	1,2	5210	18	0,3	1	0,0	<LQ	<LQ	0,010	0,025	0,050	0,110
24579-73-5	PROPAMOCARB	0,020	26	9	34,6	198	18	9,1	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,040
5598-13-0	CLORPIRIFOS-METILE	0,010	638	16	2,5	4171	17	0,4	1	0,0	<LQ	<LQ	0,025	0,025	0,025	0,370
80844-07-1	ETOFENPROX	0,020	40	12	30,0	257	17	6,6	2	0,8	<LQ	<LQ	<LQ	<LQ	0,020	0,170
55219-65-3	TRIADIMENOL	0,050	123	9	7,3	932	17	1,8	0	0,0	<LQ	<LQ	<LQ	<LQ	0,050	0,050
15972-60-8	ALACHLOR	0,010	1099	15	1,4	7022	16	0,2	2	0,0	<LQ	0,010	0,025	0,025	0,050	0,110
87-68-3	ESACLOROBUTADIENE	0,100	430	10	2,3	2870	16	0,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050

NATIONAL DATA SURFACE WATER 2012			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
63-25-2	CARBARIL	0,050	62	7	11,3	485	15	3,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,100
22224-92-6	FENAMIFOS	0,020	30	5	16,7	238	15	6,3	2	0,8	<LQ	<LQ	<LQ	<LQ	0,026	0,370
94-82-6	2,4-DB	0,020	25	11	44,0	185	15	8,1	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,050
116-06-3	ALDICARB	0,020	27	9	33,3	211	14	6,6	1	0,5	<LQ	<LQ	<LQ	0,020	0,025	0,120
67129-08-2	METAZACLOR	0,010	232	11	4,7	1510	13	0,9	2	0,1	<LQ	<LQ	<LQ	<LQ	0,025	0,510
141112-29-0	ISOXAFLUTOLE	0,020	39	13	33,3	236	13	5,5	4	1,7	<LQ	<LQ	<LQ	<LQ	0,020	0,190
1007-28-9	ATRAZINA-DESISOPROPIL	0,050	471	9	1,9	3248	12	0,4	5	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	6,400
101200-48-0	TRIBENURON-METILE	0,020	16	5	31,3	161	12	7,5	0	0,0	<LQ	<LQ	<LQ	<LQ	0,020	0,030
107-06-2	1,2-DICLOROETANO	0,100	367	10	2,7	2763	11	0,4	8	0,3	<LQ	<LQ	0,250	0,500	0,500	1,000
62-73-7	DICLORVOS	0,010	352	10	2,8	2412	10	0,4	2	0,1	<LQ	<LQ	<LQ	0,010	0,015	0,350
93-76-5	2,4,5-T	0,010	247	9	3,6	1442	10	0,7	0	0,0	<LQ	<LQ	0,010	0,050*	0,050*	0,030
69335-91-7	FLUAZIFOP	0,020	25	7	28,0	197	10	5,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,060
333-41-5	DIAZINON	0,010	325	8	2,5	2527	9	0,4	3	0,1	<LQ	<LQ	0,010	0,025	0,025	0,490
1563-66-2	CARBOFURAN	0,010	323	6	1,9	2608	8	0,3	2	0,1	<LQ	<LQ	0,010	0,010	0,010	0,200
78587-05-0	EXITIAZOX	0,020	25	4	16,0	197	8	4,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
60207-90-1	PROPICONAZOLO	0,020	225	7	3,1	1854	8	0,4	1	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,110
153719-23-4	TIAMETOXAM	0,020	25	6	24,0	197	8	4,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
309-00-2	ALDRIN	0,010	545	7	1,3	3320	7	0,2	0	0,0	<LQ	<LQ	0,015*	0,050*	0,050*	0,009
95-76-1	3,4-DICLOROANILINA	0,010	276	7	2,5	2048	7	0,3	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,050
57966-95-7	CIMOXANIL	0,020	25	7	28,0	197	7	3,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,060
105512-06-9	CLODINAFOP-PROPARGIL	0,020	25	5	20,0	197	7	3,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,070
120162-55-2	AZIMSULFURON	0,020	27	5	18,5	195	7	3,6	1	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	0,200
122-88-3	4-CPA	0,020	24	6	25,0	182	7	3,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
32809-16-8	PROCIMIDONE	0,010	581	7	1,2	4318	7	0,2	0	0,0	<LQ	0,010	0,013	0,025	0,025	0,060
34123-59-6	ISOPROTURON	0,010	561	5	0,9	3716	7	0,2	0	0,0	<LQ	<LQ	<LQ	0,010	0,025	0,040
16752-77-5	METOMIL	0,020	28	6	21,4	212	7	3,3	0	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,030
1746-81-2	MONOLINURON	0,020	25	7	28,0	197	7	3,6	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
15545-48-9	CLOROTOLURON	0,010	289	5	1,7	2011	6	0,3	0	0,0	<LQ	<LQ	<LQ	0,010	0,010	0,020
55179-31-2	BITERTANOLO	0,020	25	5	20,0	197	6	3,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
74-97-5	BROMOCLOROMETANO	0,050	13	4	30,8	85	6	7,1	3	3,5	<LQ	<LQ	0,050	0,050	0,092	11,300
121-75-5	MALATION	0,010	879	6	0,7	5959	6	0,1	2	0,0	<LQ	<LQ	0,025	0,025	0,025	0,110
58-89-9	HCH, gamma	0,010	579	5	0,9	3850	6	0,2	2	0,1	<LQ	<LQ	0,025	0,025	0,050	0,220
10265-92-6	METAMIDOFOS	0,100	247	5	2,0	1437	6	0,4	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,070
42874-03-3	OXIFLUORFEN	0,005	164	6	3,7	960	6	0,6	0	0,0	<LQ	0,010	0,025	0,025	0,025	0,050
111988-49-9	TIACLOPRID	0,020	25	5	20,0	197	6	3,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
51-03-6	PIPERONIL-BUTOSSIDO	0,050	55	6	10,9	190	6	3,2	1	0,5	<LQ	<LQ	<LQ	<LQ	<LQ	0,200
51235-04-2	ESAZINONE	0,020	158	4	2,5	1104	5	0,5	0	0,0	<LQ	<LQ	<LQ	0,025*	0,025*	0,020
1024-57-3	EPTACLORO-EPOSSIDO	0,030	161	5	3,1	1083	5	0,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,060
56-23-5	TETRACLORURO DI CARBONIO	0,100	329	2	0,6	2163	5	0,2	4	0,2	<LQ	<LQ	<LQ	0,500*	0,500*	0,200
35554-44-0	IMAZALIL	0,020	25	4	16,0	197	5	2,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
731-27-1	TOLILFLUANIDE	0,020	25	4	16,0	197	5	2,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
74070-46-5	ACLONIFEN	0,010	163	3	1,8	1369	4	0,3	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,070
41483-43-6	BUPIRIMATE	0,050	77	3	3,9	545	4	0,7	2	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	0,160
314-40-9	BROMACILE	0,050	99	4	4,0	471	4	0,8	1	0,2	<LQ	<LQ	<LQ	0,050	0,050	0,270
919-86-8	DEMETON-S-METILE	0,020	25	4	16,0	197	4	2,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
17040-19-6	DEMETON-S-METILE-SOLFONE	0,020	16	4	25,0	161	4	2,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
2212-67-1	MOLINATE	0,010	428	2	0,5	2873	4	0,1	1	0,0	<LQ	<LQ	0,010	0,025	0,025	0,140

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 2012			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	TERBUTILAZINA-DESETIL	0,020	1779	283	15,9	3651	412	11,3	35	1,0	<LQ	<LQ	0,025	0,025	0,040	0,860
6190-65-4	ATRAZINA-DESETIL	0,020	1814	200	11,0	3709	267	7,2	17	0,5	<LQ	<LQ	0,020	0,025	0,025	0,370
5915-41-3	TERBUTILAZINA	0,020	1835	146	8,0	3858	194	5,0	13	0,3	<LQ	<LQ	<LQ	0,025	0,025	2,570
1912-24-9	ATRAZINA	0,020	1835	134	7,3	3858	173	4,5	15	0,4	<LQ	<LQ	<LQ	0,025	0,025	0,520
57837-19-1	METALAXIL	0,020	1186	42	3,5	2482	128	5,2	77	3,1	<LQ	<LQ	<LQ	0,025	0,025	9,800
77732-09-3	OXADIXIL	0,025	459	45	9,8	1233	128	10,4	47	3,8	<LQ	<LQ	<LQ	0,025	0,080	4,330
105827-78-9	IMIDACLOPRID	0,010	419	49	11,7	871	114	13,1	48	5,5	<LQ	<LQ	0,010	0,030	0,110	1,300
25057-89-0	BENTAZONE	0,050	1000	79	7,9	1750	106	6,1	46	2,6	<LQ	<LQ	<LQ	0,050	0,050	37,400
51218-45-2	METOLACLOR	0,020	1881	83	4,4	3953	100	2,5	20	0,5	<LQ	<LQ	<LQ	0,025	0,025	7,600
53112-28-0	PIRIMETANIL	0,020	975	36	3,7	1921	90	4,7	9	0,5	<LQ	<LQ	<LQ	0,025	0,025	30,000
121552-61-2	CIPRODINIL	0,010	370	44	11,9	766	77	10,1	3	0,4	<LQ	<LQ	0,010	0,025	0,030	0,330
2008-58-4	2,6-DICLOROBENZAMMIDE	0,020	954	60	6,3	1840	75	4,1	18	1,0	<LQ	<LQ	0,025	0,050	0,050	1,200
110488-70-5	DIMETOMORF	0,020	585	35	6,0	1150	73	6,3	5	0,4	<LQ	<LQ	<LQ	0,050	0,050	0,400
55219-65-3	TRIADIMENOL	0,050	337	33	9,8	1011	73	7,2	9	0,9	<LQ	<LQ	<LQ	<LQ	<LQ	2,800
131860-33-8	AZOSSISTROBINA	0,020	589	32	5,4	1143	71	6,2	19	1,7	<LQ	<LQ	<LQ	<LQ	0,025	1,917
10605-21-7	CARBENDAZIM	0,020	79	40	50,6	292	71	24,3	1	0,3	<LQ	<LQ	0,020	0,030	0,040	8,800
16752-77-5	METOMIL	0,020	174	30	17,2	488	66	13,5	17	3,5	<LQ	<LQ	<LQ	0,030	0,076	1,043
94361-06-5	CIPROCONAZOLO	0,020	91	27	29,7	296	63	21,3	10	3,4	<LQ	<LQ	0,020	0,030	0,080	0,710
19666-30-9	OXADIAZON	0,020	1229	47	3,8	2682	59	2,2	29	1,1	<LQ	<LQ	<LQ	<LQ	0,025	3,240
107534-96-3	TEBUCONAZOLO	0,005	367	30	8,2	822	56	6,8	7	0,9	<LQ	0,010	0,010	0,025	0,030	0,320
94-74-6	MCPA	0,050	723	40	5,5	1339	55	4,1	2	0,1	<LQ	<LQ	<LQ	<LQ	0,050	0,390
131341-86-1	FLUDIOXONIL	0,020	188	31	16,5	477	52	10,9	4	0,8	<LQ	<LQ	<LQ	0,025	0,030	0,300
122-34-9	SIMAZINA	0,020	1834	42	2,3	3857	52	1,3	5	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,250
94-75-7	2,4 D	0,050	645	38	5,9	1217	46	3,8	2	0,2	<LQ	<LQ	<LQ	<LQ	0,050	0,810
66246-88-6	PENCONAZOLO	0,010	712	27	3,8	1335	46	3,4	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,090
153719-23-4	TIAMETOXAM	0,020	91	24	26,4	296	41	13,9	3	1,0	<LQ	<LQ	<LQ	0,028	0,040	0,400
330-55-2	LINURON	0,020	1795	29	1,6	3755	37	1,0	4	0,1	<LQ	<LQ	0,025	0,025	0,030	1,700
114-26-1	PROPOXUR	0,020	76	25	32,9	266	32	12,0	1	0,4	<LQ	<LQ	<LQ	0,020	0,028	1,600
330-54-1	DIURON	0,020	735	21	2,9	1400	29	2,1	5	0,4	<LQ	<LQ	<LQ	<LQ	0,025	0,430
93-65-2	BH (R)-MECOPROP	0,020	278	23	8,3	584	28	4,8	0	0,0	<LQ	<LQ	0,025	0,025	0,025	0,050
120-36-5	DICLORPROP	0,020	127	24	18,9	367	26	7,1	0	0,0	<LQ	<LQ	0,025	0,025	0,025	0,050
1007-28-9	ATRAZINA-DESISOPROPIL	0,020	1044	22	2,1	1846	24	1,3	4	0,2	<LQ	<LQ	0,025	0,025	0,025	0,240
188425-85-6	BOSCALID	0,020	484	13	2,7	1090	24	2,2	1	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,600
23103-98-2	PIRIMICARB	0,025	564	19	3,4	1278	24	1,9	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,053
116-06-3	ALDICARB	0,020	82	22	26,8	307	23	7,5	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,090
78587-05-0	EXITIAZOX	0,020	76	19	25,0	266	23	8,6	0	0,0	<LQ	<LQ	<LQ	<LQ	0,030	0,090
24579-73-5	PROPAMOCARB	0,020	91	15	16,5	296	23	7,8	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,090
80844-07-1	ETOFENPROX	0,020	111	16	14,4	325	22	6,8	1	0,3	<LQ	<LQ	<LQ	0,025	0,025	0,110
2921-88-2	CLORPIRIFOS	0,020	1428	16	1,1	2957	21	0,7	4	0,1	<LQ	<LQ	<LQ	<LQ	0,025	19,640
23135-22-0	OXAMIL	0,020	91	15	16,5	296	21	7,1	1	0,3	<LQ	<LQ	<LQ	0,025	0,025	0,330
1918-00-9	DICAMBA	0,050	542	19	3,5	1014	20	2,0	5	0,5	<LQ	<LQ	<LQ	<LQ	0,050	0,270
22224-92-6	FENAMIFOS	0,020	101	14	13,9	376	20	5,3	5	1,3	<LQ	<LQ	<LQ	0,025	0,025	8,390
120928-09-8	FENAZAQUIN	0,020	108	16	14,8	342	20	5,8	3	0,9	<LQ	<LQ	<LQ	0,025	0,025	0,730
60207-90-1	PROPICONAZOLO	0,020	444	15	3,4	814	20	2,5	1	0,1	<LQ	<LQ	<LQ	<LQ	0,025	0,150
135410-20-7	ACETAMIPRID	0,010	302	16	5,3	619	19	3,1	0	0,0	<LQ	<LQ	0,010	0,010	0,010	0,060
731-27-1	TOLILFLUANIDE	0,020	128	15	11,7	371	18	4,9	1	0,3	<LQ	<LQ	<LQ	0,025	0,025	0,130
63-25-2	CARBARIL	0,020	76	16	21,1	266	17	6,4	1	0,4	<LQ	<LQ	<LQ	<LQ	0,020	0,600
101200-48-0	TRIBENURON-METILE	0,020	101	17	16,8	336	17	5,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
87674-68-8	DIMETENAMIDE	0,020	473	14	3,0	929	16	1,7	9	1,0	<LQ	<LQ	<LQ	0,025	0,025	1,590
2164-08-1	LENACIL	0,010	576	12	2,1	1172	16	1,4	0	0,0	<LQ	<LQ	0,010	0,025	0,025	0,060
40487-42-1	PENDIMETALIN	0,020	1392	10	0,7	2992	15	0,5	7	0,2	<LQ	<LQ	<LQ	0,025	0,025	0,682
111988-49-9	TIACLOPRID	0,020	168	14	8,3	448	14	3,1	0	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,050
1698-60-8	CLORIDAZON	0,010	481	10	2,1	717	13	1,8	0	0,0	<LQ	<LQ	0,010	0,015	0,015	0,030
126833-17-8	FENHEXAMID	0,020	419	10	2,4	904	13	1,4	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,060
23950-58-5	PROPIZAMIDE	0,025	897	11	1,2	1839	13	0,7	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,090
1646-88-4	ALDICARB-SULFONE	0,020	76	12	15,8	266	12	4,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,030
105512-06-9	CLODINAFOP-PROPARGIL	0,020	76	10	13,2	266	12	4,5	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,060
35554-44-0	IMAZALIL	0,020	91	12	13,2	296	12	4,1	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,090
7287-19-6	PROMETRINA	0,025	350	10	2,9	964	12	1,2	1	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,150
314-40-9	BROMACILE	0,100	438	9	2,1	867	11	1,3	6	0,7	<LQ	<LQ	<LQ	<LQ	<LQ	0,160
1646-87-3	ALDICARB-SULFOSSIDO	0,020	76	10	13,2	266	11	4,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,080
51235-04-2	ESAZINONE	0,020	467	10	2,1	911	11	1,2	2	0,2	<LQ	<LQ	0,025	0,025	0,025	0,160
122-88-3	4-CPA	0,020	76	9	11,8	260	10	3,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050
2212-67-1	MOLINATE	0,020	997	8	0,8	2037	10	0,5	5	0,2	<LQ	<LQ	<LQ	<LQ	0,025	0,510
1031-07-8	ENDOSULFAN-SOLFATO	0,020	628	5	0,8	1563	10	0,6	9	0,6	<LQ	<LQ	<LQ	<LQ	0,025	4,370
1746-81-2	MONOLINURON	0,020	91	10	11,0	296	10	3,4	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,060
69806-50-4	FLUAZIFOP-BUTYL	0,020	76	8	10,5	266	10	3,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,080
81334-34-1	IMAZAPIR	0,020	76	10	13,2	266	10	3,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,050

NATIONAL DATA GROUNDWATER 2012		LQ (µg/L)	DETECTION FREQUENCY								PERCENTILE CONCENTRATION IN SAMPLES (µg/L)					
CAS	SUBSTANCES		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
32809-16-8	PROCIMIDONE	0,020	1243	8	0,6	2667	10	0,4	3	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,450
1563-66-2	CARBOFURAN	0,020	776	9	1,2	1766	9	0,5	2	0,1	<LQ	<LQ	<LQ	<LQ	<LQ	0,222
140923-17-7	IPROVALICARB	0,005	342	7	2,0	752	8	1,1	0	0,0	<LQ	0,010	0,010	0,025	0,025	0,060
69335-91-7	FLUAZIFOP	0,020	76	7	9,2	266	8	3,0	1	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	0,500
118134-30-8	SPIROXAMINA	0,005	377	8	2,1	831	8	1,0	0	0,0	<LQ	0,005	0,010	0,050	0,050	0,050
41814-78-2	TRICICLAZOLO	0,020	86	6	7,0	131	8	6,1	1	0,8	<LQ	<LQ	<LQ	<LQ	0,025	0,120
5598-13-0	CLORPIRIFOS-METILE	0,010	971	4	0,4	2029	7	0,3	3	0,1	<LQ	0,010	0,013	0,025	0,025	1,010
333-41-5	DIAZINON	0,010	487	7	1,4	985	7	0,7	0	0,0	<LQ	<LQ	0,010	0,010	0,025	0,100
142-28-9	1,3-DICLOROPROPANO	0,100	76	3	3,9	266	7	2,6	7	2,6	<LQ	<LQ	<LQ	<LQ	<LQ	0,400
111991-09-4	NICOSULFURON	0,010	25	4	16,0	70	7	10,0	0	0,0	<LQ	<LQ	<LQ	<LQ	0,016	0,020
1066-51-9	AMPA	0,100	158	6	3,8	311	6	1,9	5	1,6	<LQ	<LQ	<LQ	<LQ	<LQ	1,300
142459-58-3	FLUFENACET	0,010	482	6	1,2	719	6	0,8	0	0,0	<LQ	<LQ	0,010	0,015	0,015	0,060
57646-30-7	FURALAXIL	0,020	93	2	2,2	313	6	1,9	3	1,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,770
15972-60-8	ALACHLOR	0,020	1815	5	0,3	3830	5	0,1	0	0,0	<LQ	<LQ	0,025	0,025	0,025	0,080
34256-82-1	ACETOCLOR	0,010	251	4	1,6	423	5	1,2	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,060
95465-99-9	CADUSAFOS	0,020	93	3	3,2	312	5	1,6	3	1,0	<LQ	<LQ	<LQ	<LQ	<LQ	6,760
919-86-8	DEMETON-S-METILE	0,020	76	5	6,6	266	5	1,9	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
94-82-6	2,4-DB	0,020	76	4	5,3	259	5	1,9	1	0,4	<LQ	<LQ	<LQ	<LQ	<LQ	7,600
99-30-9	DICLORAN	0,020	890	4	0,5	1755	4	0,2	0	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,100
69327-76-0	BUPROFEZIN	0,010	319	4	1,3	666	4	0,6	1	0,2	<LQ	<LQ	0,010	0,010	0,010	1,340
101205-02-1	CICLOXIDIM	0,020	151	4	2,6	233	4	1,7	3	1,3	<LQ	<LQ	<LQ	0,025	0,025	0,090
319-85-7	HCH, beta	0,050	848	3	0,4	2149	4	0,2	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,045
41394-05-2	METAMITRON	0,010	487	4	0,8	756	4	0,5	0	0,0	<LQ	<LQ	0,010	0,015	0,015	0,010
7786-34-7	MEVINPHOS	0,020	144	4	2,8	414	4	1,0	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,020
309-00-2	ALDRIN	0,010	1067	2	0,2	2485	3	0,1	1	0,0	<LQ	<LQ	<LQ	0,010	0,025	0,070
	Σ DDT	0,100	523	3	0,6	1034	3	0,3	2	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	0,105
470-90-6	CLORFENVINFOS	0,020	486	3	0,6	999	3	0,3	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,055
500008-45-7	CLORANTRANILIPROLO	0,010	226	3	1,3	353	3	0,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,020
57966-95-7	CIMOXANIL	0,020	91	3	3,3	296	3	1,0	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,025
66215-27-8	CIROMAZINA	0,020	76	3	4,0	266	3	1,1	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,025
93-76-5	2,4,5-T	0,100	128	3	2,3	212	3	1,4	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,020
36734-19-7	IPRODIONE	0,020	843	1	0,1	1692	3	0,2	3	0,2	<LQ	<LQ	<LQ	0,025	0,025	0,135
13194-48-4	ETOPROFOS	0,020	295	1	0,3	614	3	0,5	2	0,3	<LQ	<LQ	<LQ	0,025	0,025	0,390
2032-65-7	METIOCARB	0,020	168	3	1,8	448	3	0,7	0	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,045
1897-45-6	CLOROTALONIL	0,020	908	1	0,1	2006	2	0,1	1	0,0	<LQ	<LQ	<LQ	<LQ	0,025	0,053
71626-11-4	BENALAXIL	0,025	161	2	1,2	545	2	0,4	1	0,2	<LQ	<LQ	<LQ	<LQ	<LQ	0,091
17040-19-6	DEMETON-S-METILE-SOLFONE	0,020	91	2	2,2	296	2	0,7	0	0,0	<LQ	<LQ	<LQ	0,025	0,025	0,090
56-72-4	CUMAFOS	0,020	76	2	2,6	266	2	0,8	0	0,0	<LQ	<LQ	<LQ	<LQ	<LQ	0,040
542-75-6	1,3-DICLOROPROPENE	0,100	54	1	1,9	192	2	1,0	2	1,0	<LQ	<LQ	<LQ	<LQ	<LQ	1,900
120162-55-2	AZIMSULFURON	0,020	107	2	1,9	173	2	1,2	1	0,6	<LQ	<LQ	<LQ	<LQ	<LQ	0,120
121-75-5	MALATION	0,020	1239	1	0,1	2347	2	0,1	2	0,1	<LQ	<LQ	<LQ	0,025	0,025	0,300

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

An increase in the coverage and representativeness of surveys occurred over the decade 2003-2012. Nevertheless, a difference in the controls between north and south-central Italy still remains. The monitoring in south-central Italy is less representative, both in terms of the network and number of monitored substance. On the other hand, an overall update of monitoring programs is necessary in order to take into account the new substances placed on the market. Even if the overall monitoring effort is huge in term of the number of searched substances, most of the chemicals recently introduced on the market for agricultural uses are not included in the monitoring programs. About 50 of these are classified as hazardous, in particular are hazardous to aquatic environment.

Pesticide pollution is widespread concerning about 45,5% of the sampling sites in surface water and 31 % of groundwater. In many cases the contamination is over the regulatory threshold values.
175 pesticides are detected in surface and groundwater in 2012. Herbicides are the most frequent substances, mainly because of the timing and intensity of their use in relation to the seasonal rainfall in early spring.

Compared to the past is increased, however, significantly also the presence of fungicides and insecticides. It is important to note the diffuse occurrence of imidacloprid in water, a systemic insecticide representing a concern in particular for bees. In particular, in Europe the uses as seed treatment and soil treatment of plant protection products containing imidacloprid have been prohibited according to Regulation (EC) No 1107/2009 [10].

The pollution is more widespread in the Po-Venetian plain. This depends not only from the intense use in agriculture and hydrology of the area, but also by the fact that the investigations in the northern regions are more focused and effective.

It is important to highlight the presence of mixtures of different substances, up to 36 different chemicals in a sample. Humans and other organisms are therefore exposed to a chemical "cocktail", which effects are not adequately known, for the absence of experimental data. As acknowledged by the scientific and regulatory bodies, the risk from exposure to mixtures of substances is underestimated in the authorization process, which assess individual substances and do not take into account the cumulative effects.

In Italy sales of pesticides are remarkably decreasing over the past decade (about 20 %). However, the monitoring do not reflect this trend, and continues to show a widespread occurrence of pesticides in water. The most critical issue is probably the persistence of certain substances, which along with very slow hydrological dynamics (especially groundwater) makes the environmental contamination almost irreversible.

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[3] 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.

[4] 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.

[5] 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.

[6] 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.

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[8] European Commission (2012). Final opinion on the Toxicity and Assessment of Chemical Mixtures, adopted by the SCHER on 22 November 2011, by the SCENIHR on 30 November 2011 and by the SCCS on 14 December 2011.

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[10] 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.

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