Ann Ist Super Sanità 2010 | Vol. 46, No. 3: 309-316
DOI: 10.4415/ANN_10_03_15

Pesticides and their metabolites in selected Italian groundwater and surface water used for drinking

Luca Fava[a], Maria Antonietta Orrù[a], Simona Scardala[a], Elena Alonzo[b], Maristella Fardella[b], Caterina Strumia[c], Angiolo Martinelli[d], Sabrina Finocchiaro[e], Massimo Previtera[e], Alessandro Franchi[f], Piergiuseppe Calà[g], Mauro Dovis[h], Donatella Bartoli[i], Giuseppe Sartori[l], Lia Broglia[m] and Enzo Funari[a]

[a] Dipartimento di Ambiente e Connessa Prevenzione Primaria, Istituto Superiore di Sanità, Rome, Italy
[b] Servizio Igiene Alimenti e Nutrizione, SIAN AUSL 3-Catania, Catania, Italy
[c] Assessorato alla Sanità, Regione Piemonte, Turin, Italy
[d] Agenzia Regionale per la Protezione dell'Ambiente(ARPA) Umbria, Perugia, Italy
[e] ARPA DAP Catania, Catania, Italy
[f] ARPA Toscana, Florence, Italy
[g] Coordinamento Sanità, Regione Toscana, Florence, Italy
[h] ARPA Piemonte, Vercelli, Italy
[i] ARPA Umbria, Perugia, Italy
[l] ARPA Veneto, Vicenza, Italy
[m] ARPA Lombardia, Pavia, Italy

Summary. The control of groundwater and surface water quality in relation to the presence of pesticides and their metabolites is a rather complicated task. National and local authorities with the responsibility to guarantee an adequate quality of water cannot rely on international guidelines for monitoring activities. In a national project, forty-three pesticides and pesticide metabolites were selected on the basis of sale, monitoring and physical-chemical data, and investigated from some of the main Italian agricultural areas, susceptible to pesticide contamination. Twelve compounds were found in the tested water samples at levels exceeding the 0.1 µg/L European Union (EU) limit for drinking water (European Directive 98/83/EC). Maximum levels up to 0.62 were determined. Several water samples were characterized by the simultaneous occurrence of pesticides and their metabolites (up to ten). In some samples, the total concentration of pesticides and their metabolites was higher than the EU limit of 0.5 µg/L. Total triazine concentrations up to 1.02 µg/L were found. In all the cases the highest concentrations were well below the respective guideline values defined by the World Health Organization (WHO) for drinking water quality.

Key words: pesticides, pesticide metabolites, ground water quality.

Riassunto *(Pesticidi e loro metaboliti in campioni di acque sotterranee e superficiali italiane utilizzate a scopo potabile)*. Il controllo della qualità delle acque in relazione alla presenza di pesticidi e loro metaboliti è un argomento piuttosto complicato. Le autorità nazionali e locali hanno la responsabilità di garantire il controllo delle acque destinate al consumo umano che devono far riferimento alle linee guida internazionali in materia di attività di monitoraggio. In un progetto nazionale, 43 pesticidi e loro metaboliti sono stati selezionati sulla base di dati di vendita, monitoraggio e caratteristiche fisico-chimiche, e successivamente ricercati in alcune delle principali aree ad elevata vocazione agricola suscettibili di possibile contaminazione. Dodici sostanze sono state ritrovate a livelli superiori al limite di 0,1 µg/L stabilito dall'Unione Europea (EU), fino ad un massimo di 0,62 µg/L (Direttiva Europea 98/83/EC). Numerosi campioni d'acqua sono risultati caratterizzati dalla simultanea presenza di diversi pesticidi e loro metaboliti, fino a 10 per campione. In alcuni casi la concentrazione totale di pesticidi è risultata superiore al limite definito dall'EU di 0,5 µg/L. Le triazine sono state determinate fino ad una concentrazione totale di 1,02 µg/L. In tutti i campioni analizzati la concentrazione dei pesticidi trovati era sempre inferiore ai valori guida definiti dall'Organizzazione Mondiale della Sanità (OMS) per la qualità delle acque destinate al consumo umano.

Parole chiave: pesticidi, metaboliti, qualità delle acque.

Address for correspondence: Luca Fava, Dipartimento di Ambiente e Connessa Prevenzione Primaria, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy. E-mail: luca.fava@iss.it.

INTRODUCTION

Ground and surface waters may be exposed to many contaminants, pesticides being among the most important as a consequence of their wide use.

Once in soil, pesticides can degrade, adsorb on organic matter, leach into ground water, be transported to surface water through run off or drainage, their environmental fate being controlled by their physico-chemical properties [1-3]. Beyond their intrinsic properties, other factors intervene in the contamination process of water bodies like the type of cultivation/treatment, the rate and frequency of application and total use, the nature of soil (texture and organic matter content), the hydro-geological features and climate conditions [4-6].

Pesticide contamination of surface water is seasonally dependent and generally short-lasting. Groundwater pesticide contamination is less or at all season-dependent. Groundwater generally is more protected than surface water from contamination processes and represents a source of high quality drinking water. In Italy, these waters provide more than 70% of the national drinking water need.

The European Directive 98/83/EC on drinking water quality [7] states a maximum acceptable concentration of 0.1 µg/L for single pesticide and 0.5 µg/L for their sum. These values are not based on their toxicological properties, differently from the World Health Organization (WHO) guidelines for drinking water quality [8].

In Europe, to use monitoring of drinking water quality in relation to the presence of pesticides and their metabolites is a rather complicated task, as some 500 pesticides are sold in the European market. National and local authorities with the responsibility to guarantee an adequate quality of drinking water cannot rely on international guidelines for monitoring activities. Of course, it is not possible and even useful to search all the compounds applied in the agricultural area of competence. The selection of compounds to be investigated in water samples should take into account their chemiodynamic properties as well as monitoring and sale data. A huge number of investigations have been carried out on this issue [9-25], which provide valid tools for monitoring activities.

This paper describes the approach and the results of a national research project whose aim was to specifically identify the main pesticides and their metabolites that contaminate raw waters used for drinking in the different agricultural areas in Italy.

METHODS

Design of the study

The experimental activities were planned and carried out by a national working group composed of experts of the Istituto Superiore di Sanità (National Institute of Health), with a coordinating role, five Italian Regions and seven laboratories, six of which involved in institutional monitoring activities on pesticides in drinking water.

Selection of pesticides

Pesticides were selected according to the following procedure:

- leaching indices were calculated for some 500 pesticides sold in the Italian market (data of 1998-2000 of the Ministry of Agriculture and Forest Policy) according to the Groundwater Ubiquity Score (GUS), where GUS = log soil DT_{50} × [4 - log Koc], [26]; Koc is a constant that expresses the soil organic carbon/water concentration ratio of a compound and soil DT_{50} is the time in which half of the dose of a compound disappears. Koc and soil DT_{50} values were collected from published data [27-30]. Some 80 pesticides with GUS higher than 1.8 were selected and ranked taking into account their sales in the Italian market and monitoring data [31-35].

or methods:

- alachlor, azinphos-methyl, azoxystrobin, bensulfuron-methyl, bentazone, bromacil, carbaryl, carbendazim, carbofuran, cinosulfuron, chlorpyrifos, chloridazon, chlortoluron, 2,4-D, dicamba, diazinon, dichlorprop, dichlorvos, dimethenamid, dimethoate, diuron, hexazinone, fenarimol, isoproturon, lindane, linuron, MCPA, mecoprop, metalaxyl, metolachlor, molinate, parathion-methyl, pirimicarbe propoxur, oxadiazon, oxadixyl, simazine, terbumeton, terbuthylazine.

The final number of investigated pesticides and metabolites was of 43; atrazine (which is banned since 1986 in Italy) and three triazine metabolites (deisopropylatrazine, desethylatrazine, desethylterbutilazine) were included as they are well known water contaminants [33, 36].

Selection of sampling areas and sites

Sampling areas were chosen in order to include some of the main national agricultural crops (rice, maize, cereal, citrus, flower, vine-olive and tobacco). Within these areas, groundwaters used for drinking were selected favouring those more vulnerable to pesticide contamination. At this purpose, hydrogeological features and/or monitoring data on pesticide and/or nitrate (as marker of possible pesticide contamination) concentrations were examined. Only one case of surface water used for drinking, represented by the Tuscany area, was selected. The twenty sampling sites identified by the working group from areas of 5 Regions are shown in *Figure 1*.

Sample collection

Water samples were collected in spring (April and May) and autumn (September and October) in 1-2 L amber glass bottles. Then they were kept in iced coolers or in a refrigerator, labelled and delivered to the participating laboratories within 48 hours.

Analysis

Every participating laboratory analyzed 5-10 pesticides, among those selected which coincided with those routinely monitored, in all the samples coming from the twenty sites.

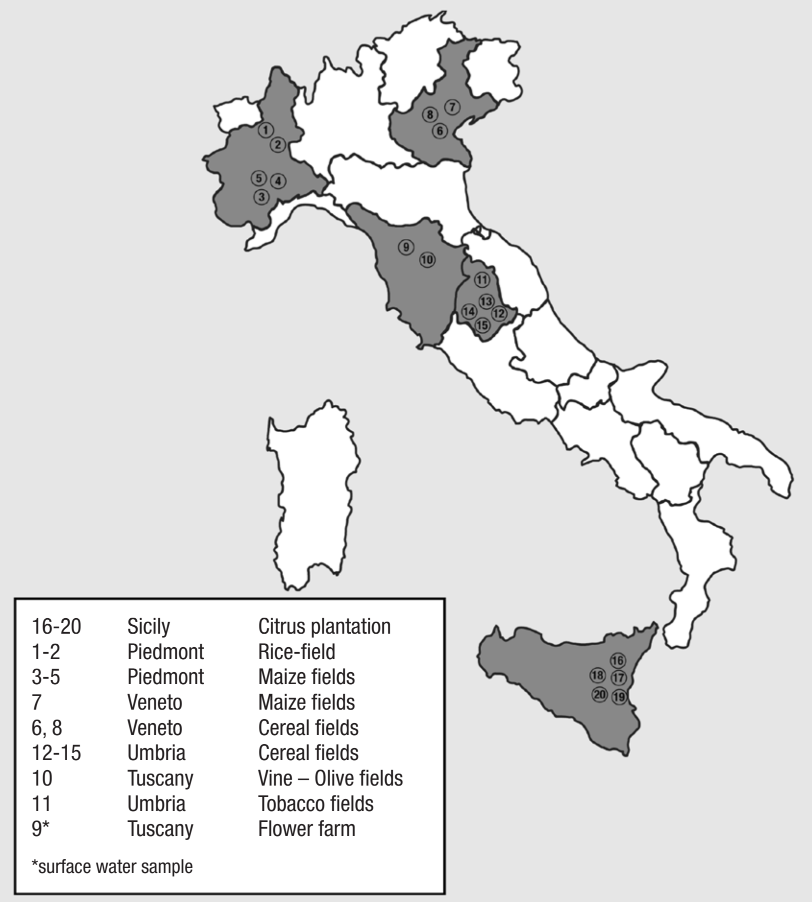

Fig. 1 | *Sampling sites of the selected Italian groundwater and surface water.*

Common to all the labs were the following: *i)*, analytical standards (> 98% purity) from various manufacturers were used to prepare fortification and standard solutions; *ii)*, pesticide sample pre-concentration was performed by Solid Phase Extraction (SPE) using polymeric or octadecyl cartridges and 500 ml of sample (this method allowed a 1000-fold concentration).

Most of the examined compounds were analysed by GC-EPD, HPLC-MS-MS and HPLC-UV methods according to published procedures [28, 37-39].

The analyses of some pesticides were performed using an HPLC equipped with single quadrupole mass spectrometer (MS) with an atmospheric pressure ionisation source operating in turbo-ionspray mode. The mobile phase consisted of 40% v/v aqueous methanol (1 mL/min) and a YMC-Pack special carbamate column (250 × 4.6 mm i.d.) protected by a guard column. A flow splitter was mounted after the HPLC column, thus allowing a flow-rate of 40 µL/min to the mass-spectrometer. The turbo-ionspray voltage was set at 5.8 kV and the decluster potential at 20V. The desolvation gas (nitrogen) temperature and flow-rate were set at 400 °C and 300 L/h, respectively. The instrument operated in the positive ion mode. The recovery of the pesticides were about 90%. A detection limit (LOD) of 2 ng/mL and a quantification limit (LOQ) of 5 ng/mL was reached for all the compounds.

RESULTS

Tables 1-5 summarize the positive detections in the selected water sites. *Table 1* shows analytical data of water samples from the two selected rice-fields. As expected, bentazone, which is specifically used in rice crop, was the main contaminant; it always exceeded the EU limit of 0.1 µg/L for drinking water. It was found in all the samples and reached a maximum concentration of 0.56 µg/L. Water samples taken in spring and autumn showed similar results. Oxadiazon and terbuthylazine were determined at trace levels only in one sample.

Table 2 reports the results obtained on water samples from the four maize-fields. Triazines were by far the main contaminants. Desethylatrazine and atrazine were found in all the samples and at the highest concentrations of 0.41 and 0.21 µg/L, respectively. Other triazines were found at much lower concentrations. Oxadiazon was evidenced in three samples at levels ranging from 0.11 to 0.18 µg/L. Metolachlor, molinate and bentazone were detected at trace levels in few samples.

Table 1 | *Concentrations of selected pesticides and their metabolites (µg/L) in groundwater samples from rice fields*

Area (S)	**S = 1**		**S = 2**	
Compounds	**Spring** **Average ± SD**	**Autumn** **Average ± SD**	**Spring** **Average ± SD**	**Autumn** **Average ± SD**
Bentazone	0.17 ± 0.04 (n = 8)	0.12 ± 0.01 (n = 4)	0.56 ± 0.08 (n = 10)	0.52 ± 0.07 (n = 6)
Oxadiazon	0.09 ± 0.03 (n = 4)	n.d.	n.d.	n.d.
Terbuthylazine	0.03 ± 0.01 (n = 4)	n.d.	n.d.	n.d.
Total concentration	**0.29**	**0.12**	**0.56**	**0.52**

S: sampling site; SD: standard deviation; n: number of analyses; n.d.: below the limit of detection (LOD = 0.01 µg/L).

All the water samples were characterized by the simultaneous occurrence of pesticides and their metabolites, up to ten in one case. Five out of eight samples exhibited total concentrations higher than the EU limit of 0.5 µg/L set for drinking water. Total triazines reached a maximum concentration of 1.02 µg/L. Spring and autumn samples gave very similar results.

Table 3 presents the analytical results from the twelve samples examined from the six cereal fields (corn, oats and maize). Triazines and their metabolites were the most frequently detected pesticides. Desethylatrazine was determined only in two samples but at the highest concentration (0.50 µg/L). Desethylterbutilazine and terbuthylazine were found in almost all the samples, where they reached levels up to 0.20 and 0.13 µg/L,

Table 2 | *Concentrations of tested pesticides and their metabolites (µg /L) in groundwater samples from maize fields*

Area (S)	**S = 3**		**S = 4**		**S = 5**		**S = 7**	
Compounds	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD
Atrazine	0.20 ± 0.07 (n = 8)	0.21 ± 0.06 (n = 10)	0.09 ± 0.01 (n = 8)	0.08 ± 0.01 (n = 8)	0.14 ± 0.01 (n = 6)	0.15 ± 0.04 (n = 8)	0.06 ± 0.03 (n = 6)	0.04 ± 0.01 (n = 8)
Desethylatrazine	0.35 ± 0.24 (n = 8)	0.42 ± 0.39 (n = 10)	0.14 ± 0.11 (n = 8)	0.17± 0.20 (n = 10)	0.32 ± 0.26 (n = 6)	0.62 ± 0.69 (n = 4)	0.34 ± 0.19 (n = 6)	0.17 ± 0.07 (n = 8)
Deisopropylatrazine	0.06 ± 0.00 (n = 2)	0.08 ± 0.00 (n = 2)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bentazone	0.02 ± 0.01 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Metolachlor	0.02 ± 0.01 (n = 4)	0.01±0.01 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Molinate	0.02 ± 0.01 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxadiazon	0.18 ± 0.06 (n = 4)	n.d.	0.11 ± 0.01 (n = 4)	n.d.	0.11 ± 0.00 (n = 4)	n.d.	n.d.	n.d.
Simazine	0.06 ± 0.03 (n = 8)	0.13 ± 0.10 (n = 4)	0.04 ± 0.01 (n = 8)	0.05 ± 0.04 (n = 4)	0.04 ± 0.01 (n = 6)	0.03 ± 0.00 (n = 2)	0.02 ± 0.00 (n = 2)	n.d.
Terbuthylazine	0.09 ± 0.07 (n = 10)	0.10 ± 0.07 (n = 10)	0.05 ± 0.05 (n = 10)	0.04 ± 0.03 (n = 10)	0.06 ± 0.06 (n = 8)	0.07 ± 0.06 (n = 8)	0.03 ± 0.00 (n = 2)	0.02 ± 0.00 (n = 2)
Desethylterbutilazine	0.06 ± 0.01 (n = 10)	0.08 ± 0.01 (n = 10)	0.03 ± 0.01 (n = 10)	0.03 ± 0.01 (n = 10)	0.06 ± 0.01 (n = 8)	0.07 ± 0.01 (n = 8)	0.03 ± 0.21 (n = 8)	0.02 ± 0.01 (n = 8)
Total concentration	**1.05**	**1.03**	**0.44**	**0.37**	**0.74**	**0.93**	**0.49**	**0.25**
Total triazine concentration	**0.84**	**1.02**	**0.34**	**0.37**	**0.63**	**0.93**	**0.49**	**0.25**

S: sampling site; SD: standard deviation; n: number of analyses; n.d.: below the limit of detection (LOD = 0.01 µg/L).

Table 3 | *Concentrations of selected pesticides and their metabolites (µg/L) in groundwater samples from cereal areas*

Area (S)	**S = 6**		**S = 8**		**S = 12**		**S = 13**		**S = 14**		**S = 15**	
Compounds	**Spring** Average±SD	**Autumn** Average±SD	**Spring** Average±SD	**Autumn** Average±SD	**Spring** Average±SD	**Autumn** Average±SD	**Spring** Average±SD	**Autumn** Average±SD	**Spring** Average±SD	**Autumn** Average±SD	**Spring** Average±SD	**Autumn** Average±SD
Alachlor	n.d.	n.d.	0.01±0.00 (n = 2)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine	0.07 ± 0.03 (n = 6)	0.05±0.02 (n = 8)	0.03±0.00 (n = 4)	0.02±0.01 (n = 8)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Desethylatrazine	0.32±0.20 (n = 6)	0.24±0.17 (n = 6)	0.04±0.00 (n = 4)	0.02±0.01 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Deisopropylatrazine	0.03±0.00 (n = 2)	0.02±0.00 (n = 2)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Metolachlor	0.01±0.01 (n = 6)	0.01±0.00 (n = 4)	0.04±0.01 (n = 8)	0.03±0.00 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	0.02±0.00 (n=2)	n.d.	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	0.09±0.02 (n=4)	n.d.	0.07±0.03 (n=4)	n.d.	0.07±0.00 (n=4)	n.d.	0.07±0.00 (n=4)	n.d.
Oxadixil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01±0.00 (n=2)	n.d.	n.d.	n.d.	n.d.	n.d.
Simazine	0.02±0.01 (n = 6)	0.01±0.00 (n = 2)	0.20±0.07 (n = 4)	0.03±0.03 (n = 4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbuthylazine	0.08±0.05 (n = 8)	0.05±0.02 (n = 8)	0.20±0.07 (n = 6)	0.05±0.02 (n = 8)	0.06±0.03 (n = 8)	0.02±0.00 (n = 8)	0.03±0.01 (n = 6)	n.d.	0.05±0.01 (n = 4)	0.03±0.01 (n = 4)	0.06±0.01 (n = 4)	0.02±0.00 (n = 4)
Desethylterbutilazine	0.12±0.06 (n = 8)	0.08±0.02 (n = 8)	0.20±0.07 (n = 6)	0.05±0.01 (n = 8)	0.09±0.04 (n = 8)	0.05±0.01 (n = 8)	0.07±0.01 (n = 8)	n.d.	n.d.	0.05±0.01 (n = 8)	n.d.	n.d.
Total concentration	**0.63**	**0.41**	**0.33**	**0.17**	**0.27**	**0.07**	**0.18**	**0.00**	**0.12**	**0.10**	**0.13**	**0.02**
Total triazine concentration	**0.62**	**0.40**	**0.28**	**0.14**	**0.18**	**0.07**	**0.10**	**0.00**	**0.05**	**0.08**	**0.06**	**0.02**

S: sampling site; SD: standard deviation; n: number of analyses; n.d.: below the limit of detection (LOD = 0.01 µg/L).

respectively. Atrazine and simazine were determined only in four samples; with respective maximum concentrations of 0.07 and 0.20 µg/L.

Deisopropylatrazine, alachlor and oxadixil were detected only in one sample, at very low concentrations.

Oxadixyl and metolachlor were found in five out of the twelve samples analysed, at levels below 0.10 µg/L.

Only one sample had total pesticide concentrations exceeding the EU limit of 0.5 µg/L. Also for water samples from cereal fields no seasonal variability was found.

Analytical results from the five selected citrus plantations are reported in *Table 4*. Only two of the selected compounds were found at trace levels in these samples: oxadiazon and terbuthylazine (maximum concentration 0.08 and 0.04 µg/L respectively).

The analytical data of selected pesticides and their metabolites in water samples from flower farm, vine-olive and tobacco fields are gathered in *Table 5*. Very few positive detections were made and always at trace levels.

Table 6 summarizes the frequency of positive detections of the selected compounds and their mean and maximum levels in the twenty water samples analysed in spring and autumn.

As shown in this table, twelve compounds, out of the forty-three selected and analysed, were determined at levels higher than the respective analytical sensitivity limits of the applied methods.

Among the selected compounds, triazines and their metabolites represented by far the major group of groundwater contaminants. Terbuthylazine and desethylterbutilazine were the most frequently detected compounds followed by atrazine and desethylatrazine, which however reached the highest concentrations.

Bentazone was found only in samples from rice-fields. Oxadiazon and metolachlor were found at a relatively high frequency in the analysed samples but at trace levels. Oxadixil, molinate and alachlor were determined at the lowest frequency. Five pesticides (atrazine, bentazone, oxadiazon, simazine and terbuthylazine) and two metabolites (desethylatrazine and desethylterbutilazine) were determined at maximum levels above the 0.1 µg/L EU limit for drinking water.

The main finding of this study was that out of forty-three pesticides and their metabolites that were selected among 500 compounds on the basis of their potential to contaminate ground and surface waters, only twelve were found at detectable levels in the analyzed water samples. Furthermore, only seven of these compounds, five pesticides (atrazine, bentazone, oxadiazon, simazine and terbuthylazine) and two metabolites (desethylatrazine and desethylterbutilazine), occurred sometimes at concentrations higher than 0.1 µg/L (EU limit for dinking water).

Triazine herbicides represented the main category of water contaminants. Terbuthylazine was found at a very high percentage in the analysed samples, but rarely at levels up to 0.2 µg/L. Often it occurred togeth-

Table 4 | *Concentrations of selected pesticides and their metabolites (µg/L) in groundwater samples from citrus plantations*

Area (S)	**S = 16**		**S = 17**		**S = 18**		**S = 19**		**S = 20**	
Compounds	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD
Oxadiazon	0.08 ± 0.01 (n = 4)	n.d.	n.d.	n.d.	0.03 ± 0.01 (n = 4)	n.d.	0.06 ± 0.02 (n = 4)	n.d.	0.06 ± 0.02 (n = 4)	n.d.
Terbuthylazine	n.d.	n.d.	0.04 ± 0.00 (n = 4)	0.02 ± 0.00 (n = 4)	0.03 ± 0.00 (n = 4)	n.d.	n.d.	n.d.	0.03 ± 0.01 (n = 4)	n.d.
Total concentration	**0.08**	**0.00**	**0.04**	**0.02**	**0.06**	**0.00**	**0.06**	**0.00**	**0.08**	**0.00**

S: sampling site; SD: standard deviation; n: number of analyses; n.d.: below the limit of detection (LOD = 0.01 µg/L).

er with its main metabolite, desethylterbutilazine. Atrazine was detected in 30% of the analysed samples at levels also beyond 0.1 µg/L, despite the fact that it was banned since 1986. Probably its presence in ground water is due either to its illegal use or the high inertia of this contamination [4].

Several water samples were characterized by the simultaneous occurrence of pesticides and their metabolites (up to ten in a sample). All the water samples from maize and one sample from cereal fields had total pesticide concentrations higher than the EU limit of 0.5 µg/L for drinking water. Total triazine concentrations up to 1.02 µg/L were found.

Atrazine, simazine, terbuthylazine, molinate, alachlor and metolachlor never reached the respective guidelines defined by the WHO [8] for drinking water quality (2, 2, 7, 6, 20 and 10 µg/L). Even considering the maximum total triazine concentrations, these values were always lower than the lowest guideline defined for a single triazine pesticide by WHO (2 µg/L).

Among the considered areas, samples from maize fields showed the highest contamination levels, probably as a consequence of the characteristics and amounts of pesticides applied and the nature of soils. These fields are indeed often located in piedmontese zones (with texture and hydro geological features favourable to pesticide leaching).

Bentazone turned out as contaminant of groundwater in rice-fields where it was found in all the analysed samples at levels above 0.1 µg/L. Nevertheless, even the highest concentration found (0.56 µg/L) was not of human health concern on the basis of the value defined by WHO [8].

Spring and autumn samples gave very similar results, showing that the process of pesticide contamination in the tested waters is not seasonally dependent.

DISCUSSION

As expected, in general the main compounds found in water samples coincided with two main features:

Table 5 | *Concentrations of selected pesticides and their metabolites (µg/L) in groundwater samples from flower farm, vine-olive and tobacco fields*

Area (S)	**S = 9 (flower field)***		**S = 10 (vine - olive field)**		**S = 11 (tobacco field)**	
Compounds	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD	**Spring** Average ± SD	**Autumn** Average ± SD
Metolachlor	n.d.	n.d.	0.07 ± 0.01 (n = 8)	n.d.	0.01 ± 0.00 (n = 2)	n.d.
Oxadiazon	0.05 ± 0.01 (n = 4)	n.d.	n.d.	n.d.	0.06 ± 0.01 (n = 4)	0.03 ± 0.01 (n = 4)
Oxadixil	n.d.	n.d.	0.03 ± 0.00 (n = 2)	n.d.	n.d.	n.d.
Simazine	n.d.	n.d.	0.02 ± 0.02 (n = 2)	n.d.	n.d.	n.d.
Terbuthylazine	0.03 ± 0.00 (n = 4)	0.02 ± 0.00 (n = 4)	0.07 ± 0.01 (n = 6)	0.02 ± 0.01 (n = 6)	0.03 ± 0.02 (n = 6)	0.03 ± 0.01 (n = 4)
Desethylterbutilazine	n.d.	n.d.	0.02 ± 0.01 (n = 4)	0.02 ± 0.01 (n = 6)	0.01 ± 0.00 (n = 2)	n.d.
Total concentration	**0.08**	**0.02**	**0.20**	**0.04**	**0.11**	**0.05**

S: sampling site; SD: standard deviation; n: number of analyses; n.d.: below the limit of detection (LOD = 0.01 µg/L).
**This site corresponds to the surface water used for drinking.*

Table 6 | *Frequency of determination, mean and maximum values of the selected pesticides and their metabolites in the analysed groundwater samples*

	Frequency of determination		Concentration (μg/l)	
Compound	**N/40**	**(%)**	**Min**	**Max**
Alachlor	1/40	(2.5)	0.01	0.01
Atrazine	12/40	(30)	0.02	0.21
Desethylatrazine	12/40	(30)	0.02	0.62
Deisopropylatrazine	4/40	(10)	0.02	0.08
Bentazone	5/40	(12.5)	0.02	0.56
Metolachlor	9/40	(22.5)	0.01	0.07
Molinate	1/40	(2.5)	0.02	0.02
Oxadiazon	15/40	(37.5)	0.03	0.18
Oxadixil	2/40	(5)	0.01	0.03
Simazine	12/40	(30)	0.01	0.16
Terbuthylazine	30/40	(75)	0.02	0.10
Desethylterbutilazine	19/40	(47.5)	0.01	0.12

they are largely used for specific crops and are characterized by a high leaching potential, on the basis of their intrinsic properties.

In few cases non expected pesticides were found in areas where the main agricultural activities did not foresee their use. These apparently contradictory results are attributed to the fact that the agricultural areas were named according to the main crops cultivated, but other minor agricultural activities can not be excluded.

The findings of this project are similar to those reported in literature with reference to the very small number of pesticides and their metabolites representing the bulk of water contamination [37, 38, 21, 22].

We hope that the approach and the results of this project might be useful for laboratories involved in drinking water monitoring in order to rationalize their efforts and improve the quality of their analytical data.

Acknowledgements

This work was partially funded by the Italian Ministry of Health.

Conflict of interest statement

There are no potential conflicts of interest or any financial or personal relationships with other people or organizations that could inappropriately bias conduct and findings of this study.

Submitted on invitation.
Accepted on 22 April 2010.

References

1. Singh BK, Walker A, Wright DJ. Degradation of chlorpyrifos, fenamiphos, and chlorothalonil alone and in combination and their effects on soil microbial activity. *Environ Toxicol Chem* 2002;21:2600-5.
2. Dagnac T, Jeannot R, Mouvet C, Baran N. Determination of oxanilic and sulfonic acid metabolites of acetochlor in soils by liquid chromatography-electrospray ionisation mass spectrometry. *J Chromatogr A* 2002;957:69-77.
3. Tarusov V, Radetsky V, Tomatis L. Dichlorodiphenyltrichl oroethane (DDT): Ubiquity, persistence and risks. *Environ Health Pespect* 2002;110:125-8.
4. Giuliano G. Groundwater vulnerability to pesticides: An overview of approaches. In: Vighi M, Funari E (Ed.). *Pesticide risk in groundwater*. Boca Raton: CRC Press; 1995. p. 101-18.
5. FOCUS 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup. (EC Document Reference SANCO/321/2000 rev. 2,). 202 p.
6. Worrall F, Kolpin DW. Aquifer vulnerability to pesticide pollution-combining soil; land-use and aquifer properties with molecular descriptors. *J Hydrol* 2004;293:191-204.
7. European Union. Directive 98/83/EC of the European Parliament and of the Council of 03 November 1998 relating to the quality of water intended for human consumption. *Official Journal of the European Communities* L 0083, 25/12/1998.
8. World Health Organization. *Guidelines for drinking-water quality Vol. 1. Recommendations.* 3. ed. Geneva: WHO; 2004.
9. Senseman SA, Lavy TL, Daniel TC. Monitoring groundwater for pesticides at selected mixing/loading sites in Arkansas. *Environ Sci Technol* 1997;31:283-8.
10. Garmouna M, Blanchard M, Chesterikoff A, Ansart P, Chevreuil M. Seasonal transport of herbicides (triazines and phenylureas) in a small stream draining an agricultural basin: Mélarchez (France). *Weed Res* 1997;31:1489-503.
11. Thurman EM, Zimmerman LR, Scribner EA, Coupe RH. Occurrence of cotton pesticides in surface water of the Mississippi embayment. *US Geological Survey Fact Sheet* 1998;FS-022-98. 4.
12. Funari E, Barbieri L, Del Carlo G, Forti S, Santini C, Bottoni P, Marinelli A, Giuliano G, Zavatti A. Comparison of the leaching properties of alachlor, metolachlor, triazines and some their metabolites in an experimental field. *Chemosphere* 1998;36:1759-73.
13. Kreuger J. Pesticides in stream water within an agricultural catchment in southern Sweden, 1990-1996. *Sci Tot Environ* 1998;216:227-33.
14. Spliid NH, Koppen B. Occurrence of pesticides in Danish shallow ground water. *Chemosphere* 1998;37:1307-16.
15. European Environmental Agency. *Groundwater quality and quantity in Europe.* (Environmental assessment report, N. 3). Copenhagen, Denmark: EEA; 1999.
16. Tuxen N, Tuchsen PL, Albrechtsen HJ, Bjerg PL. Fate of seven pesticides in an aerobic aquifer studied in column experiments. *Chemosphere* 2000;41:1485-94.
17. Scribner EA, Thurman EM, Zimmerman LR. Analysis of selected herbicides metabolites in surface and ground water of the United States. *Sci Tot Environ* 2000;248:157-67.
18. Younes M, Galal-Gorchev H. Pesticides in drinking water-a case study. *Food Chem Toxicol* 2000;38:S87-90.
19. Barbash JE, Thelin GP, Kolpin DW, Gilliom RJ. Major herbicides in ground water: results from the national water-quality assessment. *J Environ Qual* 2001;30:831-45.
20. Van Maanen JMS, De Vaan MAJ, Veldstra AWF. Hendrix WPAM. Pesticides and nitrate in groundwater and rainwater

in the province of Limburg in the Netherlands. *Environ Monit Assess* 2001;72:95-114.

21. Squillace PJ, Scott JC, Moran MJ, Nolan BT, Kolpin DW. VOCs, pesticides, nitrate, and their mixtures in groundwater used for drinking water in the United States. *Environ Sci Technol* 2002;36:1923-30.
22. Cerejeira MJ, Viana P, Batista S, Pereira T, Silva E, Valerio MJ, Silva A, Ferreira M, Silva-Fernandes MA. Pesticides in Portuguese surface and ground waters. *Water Res* 2003; 37:1055-63.
23. Papadopolou-Mourkidou E, Karpouzas DG, Patsias J, Kotopoulou A, Milothridou A, Kintzikoglou K, Vlachou P. The potential of pesticides to contaminate the groundwater resources of the Axion river basin in Macedonia; Northern Greece. Part I. Monitoring study in the north part of the basin. *Sci Tot Environ* 2004;321:127-46.
24. Lapworth DJ, Gooddy DC. Source and persistence of pesticides in a semi-confined chalk aquifer of southeast England. *Environ Pollut* 2006;144:1031-44.
25. Comoretto L, Arfib B, Talva R, Chauvelon P, Pichaud M, Chiron S, Hohener P. Runoff of pesticides from rice fields in the Ile de Camatgue. Field study and modelling. *Environ Pollut* 2008;151:486-93.
26. Gustafson DI. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ Toxicol Chem* 1989;8:339-57.
27. Tomlin C. *The pesticide manual. A world compendium. Incorporating the agrochemicals handbook. 12. ed*. United Kingdom: BCPC; 2000.
28. Fava L, Bottoni P, Crobe A, Funari E. Leaching properties of some degradation products of alachlor and metolachlor. *Chemosphere* 2000;41:1503-8.
29. Fava L, Bottoni P, Crobe A, Barra Caracciolo A, Funari E. Assessment of leaching potential of aldicarb and its metabolites using laboratory studies. *Pest Manag Sci* 2001;57:1135-41.
30. HSDB *(Hazardous Substances Data Bank)*. Available from: www. http://toxnet.nlm.nih.gov.
31. *US Geological Survey.* Available from: http://ca.water.usgs.gov/pnsp/gw/; http://idaho.usgs.gov; http://oregon.usgs.gov; http://ny.usgs.gov.
32. *UK Defra.* Available from: www.defra.gov.uk/environment/statistics/inlwater/iwpesticide.htm.
33. Kolpin DW, Thurman EM, Linhart SM. Finding minimal herbicide concentrations in ground water? Try looking for their degradates. *Sci Total Environ* 2000;248:115-22.
34. Kolpin DW, Thurman EM, Linhart SM. Occurrence of cyanazine in groundwater: degradates more prevalent than the parent compound. *Environ Sci Technol* 2001;35:1217-22.
35. Franchi A. 2001 Rapporto sui dati nazionali relative alla ricerca di fitofarmaci nelle acque – anno 2000. In: *Fitofarmaci e ambiente. Conoscenze e prospettive. 3° Seminario nazionale.* Napoli, 24 ottobre 2001. Firenze: 2001. p. 83-148.
36. Funari E, Donati L, Sandroni D, Vighi M. Pesticide levels in groundwater: value and limitations of monitoring. In: 6 *Pesticide Risk in Groundwater*. Boca Raton: CRC Press; 1995. p. 3-44.
37. Borba da Cunha AC, López de Alda MJ, Barceló D, Pizzolato TM, dos Santos JH. Multianalyte determination of different classes of pesticides (acidic, triazines, phenyl ureas, anilines, organophosphates, molinate and propanil) by liquid chromatography-electrospray-tandem mass spectrometry. *Anal Bioanal Chem* 2004;378:940-51.
38. US Environmental Protection Agency. *Determination of organic compounds in drinking water by liquid-solid extraction and capillary column GAS chromatography/mass spectrometry.* US EPA; 1995 (EPA 500, supplement III. US-EPA 525.2).
39. Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici. *Metodi analitici per le acque.* Roma: APAT; 2003 (APAT Manuali e Linee Guida, 29/2003).