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First evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture

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HIGHLIGHTS

- Occurrence of PPPs in vineyards groundwater of Tidone Valley was carried out for the first time.
- Stakeholders' engagement was essential for study development and results interpretation.
- Monitoring results revealed the presence of seven PPPs above the EQS_{gw}.
- Sampling time, territorial and wells characteristics significantly influenced PPPs concentration.
- Implementation of BMPs is mandatory to guarantee good groundwater quality in Tidone Valley.

GRAPHICAL ABSTRACT

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ABSTRACT

Agricultural practice often involves an intensive and incorrect use of pesticides and fertilizers. These chemicals can leach through the soil profile and contaminate groundwater, including drinking water. For this reason, an effective groundwater monitoring is strongly advisable.

The aim of this study was to investigate the groundwater contamination by plant protection products (PPPs) on a hilly area situated in the Tidone Valley, North-West of Italy, a region characterized by an intensive viticulture production. This area is not included in the national groundwater monitoring plan and therefore scarce information is available regarding the quality of groundwater, even though the local Environmental Agency previously revealed the occurrence of PPPs at values higher than the Environmental Quality Standard downstream this area. Hence, a monitoring wells network was developed following an upstream-downstream criterion, a list of pesticides to be monitored, based on a multi-actor approach, and an analytical method for PPPs detection and quantification. The analytical approach involved solid phase extraction followed by High-Performance Liquid Chromatography tandem mass spectrometry.

The results of three monitoring campaigns revealed the occurrence of seven PPPs at a level higher than EQS for groundwater (0.1 μg/L) in 30% of the wells. The main pesticides detected were Chlorantraniliprole, Dimethomorph, Fluopicolide, Metalaxyl-M, Penconazole, and Tetraconazole, all commonly used in viticulture, together with S-metolachlor, authorized for cereal cropping. Statistical analysis revealed a significant influence of the sampling time, slope of the soil surrounding the wells, wells depth and wells location on the concentration

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of five PPPs. Therefore, the results obtained show that the improper use of PPPs for grapevine cultivation may cause groundwater contamination and suggest the need for a deeper analysis of territorial reality, including hydrology studies and farmer behavior and for an urgent introduction of best management practices and mitigation measures to promote a sustainable use of PPPs in viticulture.

Abbreviations

ARPAE	Regional Agency for Prevention, Environment and Energy
AUSL	health local agency
EQS	Environmental Quality Standard
GLM	generalized linear model
GUS	groundwater ubiquity score
HPLC-MS/MS	high performance liquid chromatography tandem mass spectrometry
PPP	plant protection product
UPLC-QTOF-MS	ultra performance liquid chromatography quadrupole time of flight mass spectrometry
ANOVA	analysis of variance

1. Introduction

Groundwater constitutes about 30% of the world's freshwater resources. This represents 97% of the freshwater that is potentially available for human use, taking into account that 70% of freshwater resources are frozen (Morris et al., 2003). According to this, groundwater may therefore be the key to sustainability of world water supplies and needs to be managed accordingly. Groundwater is extensively used worldwide for domestic, industrial, and agricultural purposes, and both urban and rural areas rely on groundwater resources to meet their water demands (Postigo and Barceló, 2015; Swartjes and Van der Aa, 2020; Singh et al., 2015).

Moreover, thanks to its excellent biological and physical-chemical characteristics over surface water (rivers and lakes), it is mainly used as a source of drinking water. Nowadays, unfortunately, water is subject to the influence of large quantities of pollutants which cause serious environmental damage. Agriculture has direct and indirect effects on its quality, rates and compositions recharge and aquifer biogeochemistry. In particular, agricultural pollution often involves an excessive and incorrect use of Plant Protection Products (PPPs) and fertilizers which, being to some extent soluble in water, can penetrate into the soil and contaminate groundwater used for drinking (MN Khan et al., 2018; Serpa et al., 2017).

In viticulture the diseases and pest pressure are high and forces winegrowers to an intensive use of PPPs. This spraying of PPPs, however, can have a relevant impact on water quality due to their leaching to groundwater and transfer by runoff, drift and erosion to surface water (Padovani et al., 2004; Vischetti et al., 2008; Laini et al., 2012; Nario et al., 2018). The risk of such events is important in vineyards (Battany and Grismer, 2000; Lamastra et al., 2016), because vine is grown in many areas on slopes to provide grape with a good sunlight exposition and to secure the quality of berries. (Thiollet-Scholtus and Bockstaller, 2015).

The pollution of groundwater by PPPs is governed by the physico-chemical characteristics of the compounds including water solubility, groundwater ubiquity score (GUS) index, their capacity to be retained by soil components and their degradation rate (Herrero-Hernández et al., 2013). The GUS index is one of the most used indicators for screening the PPPs potential of leaching in groundwater since 2000 (Trevisan et al., 1999; Padovani et al., 2004). Furthermore, over the physicochemical characteristics, also soil characteristics, soil slope and rainfall frequency and intensity can influence the groundwater contamination after PPPs spraying. Indeed, the lower is the slope, the higher is the risk of leaching to groundwater. Precipitations, however, can dilute the groundwater within the wells and therefore the contamination may depend on the sampling period.

Moreover, the retention of a PPP by soil can prevent its short-term access to ground or surface waters and its effects on non-target organisms, but the persistence of the un-degraded pesticide or of harmful metabolites constitutes a cumulative – risk to the environment and thus to human health (Arias-Estévez et al., 2008).

In fact, it has been estimated that <0.1% of the pesticide applied to crops actually reaches the target pest; the rest enters the environment, contaminating soil, air and waterbodies (Pimentel and Levitan, 1986).

Pesticides slowly start dissipating after these are sprayed. If the conditions of good agricultural practice (GAP) such as applicable doses of the PPP and the time interval between applying the pesticide and harvesting the crop are not met, harvested crops may contain unacceptable levels of pesticide residues (Gonzalez-Rodriguez et al., 2011).

In that regard, different international regulatory bodies such as the European Union (EU), the United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) established maximum allowed concentrations for PPPs in drinking water (Donato et al., 2015) that in most of the cases corespond to the Environmental Quality Standards for groundwater (EQS_{gw}; equal to 0.1 μg/L and 0.5 μg/L, respectively for the single substance and for the sum of the substances), established by Directive 2006/118/EC (EC, 2006). This, even if the regulatory framework governing the placing on the market of PPPs, as well as aspects of their use, shape the conditions of their use on a sustainable way, through the EC Regulation No. 1107/2009 (EC, 2009a), that bases the placing of pesticide products on the market on the demonstration that their use complies with defined protection goals guaranteeing a high level of safety for humans and the environment and the Directive 2009/128/EC (EC, 2009b) also called the "Sustainable Use Directive" that extend the set of measures that, from the training and certification of users to the control of application machines and the development of effective alternative methods, should improve the safety level over the whole process (Alix and Capri, 2018). Despite of the well-defined regulatory framework, in general monitoring data from EU Member States show a diffuse pollution of surface and groundwater in several countries (SOeS, 2015; Stone et al., 2014; Petersen et al., 2012). The national monitoring plans aim to identify issues not adequately foreseen by the regulatory framework (ISPRA, 2018). In Italy the Institute for Environmental Protection and Research (ISPRA) is responsible for technical management and assessment of the monitoring. Analytical investigations are carried out by the territorial Agencies and are transmitted to the Institute, in accordance with the provisions of the Directive 2009/128/EC (EC, 2009b) and the relevant National Action Plan (DM 35/2014) (MIPAAF, 2014). However, the national monitoring network is planned to cover the institutional bodies of water, foreseen by the application of the Dir. 2000/60/CE (EC, 2000) and national application decrees that not always considers adequately local stressor realities.

In this context, the main objective of this study, part of the H2020 WaterProtect Project, is to investigate the groundwater contamination by PPPs in a hilly area situated in the Tidone Valley, Province of Piacenza, North-West of Italy, and characterized by an intensive viticulture production. In this area the groundwater wells of the institutional monitoring network are too rarefied and in positions unsuitable to adequately represent the underlying and potentially impacted aquifers. Nonetheless, downstream this area the Local Environmental Agency (ARPAE) revealed the presence of nitrates and pesticides at values higher than the Environmental Quality Standard (EQS) (data not shown). In more detail, the study aims to (i) develop a specific monitoring wells network directly in the field, in the middle of the vineyards, limiting the distance of the points and following an upstream-downstream criterium (ii) establish a list of PPPs to be monitored, following a multi-actor and analytical screening approach (iii) develop an analytical method for pesticides detection and quantification at levels below the EQS_{gw} and (iv) provide a first screening of the groundwater contamination by PPPs used in grapevine cultivation.

2. Materials and methods

2.1. Study area

Tidone Valley is placed in the North-West of Italy, Emilia Romagna Region, Province of Piacenza, and is characterized by a mix of urban, peri-urban and rural areas (Fig. 1). The area covers five municipalities: Ziano Piacentino (http://www.comune.ziano.pc.it/), Castel S. Giovanni (http://www.comune.castelsangiovanni.pc.it/), Alta Val Tidone (http://www.comunealtavaltidone.pc.it/hh/index.php), Pianello Val Tidone (http://www.comunepianellovaltidone.it/hh/index.php), and Borgonovo Val Tidone (http://www.comune.borgonovo.pc.it/) for 29.462 inhabitants and 455 declared farms. It is a hilly zone characterized by an elevation level between 100 and 350 above sea level and it is renowned for the deeply rooted tradition and vocation to viticulture. The main cultivation is vineyard, with 2941 ha in 2016 (ISTAT, 2016; http://dati.istat.it/Index.aspx?DataSetCode=DCSP_COLTIVAZ).

The study area (Action Lab) covers 206.72 km^2 and includes part of Tidone Torrent catchment and the catchments of the two streams Lora-Carogna and Carona-Boriacco. Tidone Torrent and Lora-Carogna and Carona-Boriacco streams are three tributaries of the right hydrographic bank of the Po River.

2.2. Development of the sampling network

Considering that the study area is a hilly area with a slope between 1.7 and 8.9° and aiming to highlight the impact of pesticides treatment, a *criterium* for wells individuation and selection was developed. The wells were selected taking into consideration the upstream and downstream of the small water bodies crossed by tributaries (*vallicola*) of *Tidone Torrent* and of two Streams *Lora-Carogna* and *Carona-Boriacco*, where the vineyards are treated with pesticides and fertilizers (Fig. 2). The upstream well should be the one no contaminated while the downstream well should collect all the residues of the treatments due to runoff at soil surface and transport of surface water body and drainage to groundwater.

Based on this criterium 26 wells have been selected for the monitoring network, coded from WP01 to WP32 and including 3 wells used for drinking water and part of Regional Environmental Agency (ARPAE) and the water supplier company (IRETI) networks (Table 1).

Fig. 3 shows the selected sampling sites, distinguishing between upstream and downstream wells based on the abovementioned criterium.

2.3. Development of PPPs list to be monitored

The list of PPPs to be monitored has been established following a multi-actor and analytical screening approach: (i) stakeholder consultation with the farmers and other actors involved in water use and governance of the area, (ii) results from an untargeted analysis of groundwater samples, (iii) consultation with technical experts from PPPs regional service and (iv) pesticides physico-chemical characteristics: GUS index, soil organic carbon-water partitioning coefficient (K_{oc}), half-life in soil (DT50) and water solubility.

2.3.1. Stakeholders consultation

The scope of stakeholder consultation was to collect information about PPPs with high volume of use by farmers, high probability to be find in groundwater, based on existing PPP occurrence data in groundwater and surface water of the entire province and high toxicity. In

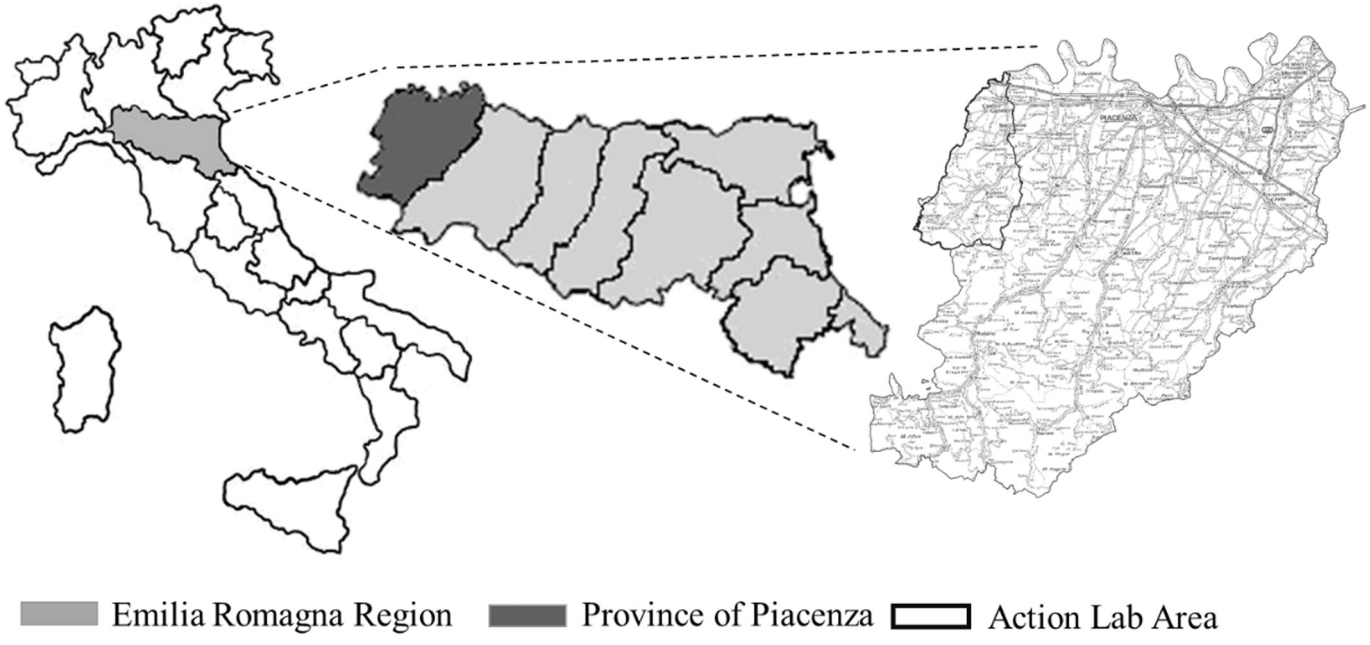

Fig. 1. The Action Lab area, an intensive viticulture region in North-Western Italy.

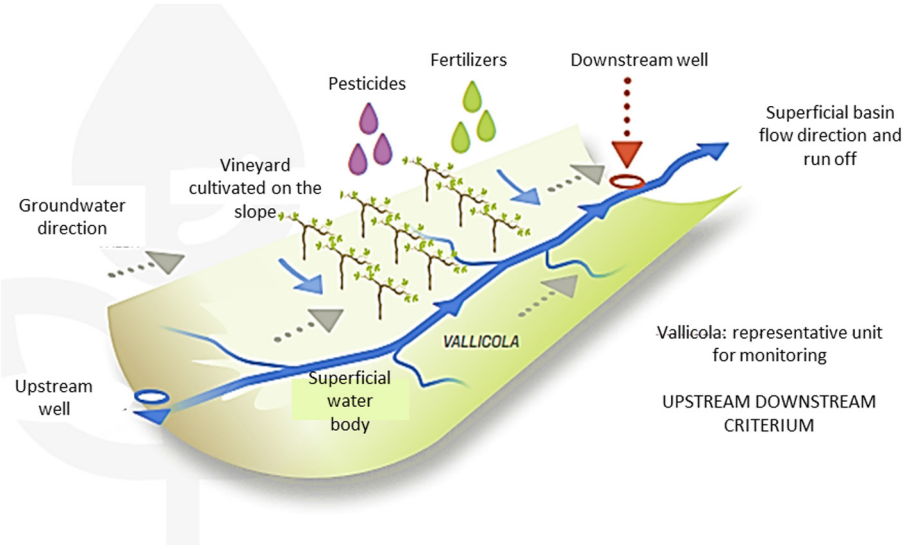

Fig. 2. Upstream-downstream criterium. Representation of the *criterium* for wells selection, with groundwater flow considered from south-west to north-east.

order to reach the scope, survey campaigns were carried out and six stakeholder categories involved: farmers (175, farmers, 97 of them are members of the local Social Winery Vicobarone), farmers associations (Confagricoltura, Coldiretti and CIA), environmental local agency (ARPAE), reclamation authority (Consorzio di Bonifica di Piacenza), water supplier company (IRETI) and local Health Agency (AUSL).

2.3.2. Untargeted analysis

In order to investigate the occurrence of pesticides in groundwater and obtain a general picture of land use, an untargeted analysis was carried out on groundwater sampled in the Action Lab area during November 2017–May 2018 for a total of 32 samples. However, 26 of these samples were then used for target analyses. The untargeted screening was done through ultra-performance liquid chromatography coupled to quadrupole-time-of-flight mass spectrometry (UPLC-QTOF-MS). Briefly, reverse phase gradient chromatography was used for separation and a data-independent tandem mass spectrometry adopted for detection. Compounds annotation was achieved using at least three fragment ions. The description of samples preparation and analysis is fully detailed as supplementary material.

2.3.3. Expert judgement

The scope of expert judgement consultation was to collect data on PPPs with the highest use and sale in the study area. The expert judgement consultation is a technique in which judgement is made based on the competences acquired in a particular area of knowledge. This knowledge base can be provided by a key member of the project team. In this case the key member is a representative of Provincial Phytosanitary Consortium, support partner of the WaterProtect Project.

Table 1
Network wells description.

Well	Municipality	Upstream/downstream	*Vallicola*	Depth (m)	Soil Slope (°)
WP01	Ziano	Downstream	Rio Gatto	2.0	6.4
WP03	Ziano	Upstream	Rio del Volto	6.0	3.2
WP04	Ziano	Downstream	Rio Lora	0.0	2.7
WP05	Ziano	Downstream	Rio Valle	3.0	0.0
WP06	Ziano	Upstream	Rio Valle	7.0	7.8
WP07	Ziano	Upstream	Rio Battilana	34.0	2.3
WP08	Castel San Giovanni	Downstream	Rio Battilana	30.1	5.1
WP09	Ziano	Downstream	Rio Guarone	6.2	8.3
WP10	Ziano	Upstream	Rio Guarone	9.0	4.7
WP11	Ziano	Upstream	Rio Bardonazzo	5.7	5.4
WP13	Ziano	Downstream	Rio Caroncella/Bardonazzo	5.4	7.8
WP14	Ziano	Upstream	Rio Montalbo	4.5	7.9
WP15	Ziano	Downstream	Rio Montalbo	4.6	2.8
WP17	Pianello Val Tidone	Upstream	Rio Lisone	11.5	5.4
WP18	Pianello Val Tidone	Downstream	Rio Lisone	3.5	5.7
WP19	Alta Val Tidone	Action lab upstream/drinkable	Rio Gualdora	0.0	8.8
WP20	Castel San Giovanni	Action lab downstream	Rio Ganaghello	117.0	1.7
WP21	Pianello Val Tidone	Drinkable	Torrente Tidone	11.0	3.2
WP22	Ziano	Upstream	Rio Lora	5.4	7.9
WP24	Ziano	Upstream	Rio Gatto	3.7	8.9
WP25	Ziano	Upstream	Rio Caroncella	11.2	7.6
WP26	Borgonovo Val Tidone	Upstream	Rio Carona	8.8	1.7
WP28	Ziano	Downstream	Rio Bardonazzo	5.0	2.4
WP29	Ziano	Upstream	Rio del Volto	2.9	5.8
WP30	Ziano	Downstream	Rio del Volto	7.8	2.9
WP32	Ziano	Downstream/drinkable	Rio Carona	15.0	1.7

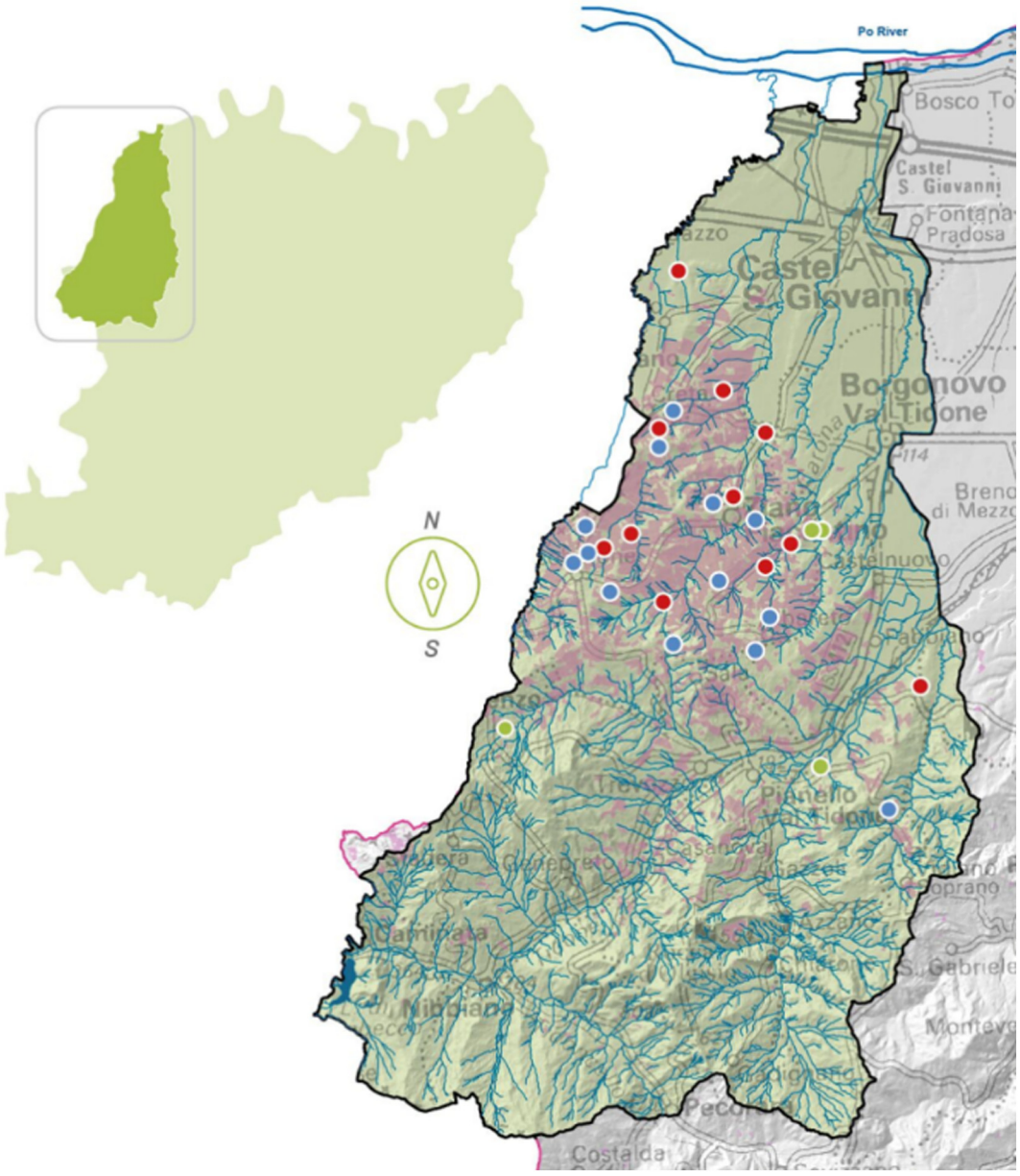

Fig. 3. Map of the wells network. Blue - upstream wells, red – downstream wells, green - drinking water wells. In pink the area with grapevine cultivation.

All the obtained information, in form of lists of PPPs, were then compared with the indications given by the integrated pest Management guidelines of Emilia - Romagna Region (http://agricoltura.regione.emilia-romagna.it/produzioni-agroalimentari/temi/bio-agro-climambiente/agricoltura-integrata/disciplinari-produzione-integrata-vegetale/Collezione-dpi/2019/norme-generali-2019) for the active ingredients authorized for grapevine cultivation and the most recent data concerning the active ingredients quantity sold in Emilia Romagna Region, and the list of PPPs to be monitored was established.

2.4. Reagents and standards

Methanol and acetonitrile HPLC grade were purchased from Carlo Erba reagents S.R.L (Milan, Italy). Formic acid was purchased from Sigma-Aldrich S.R.L. (Milan, Italy). SPE Bond Elut PPL cartridges were purchased from Agilent Technology (Milan, Italy). Pesticide standards were supplied by VWR International S.R.L. (Milan, Italy). Individual stock solutions (100 mg L^{-1}) of each analyte was prepared in methanol and then mixed standard solutions (5, 2.5, 1, 0.5, 0.1, 0.05, 0.025, 0.010, 0.001 mg L^{-1}) of all analytes were prepared in methanol.

2.5. Groundwater sampling and instrumental analysis

Sampling of the 26 network wells was carried out between November 2017 and September 2018. The samples were collected in triplicate and filled into 1500 mL plastic bottles after well flush out. All bottles were kept at −28 °C until analysis. Before SPE extraction, the samples were thawed at room temperature and three aliquots of 500 mL were filtered with a bottle-top vacuum filtration unit through a glass microfiber filter (1.6 μm average pore size, 90 mm diameter, 0.26 mm thickness) into 500 mL glass flasks.

A method based on solid phase extraction from groundwater, suitable for the selected PPPs, and their analysis through HPLC-MS/MS, was then developed following the Guidelines for the detection of Residues for post-registration control and monitoring, proposed by

European Commission (https://ec.europa.eu/food/plant/pesticides/approval_active_substances/guidance_documents_en; https://esdac.jrc.ec.europa.eu/projects/focus-dg-sante) (EC, 2010).

Shortly, several types of cartridges and absorbents were chosen and tested, based on the sorbent characteristics, properties of the selected pesticides and literature search. SPE cartridges tested for the recovery tests were Oasis HLB, Bond Elut ENV, Bond Elut PPL and C18. After several recovery test the cartridge that showed the highest recovery for all selected pesticides (recovery between 41% and 103%) was PPL cartridge (styrene-divinylbenzene adsorbent), whereas the elution solvent was methanol.

For the analysis of the extracts, a 1200 series liquid chromatograph system equipped with quaternary pump, electrospray ionization system and coupled to a G6410A triple quadrupole mass spectrometer detector (all from Agilent technologies, Santa Clara, CA, USA) was used. The chromatographic separation was achieved on a EC-C18 column (4.6 × 100 mm, 2.7 μm, Agilent technologies, Milan, Italy) using ultrapure water with 0.1% formic acid (phase A) and 0.1% formic acid in methanol (phase B) as mobile phases. Injection volume was 20 μL, run time was 30 min and the flow rate was 0.2 mL/min. The proposed method was validated by evaluating linearity, matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability). The linearity was evaluated through the coefficient of determination (R^2) of the analytical curves at concentration levels between 1 and 2500 μg/L. The solutions for instrumental calibration were prepared in methanol. Matrix effect was calculated comparing the slope of curves prepared in solvent and in the blank extract. Precision was evaluated in terms of repeatability and intermediate precision, by estimating the relative standard deviation (RSD) of the recovery percentage for each spiked level. The LOD and LOQ were calculated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1. The complete description of the analytical method and the results of recovery test are presented in the supplementary material.

2.6. Statistical analysis

The normal distribution of the data was verified by using UNIVARIATE procedure (SAS Inst. Inc., Cary, NC; release 8.0) by NORMAL option. Data were not normally distributed, and a log normal transformation was applied to satisfy normality and homogeneity of variance assumptions underlying linear models. Through the text, in tables and graphs, the average data were presented in their original scale, whereas pooled error terms (i.e., root means square error or √MSE) were associated to log normal transformed data (Petrie and Watson, 2006). Two experimental designs have been elaborated. One experimental design corresponded to a completely randomized design with a 2 × 3 × 4 factorial arrangement of treatments. A generalized linear model (GLM procedure) was applied to *log* transformed data and main tested effects in the model were the location of the wells (Stream, $n = 2$; upstream vs downstream), the wells depth (Deep, $n = 4$) and the sampling period (Period, $n = 3$). First and second order interactions of main tested effects were also included in the model.

The second experimental design corresponded to a completely randomized design with a 2 × 3 × 2 factorial arrangement of treatments. Also in this case a GLM procedure was applied to *log* transformed data and the tested effects were the location of the wells (Stream, n = 2; upstream vs downstream), the degree of the slope of the soil in which the wells are located (Slope, n = 2) and the sampling period (Period, n = 3).

In particular, the sampling periods considered were November 2017, July 2018 and September 2018, whereas two slope levels were defined, slope level I, with a slope between 0 and 3° and slope level II, with a slope > 3°. Based on the wells depth, four levels were defined, level I, with a depth < 6 m, level II, with a depth between 6 and 10 m, level III, with a depth between 10 and 15 m and level IV, with a depth > 30 m.

3. Results and discussion

3.1. PPPs selection for groundwater monitoring

In order to define the final list of PPPs to be monitored in groundwater, thus highlighting the impact of viticulture on groundwater pollution, the results from untargeted analysis, the stakeholders' consultation and expert judgement outcomes and the PPPs' physico-chemical characteristics were considered.

The untarget analysis showed the presence of fourteen PPPs in the groundwater samples: five insecticides (Chlorantraniliprole, DEET, Dimetan, Pirimicarb, Trimethacarb), three herbicides (Defenuron, Glufosinate, Isopropalin) and five fungicides (Dimethirimol, Dimethomorph, Fluopicolide, Isopamphos, Metalaxyl-M). Among the insecticides and the herbicides found, three were revoked from the market (not longer authorized as pesticides): DEET (Diethyltoluamide), Dimetan and Isopropalin. Furthermore, untargeted analysis revealed the occurrence of other chemicals such as PPPs metabolite products, pharmaceuticals, anthelmintic, rodenticides, molluscicides, bronchodilatators and surfactants. Table 4S in supplementary material reports all the chemicals found by the untargeted analysis and the physico-chemical properties and GUS index for each PPP detected.

The outcomes of stakeholders and expert judgement consultation produced a list of twenty-one PPPs, with high interest for the local stakeholders and high use on the territory (Tables 5S and 6S in the supplementary materials). In particular, farmers and other stakeholders indicated seven herbicides (Acetolachlor, Flufenacet, Isopropalin, Metsulfuron-methyl, S-metolachlor, Terbuthylazine and Tribenuron-methyl), two insecticides (Chlorantraniliprole and Parathion-methyl) and two fungicides (Benomyl and Fluopicolide), whereas the expert judgement consultation indicated three insecticides (Chlorpyrifos, Chlorpyrifos-methyl and Thiamethoxam) and six fungicides (Cyflufenamid, Cyprodinil, Mancozeb, Metiram, Penconazole and Tetraconazole) as high used pesticides on the study area. Tables 5S and 6S in the supplementary material show their physicochemical properties and GUS Index.

For what concern the physicochemical properties of the pesticides previously detected/indicated by the stakeholders, the dissipation of a substance is usually expressed through the DT_{50} and contributes, in combination with the K_{oc}, to the leaching potential through the GUS index: $GUS = \log(DT_{50}) \times [4 - \log(K_{oc})]$. This is an empirical index and represents a potential indicator since environmental conditions are not considered. GUS values higher than 2.8 indicate that the leaching of the substance is probable, while this is not likely to happen with GUS values <1.8. Intermediate values point indicates a limited leaching potential. The partition coefficient K_{oc} is expressed on the basis of the organic carbon content of the sediment. This parameter gives indications on the chemical compound's ability to bind to the soil according to its characteristics. The higher value represents the stronger tendency to be tied to the ground, while the lower value represents the greater tendency to move with percolation water. The half-life of the pesticides in the soil (soil DT_{50}), expressed in days, indicates the time in which the substance is halved compared to the initial concentration: greater is the value, more persistent is the substance in the soil. For this last parameter, three different values are provided: laboratory, field and typical. The typical value is that reported in the literature and it is often the average of all field and laboratory studies. (Vassiliou, 2016).

Therefore, merging all the information obtained from the untargeted analysis, the outcomes of stakeholders and expert judgement consultation, the physicochemical properties (K_{oc}, DT_{50} and water solubility) and finally the GUS Index, the pesticides list showed in Table 2 was selected. Higher priority was given to the PPPs authorized for grape

Table 2
List of PPPs to be monitored.

Compound name	Type	GUS index[a]	K_{oc}[a] (mL/g)	DT50[a] (days)	Water solubility[a] (mg L^{-1})
Chlorpyrifos	Insecticide	1.04	5509	27.6	1.05
Chlorpyrifos-methyl	Insecticide	0.92	4645	12	2.74
Chlorantraniliprole	Insecticide	4.22	362	204	0.88
Cyflufenamid	Fungicide	1.85	1592	25.3	0.52
Cyprodinil	Fungicide	1.11	2277	45	13
Dimethomorph	Fungicide	2.56	348	44	28.95
Flufenacet	Herbicide	2.02	401	39	51
Fluopicolide	Fungicide	3.63	321.1	138.8	2.8
Isopropalin	Herbicide	0.00	10,000	100[b]	0.11
Metalaxyl-M	Fungicide	1.71	78.9	14.1	26,000
Metsulfuron-methyl	Herbicide	3.99	12	13.3	2790
Penconazole	Fungicide	1.36	2205	90	73
S-metolachlor	Herbicide	1.91	226.1	21	480
Tetraconazole	Fungicide	1.81	1152	430	156.6
Tribenuron-methyl	Herbicide	2.4	35	3.6	2483

[a] Lewis et al. (2016). An international database for pesticide risk assessments and management. International Journal of Human and Ecological Risk Assessment.
[b] Typical value in the above database.

cultivation and with high number of treatments, following the integrated pest Management guidelines of Emilia - Romagna Region. It consists in three insecticides (Chlorantraniliprole, Chlorpyrifos and Chlorpyrifos methyl), used on grapevine against *Eupoecilia ambiguella*, seven fungicides (Cyflufenamid, Cyprodinil, Dimethomorph, Metalaxyl-M, Penconazole, Tetraconazole, Fluopicolide) used on grapevine against downy and powdery mildew, *Ascomycetes*, *Basidiomycetes*, *Deuteromiceti*, *Septoria* and *Rhynchosporium*, and five herbicides (Flufenacet, Isopropalin, Metsulfuron-methyl, S-metolachlor, Tribenuron-methyl) not authorized for grapevine cultivation but commonly used for cereals in conventional farming. Indeed, the selected herbicides were included in the final list (Table 2) in order to assess a possible inappropriate use for grapevine cultivation or a possible impact of cereals cultivation. The ISTAT data, elaborated by AAAF (Gruppo di lavoro Fitofarmaci) group, concerning the active ingredients quantity sold in Emilia Romagna Region in 2012 (no other recent data available) confirm the high use of Chlorpyrifos, S-Metolachlor, Dimethomorph, Chlorpyrifos-methyl, Cyprodinil, Metalaxyl-M, Chlorantraniliprole, Fluopicolide, Penconazole, Flufenacet, Tetraconazole, Metsulfuron-methyl and Cyflufenamid, with values ranging between 16 kg (Cyflufenamid) and 117,069 kg (Chlorpyrifos) (http://www.appa.provincia.tn.it/fitofarmaci/programmazione_dei_controlli_ambientali/Criteri_vendita_prodotti_fitosanitari/pagina123.html).

Based on the physicochemical properties and GUS Index, Chlorantraniliprole, Fluopicolide and Metsulfuron-Methyl are the compounds with the highest leachability potential, while Chlorpyrifos, Chlorpyrifos-Methyl, Cyprodinil, Isopropalin, Metalaxyl-M and Penconazole have the lowest leachability potential. The other six selected pesticides, Dimethomorph, Flufenacet, S-metolachlor, Tetraconazole and Tribenuron-Methyl, are classified as compound with limited leaching potential. Concerning their persistence in soil, the PPPs with the highest persistence are Chlorantraniliprole, Fluopicolide, Isopropalin and Tetraconazole, while the non-persistent compounds are Chlorpyrifos, Chlorpyrifos-Methyl, Cyflufenamid, Metalaxyl-M, Metsulfuron-Methyl, S-metolachlor and Tribenuron-Methyl. Cyprodinil, Dimethomorph, Flufenacet and Penconazole have a moderately persistence in soil.

3.2. PPPs occurrence in groundwater

An HPLC-MS/MS analysis was applied in order to determine the occurrence of PPPs in groundwater samples from the 26 wells, and to gain insights onto the possible impact of viticulture on groundwater quality. The results of the groundwater analysis of three monitoring campaigns (November 2017, July 2018 and September 2018) revealed the occurrence of seven pesticides at a level higher than EQS for groundwater (0.1 μg/L), in 30% of the wells. The PPPs found were: Chlorantraniliprole, Dimethomorph, Fluopicolide, Metalaxyl-M, Penconazole, S-metolachlor and Tetraconazole. The most critical pesticides were Metalaxyl-M, Fluopicolide and Penconazole with a presence in groundwater of 71%, 38% and 29%, respectively (Fig. 4). All these PPPs are fungicides commonly used in viticulture, while the herbicide S-metolachlor, which is not authorized for the cultivation of the grapevine, was found in wells surrounded by cereal crops. The pesticides Chlorpyrifos Chlorpyrifos-methyl, Cyflufenamid, Cyprodinil, Flufenacet and Isopropalin were at no time found in the groundwater samples.

In particular, in the first monitoring campaign, carried out in November 2017, the pesticides Chlorantraniliprole, Fluopicolide, Metalaxyl-M, Penconazole and S-Metolachlor were found at a concentration above the EQS in 6 wells out of 26. In the second monitoring campaign, carried out in July 2018, the pesticides Chlorantraniliprole, Dimethomorph, Fluopicolide, Metalaxyl-M, Penconazole, S-metolachlor and Tetraconazole were found at concentrations above the EQS in 11 out of 26 wells, whereas in the third monitoring campaign, carried out in September 2018, only the pesticides Fluopicolide, Metalaxyl-M and Penconazole were found at concentrations above the EQS in 5 out of 26 wells. The period with the highest number of wells having concentration of PPPs above the EQS was July 2018. Indeed, this period is just after the period of application for pesticides. Normally, almost 95% of pesticide treatments for grape protection have been already carried out by that date (expert judgement). The wells with concentrations of PPPs higher than EQS in all three monitoring campaigns were well WP09, well WP13, well WP14, well WP15, well WP17, well WP 22, well WP 28 and well WP 30. Fig. 5 shows the concentration levels of the pesticides that exceed the EQS, for all the wells (expressed only with the number that characterized the code) and the three sampling campaigns.

Based on the physico-chemical properties and GUS Index, Metalaxyl-M, Penconazole, S-metolachlor and Tetraconazole are not persistent in the soil and have a low leaching potential (1.71; 1.36; 1.91; 1.81), making them unlikely to be found in groundwater. On the contrary, Chlorantraniliprole, Fluopicolide and Dimethomorph are compounds with high persistence in soil and high leaching potential (4.22; 3.63; 2.56). However, further study on territorial hydrology, discussed by Suciu et al. (2020, under submission in this special issue), highlighted that for a sub-area of 7 km^2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25), the occurrences and concentrations of PPPs are due to both point and diffuse contamination sources, but the position of the well in the territorial context may help to discriminate which of the two sources is the most influent.

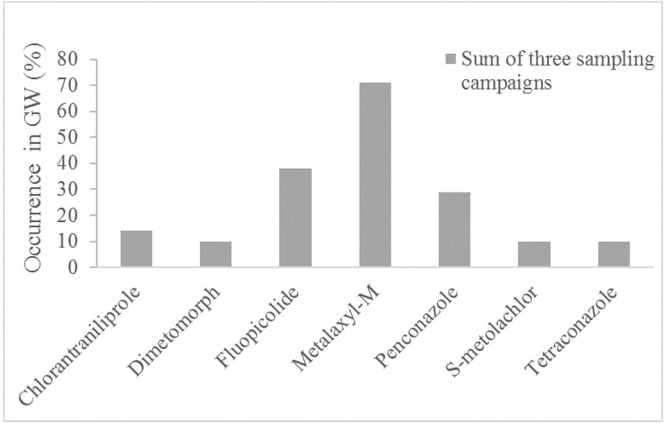

Fig. 4. % of groundwater samples above EQS during the three sampling campaigns.

Several studies were conducted on the impact of viticulture on groundwater, surface water or soils (Pose-Juan et al., 2015; Hildebrandt et al., 2008; Herrero-Hernández et al., 2013). The study of Pose-Juan et al. (2015), about the PPPs occurrence in vineyard soils in Spain, showed the presence in soil of herbicides, fungicides and insecticides typically used in viticulture, with the highest number detected in June. One of the highest concentrations was determined for the fungicide Metalaxyl, at a value of 11.5 μg/kg. Furthermore, the study revealed

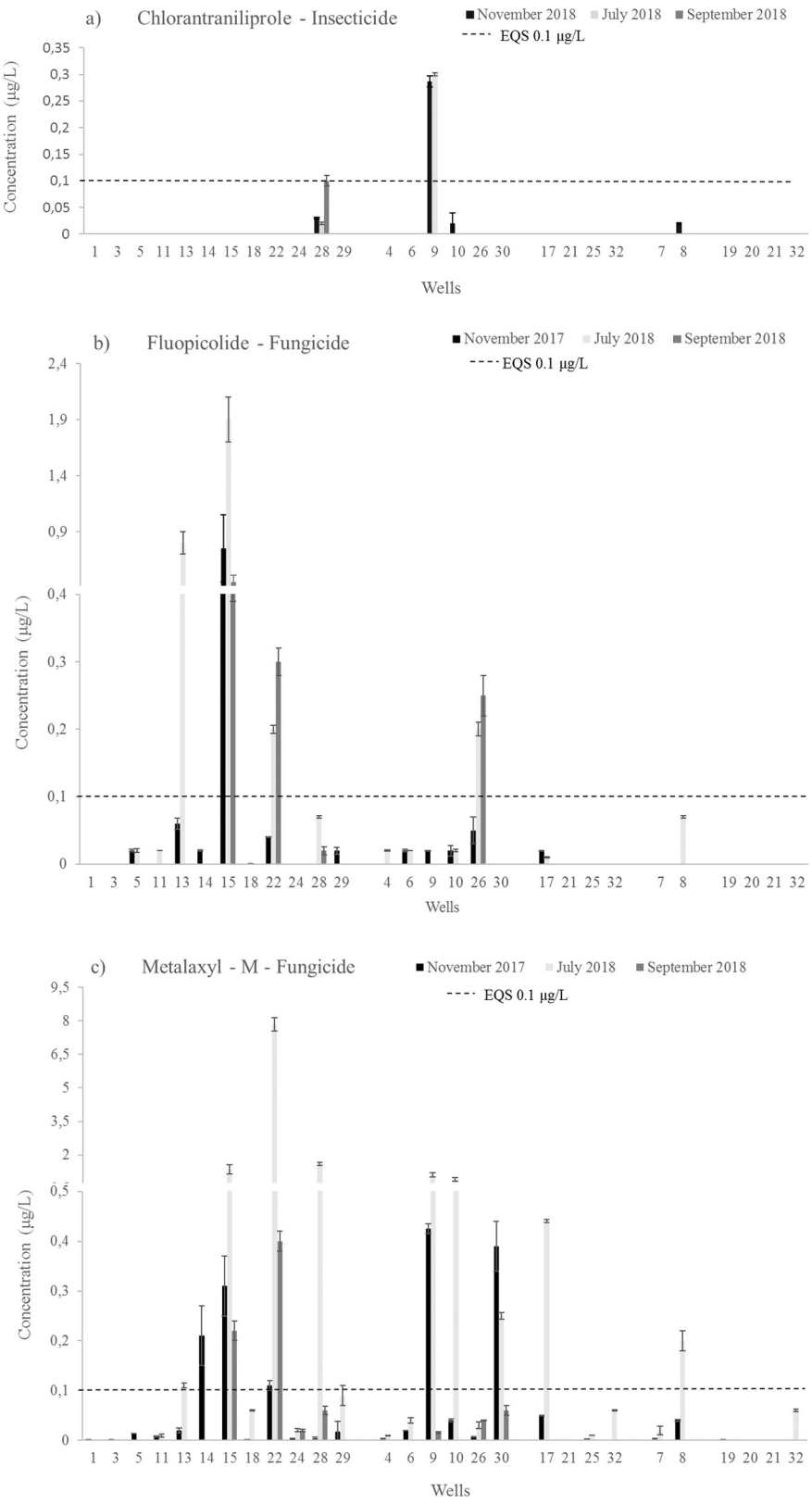

Fig. 5. Concentration (μg/L) of the pesticides that exceed the EQS during the three sampling campaigns; a) Chlorantraniliprole, b) Fluopicolide, c) Metalaxyl-M, d) Penconazole, e) S-metolachlor, f) Tetraconazole and g) Dimethomorph.

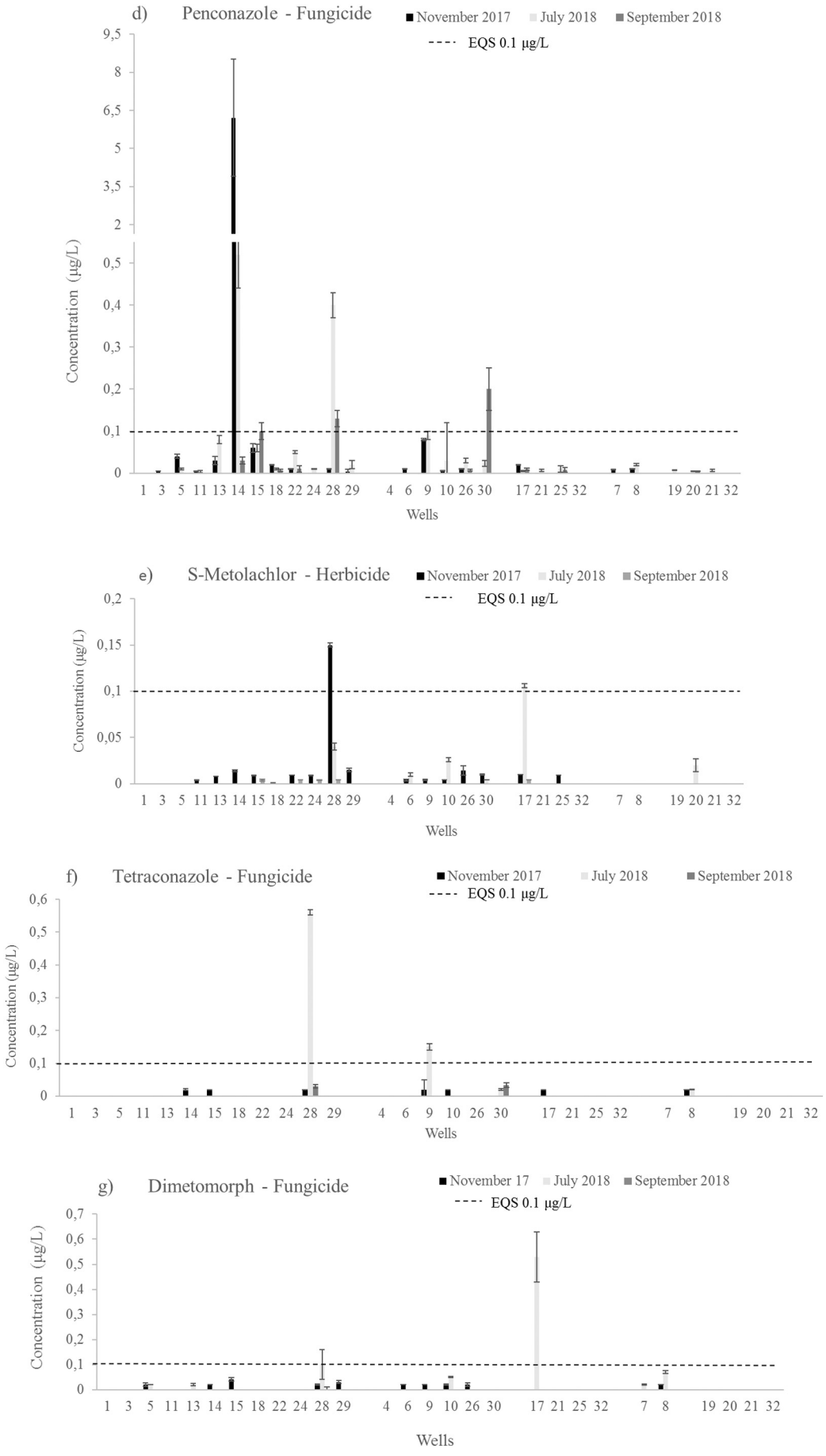

Fig. 5 (*continued*).

a more intensive use of herbicides in March, while the use of insecticides and fungicides may depend on the specific needs of crops and/or the onset of diseases. Their results were consistent with the residues found in groundwater in that region (Herrero-Hernández et al., 2013). Four of the forty-seven PPPs analyzed in the Spanish study are common with the present study: Chlorpyrifos, Cyprodinil, Dimethomorph and Penconazole, while for S-metolachlor and Metalaxyl – M, analyzed in the present study, the enantiomers Metalaxyl and Metolachlor were searched in Spanish groundwater. Metalaxyl, Penconazole, Dimethomorph and Metolachlor were found in 50%, 46%, <5% and <15%, respectively, of Spanish ground water samples, with the highest concentration of Metalaxyl and Penconazole equal to 8.015 μg/L and 18.72 μg/L, respectively. Similarly, in the present study Metalaxyl-M and Penconazole show the highest presence (Fig. 4), with maximum concentrations equal to 7.85 μg/L (July 2018) and 6.21 μg/L (November 2017), respectively.

Another study, conducted by Hildebrandt et al. in 2008, investigated the occurrence of eight PPPs (including Metolachlor and Metalaxyl) in the surface and groundwater of agricultural and vineyard areas in the north of Spain. Overall, the analytical results show that only 12% of examined water samples exceeded the 0.1 μg/L limit. However, sporadic high levels up to 2.46 μg/L in groundwater and 0.63 μg/L in surface water were detected. Furthermore, the groundwater samples showed higher concentration of PPPs than surface water samples, suggesting that groundwater should be considered a more vulnerable ecosystem.

3.3. Statistical analysis

A statistical analysis was performed in order to investigate if the slope of the soil surrounding the wells, the sampling time, the wells depth and the location of the wells (upstream vs downstream) may affect the groundwater contamination by PPPs. Tables 3 and 4 show the results obtained by ANOVA analysis. The formers report the sampling time, the slope of the soil, the wells location and the wells depth in relation to the root mean squared error ($\sqrt{MSE}$) and the *P* values in two different tables. The values indicate the average values of the PPPs concentrations, expressed in μg/L, in all 26 wells taken into consideration. When PPPs were not detected, the half value of the LOD was used to allow the log transformation of data as suggested by Ogden (2010), Croghan and Egeghy (2003) and according to the Guidance for Data Quality Assessment of EPA (2000).

As shown in Table 3, the pesticides Dimethomorph and Tetraconazole did not show a significantly differences of concentrations among the period of sampling campaigns, the degree of the soil slope and the location of the wells ($P > 0.05$ for all terms). Instead, the wells location have shown to affect significantly the concentration of the insecticide Chlorantraniliprole ($P < 0.05$), with the highest concentration found in the downstream wells, indicating that these wells may have collected the residues of the treatments due to run-off at soil surface, transport of surface water body and drainage to groundwater. This seems to be supported by the value of GUS index of Chlorantraniliprole, 4.22, that indicates its high leaching potential and high persistence in soil. For the fungicide Fluopicolide, the slope of the soil surrounding the wells showed to slightly influence its concentration in groundwater ($P = 0.1$), with a higher concentration detected in the wells characterized by a slope of type 1 (0–3°), indicating that the cause of contamination may be attributed to the rainfall events which facilitate its leaching to groundwater. Again, this seems to be supported by the Fluopicolide GUS index, 3.63, that indicates a high leaching potential. Moreover, the concentration of Fluopicolide slightly decreases from wells with low depth (level I) to the deeper ones (levels II, III and IV) and increases from upstream to downstream wells ($P = 0.1$ deep × stream) (Table 4), indicating a higher vulnerability of shallower wells due to the higher proximity to the soil surface. Similar results, higher concentrations in shallower wells were observed by Herrero-Hernández et al. (2013), in a similar study.

Furthermore, the most influencing variable was the sampling time (Tables 3 and 4). Indeed, the concentration of the fungicide Metalaxyl-M was significantly higher in July 2018, whereas those of Penconazole and S-Metolachlor were significantly higher in November 2017 ($P < 0.05$). Metalaxyl-M is a fungicide used against *downy mildew*, with the most treatments before July (expert statement). Hence, sampling the water in July may have influenced its occurrence and concentration in groundwater. This is in accordance with its physicochemical properties, as it is not persistent in the soil and it has a low leaching potential (1.71). Furthermore, the wells location slightly affects the contamination of groundwater from Metalaxyl-M ($P = 0.1$), with higher concentration in the upstream wells. Therefore, this may indicate a possible point source contamination of wells by Metalaxyl-M. Indeed, Suciu et al. (2020) in the study on territorial hydrology of a sub-area of 7 km^2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25), show that the contamination of upstream wells (ex: WP25, WP26) is mainly due to point contamination sources, as water movement in the period November 2017–November 2018 was very low.

The fungicide Penconazole is mostly used for grape cultivation against *powdery mildew* and often the treatments go on until end of August (expert statement). However, a very high concentration in November 2017 was detected in well WP14 (Fig. 5), that could be attributed just to a point-source contamination, as Penconazole is not persistent in the soil and it is characterized by a low leaching potential (1.36). Furthermore, its concentration decreases slightly from the wells with a level I of deep (<6 m) to a well with a level IV of deep (>30 m) ($P = 0.1$) (Table 4).

The concentration of the herbicide S-metolachlor decreases significantly over time, 0.01 μg/L in November 2017, 0.007 in July 2018 and 0.0008 in September 2018. S-metolachlor is an herbicide not authorized for the use in grapevine cultivation and its occurrence was in wells where the territory is used also for cereals cultivation. Furthermore, the concentration of S-metolachlor increased in the wells with a slope of type 1 (0–3°) and located downstream, and decreased in the wells with a slope of type 2 (>3°) and located upstream ($P < 0.05$ slope × stream). This is in accordance with the upstream-downstream approach, even if S-metolachlor is characterized by a low GUS index (1.91) and its leaching to groundwater is unlikely.

4. Conclusions

In this work, the quality of groundwater in an area with intensive viticulture activity, located in North-West of Italy and out of the national groundwater monitoring plan, was investigated for the first time. With this aim, a specific list of PPPs with high use in the area and high interest for the local stakeholders was developed based on a multi-actor approach and untargeted screening analysis in groundwater. Furthermore, considering the territorial characteristics and following an upstream-downstream criterium, a specific groundwater wells network was settled. The untargeted screening revealed the occurrence of several contaminants in addition to PPPs and PPPs metabolites, including pharmaceuticals and surfactants. Thereafter, 78 groundwater samples were collected between November 2017 and September 2018 and a target analytical method, comprising solid phase extraction and HPLC-MS/MS detection, was developed and applied for the detection of the 15 PPPs.

Groundwater analysis showed the occurrence of nine PPPs in 80% of the twenty-six wells monitored, and in 30% of them the values were above the EQS limit for groundwater. The most critical PPPs were Chlorantraniliprole, Dimethomorph, Fluopicolide, Metalaxyl-M, Penconazole and Tetraconazole, all fungicides used for grapevine cultivation, and S-metolachlor, an herbicide authorized for cereal cultivation.

ANOVA statistical analysis revealed significant influence of the sampling time, the slope of the soil surrounding the wells, the wells depth

Table 3
Effect of the sampling time (November 2017; July 2018; September 2018), the 2 levels of the slope degree of the soil (type 1 = 0°–3°; type 2 = >3°) and the wells location (upstream vs downstream) on PPPs concentration (μg/L).

PPPs		Sampling time			Slope (°)		Stream		√MSE[a]	P of the model[a]						
		Nov. 2017	Jul. 2018	Sept. 2018	1	2	Ups.	Downs.		Period	Slope	Period * slope	Stream	Period * stream	Slope * stream	Period * slope * stream
Chlorantraniliprole	μg/L	0.01	0.01	0.005	0.008	0.03	0.002	0.02	1.03	0.8	0.7	0.5	<0.05	0.8	0.7	0.5
Dimethomorph	μg/L	0.006	0.03	0.002	0.008	0.02	0.02	0.01	1.14	0.2	0.8	0.6	0.7	0.9	0.6	0.8
Fluopicolide	μg/L	0.02	0.08	0.03	0.1	0.05	0.02	0.06	1.93	0.5	0.1	0.5	0.8	0.4	0.5	0.9
Metalaxyl-M	μg/L	0.07	0.4	0.02	0.1	0.3	0.2	0.1	2.94	<0.05	0.8	0.4	0.1	1	0.5	0.7
Penconazole	μg/L	0.1	0.04	0.01	0.04	0.1	0.1	0.02	2.11	<0.05	0.9	0.3	0.2	0.9	0.9	0.4
S-metolachlor	μg/L	0.01	0.007	0.0008[b]	0.01	0.004	0.006	0.01	1.42	<0.05	0.3	0.5	0.8	0.8	<0.05	0.4
Tetraconazole	μg/L	0.003	0.02	0.004	0.02	0.01	0.004	0.01	1.07	0.3	0.8	0.6	0.2	0.4	0.4	0.8

[a] The values reported are in $\log_e$.
[b] This value corresponds to the average of the results in which S-metolachlor was never found except for one well, with a concentration equal to 0.0047 μg/L. Therefore, for wells in which S-metolachlor was no detected, for statistical calculation the half of the limit of detection (0.0006 μg/L) was considered.

Table 4
Effect of the sampling time (November 2017; July 2018; September 2018), the wells depth (type 1 = <6 m; type 2 = 6–10 m; type 3 = 10–15 m; type 4 = over 30 m) and the wells location (upstream vs downstream) on PPPs concentration (μg/L).

PPPs		Sampling time			Stream		Depth (m)				√MSE[a]	P of the model[a]						
		Nov. 2017	Jul. 2018	Sept. 2018	Up.	Down.	1	2	3	4		Period	Depth	Period * depth	Stream	Period * stream	Depth * stream	Period * stream * depth
Chlorantraniliprole	μg/L	0.01	0.01	0.005	0.002	0.02	0.007	0.03	0.002	0.002	1.03	0.8	0.5	0.9	<0.05	0.8	0.5	0.9
Dimethomorph	μg/L	0.006	0.03	0.002	0.02	0.01	0.008	0.006	0.03	0.01	1.14	0.2	0.7	0.7	0.7	0.9	0.1	0.5
Fluopicolide	μg/L	0.02	0.08	0.03	0.02	0.06	0.1	0.03	0.002	0.01	1.93	0.5	0.3	1	0.8	0.4	0.1	0.9
Metalaxyl-M	μg/L	0.07	0.4	0.02	0.2	0.1	0.3	0.2	0.03	0.05	2.94	<0.05	0.2	0.8	0.1	1	0.8	1
Penconazole	μg/L	0.1	0.04	0.01	0.1	0.02	0.2	0.03	0.003	0.007	2.11	<0.05	0.1	1	0.2	0.9	0.7	1
S-metolachlor	μg/L	0.01	0.007	0.0008[b]	0.006	0.004	0.008	0.004	0.007	0.0006	1.42	<0.05	0.6	0.8	0.8	0.8	0.4	0.6
Tetraconazole	μg/L	0.003	0.02	0.004	0.004	0.01	0.02	0.02	0.002	0.002	1.07	0.3	0.5	0.9	0.2	0.4	0.9	1

[a] The values reported are in $\log_e$.
[b] This value corresponds to the average of the results in which S-metolachlor was never found except for one well, with a concentration equal to 0.0047 μg/L. Therefore, for wells in which S-metolachlor was no detected, for statistical calculation the half of the limit of detection (0.0006 μg/L) was considered.

and the location of the wells (upstream vs downstream) on the concentration of five of the fifteen PPPs monitored. Furthermore, study of territorial hydrology for a sub-area of 7 km^2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25) (Suciu et al., 2020, under submission in this special issue) helped to discriminate which of the two between point and diffuse contamination sources was more influent, in some cases, although additional information about farmers' practices are necessary to fully understand the actual contamination pathway(s). In conclusion, intensive viticulture may affect groundwater quality, thus suggesting the need for an urgent introduction of the best management practices and mitigation measures for a sustainable use of PPPs to enhance groundwater governance and ensure good groundwater quality (Calliera et al., 2020, under submission in this special issue).

CRediT authorship contribution statement

Roberta Zambito Marsala: Methodology, Writing - original draft, Visualization, Investigation, Data curation. **Ettore Capri:** Supervision, Funding acquisition, Conceptualization, Writing - review & editing, Methodology. **Elisabetta Russo:** Methodology, Investigation, Resources, Writing - review & editing. **Miriam Bisagni:** Investigation. **Ruggero Colla:** Investigation, Writing - review & editing. **Luigi Lucini:** Formal analysis, Writing - review & editing. **Antonio Gallo:** Formal analysis, Writing - review & editing. **Nicoleta Alina Suciu:** Project administration, Methodology, Validation, Investigation, Writing - review & editing, Data curation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.139730.

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