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## Integrated forecasting models of pesticide concentrations and environmental monitoring campaigns

Ana Masiá,<sup>1\*</sup> Yolanda Picó,<sup>1</sup> Maura Calliera,<sup>2</sup> Ettore Capri,<sup>2</sup> Lucrezia Lamastra,<sup>3</sup> Federico Ferrari<sup>4</sup>

<sup>1</sup>Food and Environmental Safety Research Group, Department of Preventive Medicine, Faculty of Pharmacy, University of Valencia, Valencia, Spain. <sup>2</sup>OPERA research center, Università Cattolica del Sacro Cuore, Piacenza, Italy. <sup>3</sup>Institute of Agricultural and Environmental Chemistry, Università Cattolica del Sacro Cuore, Piacenza, Italy. <sup>4</sup>Aeiforia srl, Fidenza, Italy

**\*Correspondence:**

Ana Masiá-Reyes  
Department of Preventive Medicine  
Faculty of Pharmacy  
University of Valencia  
Av. Vicent Andrés Estellés, s/n  
46100 Burjassot, València

E-mail: ana.masia@uv.es



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**Summary.** By integrating agri-environmental databases, mathematical models and geographic information systems, maps showing the potential vulnerability of soils to the leaching of plant protection products can be generated. However, these forecasts may not be subsequently corroborated by monitoring data. Here we present a case study based on glyphosate in Lombardy (Italy) and triazine herbicides in the Autonomous Community of Valencia (Spain). Glyphosate was found in the groundwater of Lombardy, despite modeling results clearly indicating the non-potential risk of groundwater contamination. Among the triazine herbicides in Valencia, simazine, although present in surface waters, was not found in groundwaters, contrary to its expected behavior as a potential leachate. The discrepancy in the behavior of glyphosate can be explained by infiltration and point contamination sources, and the absence of simazine by the facility of its degradation. Our study highlights the importance of integrating monitoring modeling and mapping approaches to improve knowledge and to obtain quality data. [Contrib Sci 10:151-160 (2014)]

### Introduction

The new European Union (EU) regulation 1107/2009 on the placing of plant protection products on the market replaces Directive 91/414 and provides a comprehensive risk assessment procedure to be applied before each active substance can be authorized for use and marketing. In addition, the Groundwater Daughter Directive (2006/118/EC) and the Wa-

ter Framework Directive (WFD 2000/60/EC) establish a legal framework to protect and restore clean water in sufficient quantity across Europe. Specifically, in accordance with Article 17, the WFD establishes EU-wide quality standards for nitrates and pesticides that must be met to comply with "good groundwater chemical status." The goal of the WFD is to reach a coherent and integrated approach to water management across the EU, including surface waters. Directive

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2008/105/EC and, more recently, Directive 2013/39/EU set limits on the concentrations of priority substances in surface waters, including atrazine, diuron, isoproturon and simazine.

To evaluate the chemical status of water bodies, the WFD introduced criteria establishing a list of priority substances and priority hazardous substances, for which specific measures such as quality standards and emission controls must be taken in order to reduce or eliminate emissions, discharges and losses. Plant protection products (PPPs) are released directly into the environment and are, therefore, an obvious target for monitoring activities.

One of the shortcomings of the legal framework concerning pesticides is that the actual use phase, which is a key element for the determination of the overall risks posed by these chemicals, is not sufficiently addressed. To achieve a more sustainable use of pesticides, in 2009 the European Parliament approved Directive 128, regarding the Sustainable Use of Pesticides (2009/128/EC), proposed measures for the determination of the overall risks that pesticides pose with respect to the use-phase of their life-cycles. The aims of the Directive are to improve the methods and tools of pesticide evaluation and to develop innovative approaches that will inform the policy-making process for sustainable development, thereby addressing this deficiency. In this legal framework, monitoring should assume an important role in environmental risk management for chemicals. However, there are a number of different drivers that complicate the planning of PPP monitoring campaigns.

In Italy, monitoring and environmental control are guaranteed by a large number of institutional bodies. Each region, through its environment protection agency (ARPA) applies its monitoring plan by carrying out sampling and analysis, and collecting information at the local level. The data are then annually delivered to the national authority, which coordinates the overall monitoring plans and provides technical protocols, data processing and statistical assessment. Systematic pesticide monitoring for environmental purposes was carried out at the time of this study in 85% of Italian regions. In general, there was a gradual increase in the coverage and significance of the surveys. However, the creation of a national framework on the presence of pesticides has been hindered by differences between regions with respect to the extension of the monitoring network, the frequency of sampling and the number of target substances. However, efforts at improvement are on-going. In Spain, pesticides in surface and groundwater are monitored by the hydrographic confederations of each river basin, which in turn depend on the Ministry of Agriculture, Food and Environment [26]. Consequently, both the net-

works and the protocols needed to monitor pesticides included in the WFD are well-established. However, in both Spain and Italy, these networks face challenges regarding seasonal and temporal sampling frequency, given that, unless many samples are collected within a defined period of time, the results might not be representative. Conversely, tests aimed at detecting typical conditions may miss evidence of problems that only occur infrequently. For PPPs, the current trend is to manage the risk not only at the level of registration and control (by monitoring residues) but also at the territory level. This is clearly evident in the WFD, which refers to the management of chemical risks at the level of river basins, such as the identification of vulnerable areas, and in the Directive for the sustainable use of PPPs, in which the main objective is the reduction of risk during the use-phase of these substances. To overcome these problems, the use of simulation models coupled with a geographical information system (GIS) has been proposed as a valuable tool to predict the pollution risk and to prevent contamination [1,6,8]. This is an effective approach for the regional-scale evaluation of herbicides leaching into groundwater and can guide decision-making regarding protection from and the prevention of pollution.

Some regions of Italy and Spain have started projects aimed at identifying the driving forces of the processes involved in pesticide movement. They have therefore developed tools to simulate the behavior of pesticide at different scales. Applications include defining pesticide use permissions (or restrictions) at a regional level, planning monitoring programs and optimizing the study budget by focusing sampling on the areas where higher pesticide concentrations are likely to be found.

## Material and methods

**Studied areas.** Agriculture in the plains areas of Lombardy and northern Italy is more intensive than almost anywhere else in the world. Accordingly, preserving water quality and aquatic ecosystems is of high priority. An early definition of critical environmental areas was carried out through a preliminary recognition survey at a scale of 1:250,000 based on a combined analysis of the environmental factors that can contribute to groundwater contamination, including the intrinsic vulnerability of aquifers, the loads of anthropogenic origin imposed on the territory, the pressure on groundwater quality and the chemical quality of the water.

Regarding the pressure exerted by pesticides, already in 1997, ERSAF (Ente Regionale Servizi Agricoltura e Foreste) de-

veloped SuSAP (Supplying Sustainable Agriculture Production), a decision support system, developed in a GIS environment, that takes into account the protective capacity of the soil, the loads distributed, the spatial distribution of crops, irrigation practices and the chemical and physical properties of the compounds under investigation. The integration of an agri-environmental database and a mathematical model within a GIS (Arc/Info GIS) allows mapping of the potential vulnerability of soils to PPP leaching.

The Autonomous Community of Valencia (ACV, Spain) produces the majority of the oranges and tangerines consumed locally and much of those exported to Europe and other countries. During the 2010–2011, citrus production exceeded  $3 \cdot 10^6$  tons, of which approximately  $2.8 \cdot 10^5$  tons were destined for export. This intensive agricultural activity constitutes a non-point pollution source that threatens surface and groundwater quality, both of which are used to supply the population with drinking water. In the ACV, 65% of the population is supplied with groundwater and the rest with surface water. The inappropriate use of herbicides in this area results in the contamination of surface and groundwater. Although herbicides are normally less toxic for humans than other pesticide families, their inclusion in priority lists of monitoring programs is of great importance to obtain comprehensive knowledge of groundwater pollution, as these compounds have been the main pesticide contaminants in groundwater. In addition, the herbicides diuron, atrazine, simazine, terbuthylazine and terbutometon have been detected in surface waters and in some wells in the ACV, with similar reports from other countries [5,18,20,24]. Therefore, studies at the regional level are warranted.

Several models integrated in an Arc/Infor GIS have been applied in citrus-growing areas of the ACV to evaluate and rank the potential leaching risk of the most frequently applied herbicides [9,10,17]. However, the limitations of Arc/Info GIS maps should be noted. Even if they constitute an important contribution to identifying areas where the potential risk of leaching is higher, they assume that a treatment with one active ingredient involves a single crop throughout the area under investigation. Therefore, at present, there is no real mapping of vulnerabilities to pesticides, although good maps for the evaluation of nitrate vulnerability have been produced and they provide useful information for a preliminary investigation. This limitation highlights the need to develop decision support systems that integrate different forecasting models for the calculation of surface water or groundwater pesticide concentrations with information derived from environmental monitoring campaigns.

An interesting example is that of the active ingredient glyphosate. Based on the results of many studies and reports, glyphosate was determined to have little propensity to leach into groundwater. Despite being one of the best-selling substances in Italy, where it was designated as a priority substance for both surface and groundwater, glyphosate monitoring was initiated for the first time only in 2005, and only in the Lombardy region, by the regional ARPA. Additional examples are triazines (terbutometon, atrazine, propazine, simazine and terbuthylazine) and ureas (diuron and isoproturon), which are the most commonly used herbicides in Spain, together with glyphosate and diquat. Triazines and ureas are among the most frequently detected herbicides due to their high mobility in the soil-water environment. Once pesticides come in contact with this environment, these compounds can be degraded via different pathways into a variety of transformation products (TPs). Although TPs are usually less active and harmless than their parent compounds, they can still have a certain degree of toxicity. Because of their polarity, they normally have a higher mobility in the soil-water environment and can reach groundwater more easily than their parent compounds. Therefore, the inclusion of relevant TPs in the analytical methodology applied in water monitoring programs is necessary to provide a realistic overview of pesticide pollution.

Modeling results noted the leaching potential of terbutometon, and simazine, which because of their high mobility pose a high pollution risk. According to the simulated attenuation factor for terbutometon, up to 58% of the applied herbicide may leach out into the surrounding aquatic medium. By contrast, terbuthylazine and diuron are strongly adsorbed by the soil and within 99% of the study area posed a risk below the minimum value. A theoretical ranking of the highest to lowest risk, as determined from this model was: terbutometon > propazine > simazine > atrazine > terbuthylazine > diuron > isoproturon > glyphosate. However, as noted above, the experimental data obtained from monitoring studies are not always in agreement with the established ranking. The physico-chemical characteristics of all the herbicides covered in these examples and their leaching potential are listed in Table 1.

**Potential glyphosate groundwater contamination in Lombardy (northern Italy).** Glyphosate (N-(phosphonomethyl)glycine,  $C_3H_8NO_5P$ ) is the world's largest-selling herbicide. It is used in agriculture and forestry, orchards, viticulture, horticulture in private gardens and on non-cultivated areas, such as railway tracks, roadsides, and public squares. Its agricultural use comprises, besides pre-

**Table 1.** Herbicide properties

Herbicide	T <sub>1/2</sub> * (days)	K <sub>oc</sub> ** (ml/g)	GUS	Leaching risk
Terbumeton	300	158	4.46	High
Propazine	35–231	8910	3.84	High
Simazine	60	130	3.35	High
Atrazine	17–271	501	3.30	High
Terbuthylazine	60	250	2.85	Moderate
Diuron	90	480	2.58	Moderate
Isoproturon	30	316	2.07	Moderate
Glyphosate	47	24,000	−0.64	Low

\*T<sub>1/2</sub>: pesticide half-life.

\*\*K<sub>oc</sub>: pesticide sorption coefficient.

GUS: groundwater ubiquity score.

emergence weed control, pre-and post-harvest applications to facilitate the harvest and to control volunteer crops, respectively. The application rates of glyphosate for weed control range from a few hundred g/ha to several kg/ha [2].

The mobility, and hence the leachability, of glyphosate in soil depends on its inactivation in soil, which is a function of its relatively fast degradation and its sorption. These two processes can be very different from soil to soil, but compared with other pesticides the sorption characteristics of glyphosate in soil are unique [3].

Studies on glyphosate that focused on its mobility and leaching from agricultural soils concluded that both are mainly governed by macropore flow [3,34]. Transport by soil particles (colloidal transport) of strongly adsorbed pesticides, such as glyphosate, through macropores (preferential flow) has been demonstrated. A slight increase in the otherwise low leachability of glyphosate in soils where preferential flow is a significant process, such as in many structured clayey soils, was, therefore, predicted. A decisive condition is a heavy rainfall event shortly after glyphosate application; by contrast, vegetation, tillage and phosphate concentration have little or no effect on the transport of glyphosate into drainage systems by preferential flows. Rather, leaching is limited in uniform, non-structured soils, without macropores, such as in sandy soil. The risk of contamination persists, however, in sandy oxide-poor soils in which there is a shallow groundwater table [3]. The strong, but not fully understood, soil dependency indicates that determination of glyphosate sorption, and hence leachability, in a certain soil is not simple as it seems to depend on several soil characteristics such as mineralogical composition (mineral types, contents and crystallinity), pH, phosphate content and maybe soil organic matter content [3]. Subsequent to glyphosate application for

weed control and in new agricultural systems, notably glyphosate-tolerant crops [2,25], glyphosate and its degradation product AMPA were often detected in surface waters and partially in groundwater [4,30].

In a survey in Lombardy in 2007, glyphosate was found in 65 of the 154 surface water samples collected in 53 monitoring sites. In 33.8% of the positive samples the concentration was >0.1 µg/l; in 2008, glyphosate was detected in 37 of the 205 surface water samples collected in 48 monitoring sites, with 34.1% of the positive samples having concentrations >0.1 µg/l. Otherwise, monitoring did not detect glyphosate exceeding the legal limit of >0.1 µg/l in the groundwater of Lombardy in 2005, 2006 and 2009. Glyphosate concentrations above the drinking water limit were detected only in some groundwater monitoring sites during May 2007 monitoring campaign, when 84 samples were collected from 57 selected wells. All the contaminated wells are located in the south east part of the region (Fig. 1 and Table 2).

In summary, taking into account the state of knowledge with respect to the mobility and leaching of glyphosate from agricultural soils as described above, the finding of the active ingredient glyphosate can be explained by several causes/hypothesis such as point source contamination, chemical-physical properties of the soil, competition with inorganic phosphate for sorption sites, macropore flow; (shallow groundwater), inflow of surface water or bank filtrate.

In contrast to Lombardy, contamination by glyphosate was detected in only 4% of the wells analyzed in the provinces of Lodi, Cremona, and Mantova. These results show an extremely localized contamination. Therefore, the aim of this study was to clarify the causes of glyphosate contamination (concentrations ≥0.1 µg/l) of groundwater using site inspection and evaluation together with water sample collection

and analysis. Parallel samples from contaminated sites and from surrounding areas where piezometers were available were collected to assess residue concentrations of glyphosate, characterize the water, and investigate possible different analytical methods. In general, the groundwater-flow direction was either known or it was deducible on the basis of scientific expert assessment. However, neither the hydrological connectivity between the treated areas and the aquifer accessed by a well nor the solute travel time from the surface to the aquifer were known.

Sampling campaigns to collect groundwater from the contaminated wells were organized from November 2010 to January 2011. All of the monitored wells are part of the monitoring network of ARPA Lombardy. Samples were collected in polypropylene bottles (1000 ml) and immediately stored in an insulated container chilled using ice packs for transport to the laboratory within 12 h. The samples were stored in a laboratory freezer for a maximum of 2 weeks and then extracted using an analytical method based on the one described by Hanake et al. [19]. An HPLC-MS Thermo MSQ (single quadrupole ESI/APCI) with autosampler was used to confirm the identity of the samples analyzed and quantified using a high-performance liquid chromatography with fluorescence detection system. Due to the low recovery in natural water, a purification step using a strong anion exchange chromatographic technique was added.

**Monitoring of herbicides in waters of the Autonomous Community of Valencia.** Triazine compounds are inhibitors of electron transport in photosynthesis and are often used as the basis for various herbicides, such as atrazine, propazine, simazine, terbuthylazine and tebumeton. As herbicides, triazines may be used alone or in combination with other herbicidal active ingredients to increase the weed control spectrum. Tolerant plants metabolize the active ingredient, whereas susceptible plants do not. Triazines are some of the oldest herbicides, with research initiated on



Fig. 1. Map of the studied area in Italy.

their weed control properties at the beginning of the decade of 1950. Some of their uses are classified as restricted because of groundwater and surface water concerns. Urea herbicides are generally used for weed control in agricultural and non-agricultural practices and, like the triazines, inhibit photosynthesis. They can be very unrelenting in the environment and are often detected in drinking water.

The topography of the ACV is largely flat, and the climate is mainly Mediterranean semiarid and mesothermic. Average annual precipitation ranges from 391 to 584 mm, with intensive rain during October (80–110 mm) and dry summers (6–13 mm in July). The temperature ranges from a minimum of 4°C in January to a maximum of 36°C in July. Most of the soils are calcareous fluvisols with heavy textures in deeper horizons. There are also large areas of calcisols (petric and haplic) containing low levels of organic matter and a high calcium carbonate content; their textures are lighter than those of

Table 2. Monitoring results compared with those of ARPA. Data in µg/l

Monitoring site	Date	Glyphosate ARPA*	Glyphosate UCSC**	Date
Site 1	10.05.2007	0.9	< loq	28.11.2010
Site 2	22.05.2007	0.2	0.252	28.11.2010
Site 3	08.05.2007	0.2	0.163	30.11.2010
Site 4	05.06.2007	0.7	0.525	16.10.2010
Site 5	06.06.2007	1.2	1.375	12.01.2011

\* Agenzia Regionale per la Protezione dell'Ambiente.

\*\* Università Cattolica del Sacro Cuore.

the fluvisols. Less frequent are the luvisol soils, which are favored by citrus farmers. The heavy textures in the deeper horizons of these soils protect the aquifers from non-point source pollution. Regosols and arenosols, with their light textures and low organic matter contents, are also found in the region, but they are not important in citrus-growing areas. The study area (Fig. 2) was selected because it is the only area in the ACV for which both vulnerability maps [8] and data on several monitoring campaigns [20] are available.

There are several studies on the presence of triazines, ureas, and other pesticide families in the surface water, groundwater, and air of the ACV. Pesticide concentrations in groundwater depend on many factors, such as crop and soil type, weather, season, degradation rates in the environment, the physical and chemical characteristics of the pesticide, the application rate, and management practices.

In the ACV, one of the most important citrus cultivation sites of Southern Europe, the presence and changes over time of pesticide residues in groundwater have been monitored. Several wells representing the different types of aquifers present in this area were monitored during two sampling periods, in 2000 and 2003 [20]. In 2000, 50 pesticides and TPs were included in the monitoring. In 2003, the analyses focused on the compounds most frequently detected in the previous monitoring, mainly herbicides and their TPs. Simazine, terbuthylazine, terbumeton, terbutryn and diuron were frequently found at concentrations  $\geq 0.1 \mu\text{g/l}$  in most of the samples collected during both sampling periods. There are also data on the pesticides present in the inhalable fraction of particulate matter  $10 \mu\text{m}$  or less in diameter ( $\text{PM}_{10}$ ) in stations located in this area. The herbicide terbuthylazine and its metabolites appeared in 75% and 31–60% of the samples, respectively [7].

In this study, a large group of triazines and ureas were monitored in 2012 in superficial waters of the Turia River basin, the most important river of the area, and in groundwaters from two representative wells: well 1, located in Carcaixent, and subject to extensive citrus crop activity, and well 2, located in Alborai. The sampling campaign was carried out from the end of September to the first of October. Atrazine, deisopropylatrazine, deethylatrazine, propazine, simazine, terbumeton, deethyl-terbumeton, deethyl-terbuthylazine, terbuthylazine-2-hydroxy, terbutryn, diuron and isoproturon were monitored.

Twenty-five water samples were collected in clean amber glass bottles from the middle of the river's width. Before sample collection, each bottle was thoroughly rinsed with MilliQ water and then with the same water to be collected.

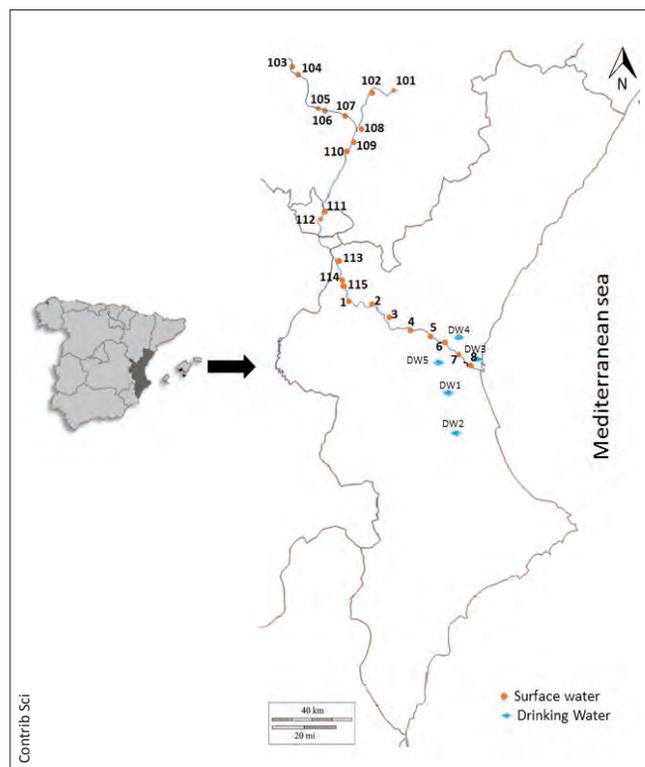


Fig. 2. Location of the studied area in Spain.

All samples were transported to the laboratory (located in Valencia, Spain) in hermetic boxes cooled with ice. In the laboratory, the water samples were stored at  $4^{\circ}\text{C}$  within 24 h to avoid degradation and pre-treated during the 5 subsequent days. Before the analysis, the water samples were vacuum-filtered through  $1\text{-}\mu\text{m}$  glass-fiber filters followed by  $0.45\text{-}\mu\text{m}$  nylon membrane filters (VWR, Barcelona, Spain).

The method used for water extraction was based on the off-line solid phase extraction (SPE) procedure [27]. Briefly, water samples (200 ml) were vacuum-passed through the SPE column (Oasis HLB SPE cartridge 200 mg sorbent/6 ml cartridge, Waters, Milford, MA, USA). The cartridges were dried under vacuum for 10 min and the analytes were eluted with 10 ml of dichloromethane-methanol (50:50, v/v). The extracts were evaporated to dryness and reconstituted with 1 ml of methanol.

For chromatographic separation and determination, an HP1200 series liquid chromatograph coupled to an Agilent 6410 triple quadrupole (QQQ) mass spectrometer equipped with an electrospray ionization (ESI) interface was used. Operation in multiple reaction monitoring provided higher sensitivity and selectivity. The data were processed using a MassHunter Workstation Software for qualitative and quantitative analysis (AGL Sciences, Tokyo, Japan).

**Table 3.** Herbicides detected in surface waters in 2012. Data in ng/l

Compounds	Min.	Max.	Mean <sup>1</sup>	Mean <sup>2</sup>	Freq. (%)
TRIAZINES					
Atrazine	< LOD	< LOD	< LOD	< LOD	–
Deisopropylatrazine	< LOD	< LOD	< LOD	< LOD	–
Deethylatrazine	1.38	3.95	0.79	2.50	73
Propazine	< LOD	< LOD	< LOD	< LOD	–
Simazine	13.89	13.89	0.63	13.89	5
Terbumeton	< LOD	< LOD	< LOD	< LOD	–
Deethyl-terbumeton	1.43	6.76	0.45	3.29	14
Terbuthylazine	4.01	8.15	2.12	6.14	41
Deethyl-terbuthylazine	10.65	14.86	0.48	12.76	9
Terbuthylazine-2-hydroxy	1.77	7.83	0.75	3.81	36
Terbutryn	4.98	4.98	0.00	4.98	5
UREAS					
Diuron	< LOD	< LOD	< LOD	< LOD	–
Isoproturon	3.39	3.53	0.15	3.46	9

LOD = limit of detection.

<sup>1</sup>Mean value considering not detected as zero.

<sup>2</sup>Mean value of those samples that presented the pesticide.

## Results

**Italy.** The results for the four wells are summarized in Table 2. They confirm the findings of the ARPA obtained during the 2007 monitoring campaign, in which the persistence of groundwater contamination by glyphosate was demonstrated. The results of the analytical method adopted in this study were comparable with those obtained using the ARPA method, particularly regarding the limit of quantification (LOQ) and recovery values.

The data for the four wells provided evidence of the existence of localized hot spots of contamination in the area. However, the analysis of water from additional wells in the same catchment where glyphosate was not detected confirmed that groundwater contamination is not generalized.

**Spain.** The results obtained for the surface water and groundwater samples are shown in Tables 2 and 3. They confirm the previous findings determined for this area, in which several triazines and ureas were detected in surface waters (indicative of their use in the area).

## Discussion

Glyphosate, as showed in different studies, is a strongly sorptive and rapidly degrading compound. On the basis of its sorption properties and given its high adsorption constants ( $K_{oc}$  or  $K_f$  values) it can be considered immobile in soil [34]. The chemical-physical characteristics are supported by the groundwater monitoring results showing a low-level occurrence of glyphosate in Europe [34]. However, in Catalonia the detected concentrations were above the legal limit of 0.1 µg/l [30]. Together with the chemical-physical properties of the active ingredient, which affect its leaching and degradation capacities, the results of the monitoring campaign will help to shed light on the processes that may be responsible for well contamination. Site inspections and evaluations through different approaches are useful to define the susceptibility and the vulnerability of wells to contamination. Vulnerability is the probability of a pollution event occurring, and it is a part of the risk assessment processes. At present, in Lombardy, mapping of the vulnerabilities to pesticides has yet to be carried out, but there are good intrinsic vulnerabil-

ity maps for the evaluation of nitrate vulnerability. These maps can provide useful information for a preliminary investigation. The intrinsic vulnerabilities of the selected aquifers are defined using index-based methods in which different variables are empirically combined to produce a vulnerability index. In Lombardy, the index is obtained by integrating data on the hydrogeological vulnerability and soil protective capacity towards groundwater. The latter describes the soil's ability to control the transport of soluble pollutants from deep percolation waters into subsurface water resources and is a key element for assessing the vulnerabilities of aquifers. Soil properties that could influence the soil protective capacity are permeability, depth of the shallow groundwater, particle size, pH, and cation exchange capacity, used as an indicator of the buffering capacity of soils. The hydrogeological vulnerability of an aquifer is essentially linked to the possibility of penetration and propagation of any pollutant in the aquifer itself. The ability of a deposit to be penetrated by a possible pollutant is based on several factors including the thickness and lithology of the unsaturated level [28]. All the contaminated sites examined in this study are situated in southeast of Lombardy, an area characterized by different levels of intrinsic vulnerability, including a high level. The potential vulnerability maps for glyphosate were developed by the regional decision support system, in a GIS environment. They take into account the protective capacity of the soil, the loads distributed, the spatial distribution of crops, irrigation practices and the chemical and physical properties of the compounds under investigation, none of which exceeded the threshold limit except glyphosate. The hydrological vulnerability and in particular the depth to the water table play a key role in the case of glyphosate.

For surface water samples analyzed in Valencia Community, the most detected compounds regarding their frequency were deethylatrazine, terbuthylazine and terbuthylazine-2-hydroxy. The maximum concentration was detected for simazine (13.89 ng/l) and deethyl-terbuthylazine (14.86 ng/l), but their average concentrations never surpassed the 100 ng/l limit established for individual concentrations in drinking water according to EU legislation (2006/118/EC). Note that TPs appear in higher concentrations than the parent compounds because of their long degradation process. In addition, the use of terbuthylazine has increased because it is a substitute for atrazine, a persistent groundwater contaminant banned in the EU in 2004. However, due to its long half-life atrazine may still be present in the environment.

In Spain, the hydrographic confederations have not developed pesticide vulnerability maps, but those existing for ni-

trates [26] provide a general idea of the risk of leaching as a function of soil type. A GIS-attenuation factor/retardation factor model to assess the risk of herbicide leaching in the southern part of the studied area, mostly devoted to a citrus orchard, was also evaluated [8]. The resulting maps identify areas of potential risk in terms of herbicide leaching, with the highest risk posed by terbumeton, bromazil and simazine herbicides.

However, the results of the monitoring campaigns carried out in this study agree only partly with the simulation. In the groundwater samples analyzed, atrazine, terbumeton and terbuthylazine were always detected. The degradation product of terbumeton, deethyl-terbumeton, was always found at higher concentrations than the parent compound. However, in contrast to its predicted behavior as a potential leachate, simazine, although present in surface water, was not detected, perhaps because it is readily degraded under environmental conditions.

## Conclusions

A study was developed to investigate the groundwater concentrations of glyphosate  $\geq 0.1$   $\mu\text{g/l}$  at monitoring sites in southeastern Lombardy. To clarify the causes, site inspection, well status, and site evaluations at areas surrounding wells were carried out and local authorities or the owners of the wells contacted regarding the results, which showed:

- (i) Glyphosate contamination was confirmed at three of the four previously contaminated wells. The findings are comparable with those obtained by ARPA during its 2007 monitoring campaign and confirm the persistence of the contamination. The extreme locations of the three contaminated wells underlines the non-agricultural source of the contamination.
- (ii) The data at the site 4 well were not confirmed, but the well conditions and the adopted management options in areas close to the well could explain the previous contamination. However, the four analyzed wells seem to be mainly contaminated by point sources originating from losses of herbicide near farm houses or from the cleaning of sprayers and trucks in the proximity of the wells. Moreover, the water may have been polluted via the surface waters by bank filtration or infiltration during artificial groundwater recharge, resulting in polluted surface water and unrelated to the active ingredient.
- (iii) Some of the sampled wells did not meet the requirements for groundwater-quality wells. In general, the condi-

tions and positions of the wells were not suitable for the collection of groundwater-quality samples for the assessment of contamination caused by trace levels of PPPs.

A similar study was developed to investigate the findings of triazine and urea herbicides in groundwater of the ACV. The behavior of simazine was other than expected from the vulnerability maps because it is a potential leachate. However, it was detected only in surface water and not in groundwater. Compounds with less leaching potential, such as atrazine or terbuthylazine, were present in groundwater as expected. The concentrations of atrazine metabolites were higher than those of the parent compound, both in surface and in groundwater. The use of atrazine was banned in the EU in 2004 and atrazine was finally retired from the market in 2007 (Decision 2004/248/CE); thus, the presence of this pesticide represents illegal continuation of its use, slow propagation from a reservoir to the water system, and/or its long persistence.

Vulnerability studies have increasingly become an essential part of groundwater protection strategies in the WFD and could represent a valuable tool in environmental management. The analyzed wells differed in their vulnerability although the results obtained in this study were apparently independent of the vulnerability of the soil. This observation confirmed either point source contamination or the infiltration of contaminated surface water as the main cause of the findings in groundwater and the importance of integrating monitoring data and model predictions to underline specific problems linked to poor agricultural practices and territory specificities.

The two studies presented in this article were conducted in two different countries and their results highlight the discrepancy between modeling and monitoring. They also demonstrate the importance of integrating the two approaches to alert decision makers to the need to identify the causes of contamination and then make the most appropriate choices, whether a greater investment in knowledge of the area and quality production data or the application of appropriate mitigation measures. 

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