Science of the Total Environment 749 (2020) 141495

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluation of groundwater contamination sources by plant protection products in hilly vineyards of Northern Italy

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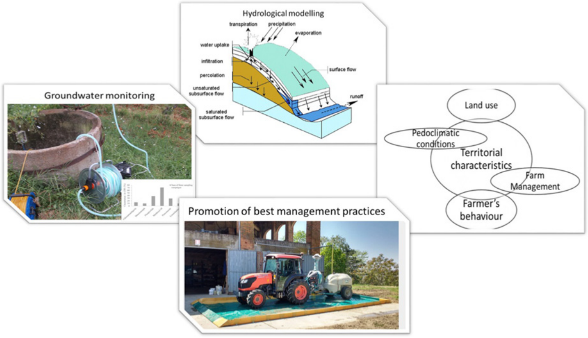
HIGHLIGHTS

- Sampling time influences significantly PPPs occurrence and amounts in groundwater.
- Well location and use were fundamental for the detections of contamination.
- A wide permanent aquifer does not exist in the Tidone Valley.
- Both diffuse and point sources are responsible for GW contamination in Tidone Valley.
- The results obtained were used to raise awareness and promote specific Best Management Practices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 June 2020
Received in revised form 24 July 2020
Accepted 3 August 2020
Available online 6 August 2020

Editor: Miren Lopez De ALda

Keywords:
Pesticides
Vineyards
Tidone Valley

ABSTRACT

In Europe, 25% of groundwater has poor chemical status. One of the main stressors is agriculture, with nitrates and plant protection products (PPPs) causing failure in 18% and 6.5%, respectively, of groundwater bodies (by area). EU legislation for the placement of the PPPs on the market is one of the most stringent in the world. However, recent monitoring studies in hilly vineyards of Tidone Valley, north-west of Italy, show presence of PPPs used for grapevine cultivation in 15 out of 26 groundwater wells monitored, at values above the Environment Quality Standard (EQS) for groundwater (0.1 μg/L). However, no information about the contamination sources are available. Therefore, the objective of the present work is to evaluate the groundwater contamination sources by PPPs, in a small catchment with intensive viticulture, by collecting and integrating monitoring data, subsurface water movement data and territorial characteristics. The results show that in wells used for PPP's mixture preparation and sprayer washing located at the top of hilly vineyards, with low slope and no water movement in the surrounding soil, the contamination is most likely from point sources. On the contrary, for wells located in a

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Abbreviations: ARPAE, Agenzia Regionale per la Prevenzione, l'Ambiente e l'Energia dell'Emilia-Romagna; BMP, Best Management Practice; CD, Cumulated Drainage; CWI, Cumulated Water Inflow; CIA, Confederazione Italiana Agricoltori; DEM, Digital Elevation Model; DOS, Degree Of Saturation; EEA, European Environmental Agency; EFSA, European Food Safety Authority; EFSA PPR, European Food Safety Authority - Panel on Plant Protection Products and their Residues; EPA, Environmental Protection Agency; EQS, Environment Quality Standard; FOCUS, FOrum for the Co-ordination of pesticide fate models and their UseGLM - Generalized Linear Model; GIS, Geographic Information System; LOD, Limit of Detection; LOQ, Limit of Quantification; MM, Mitigation Measure; MSE, Mean Squared Error; PPPs, Plant Protection Products; SAS, Statistical Analysis Software; SETAC EMAG-Pest GW, Society of Environmental Toxicology And Chemistry - Environmental Monitoring Advisory Group on Pesticides - Groundwater expert group; VFS, Vegetated filter strip; WFD, Water Framework Directive; WL, Water Level; WWAP, World Water Assessment Programme.

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https://doi.org/10.1016/j.scitotenv.2020.141495

Groundwater monitoring
Stakeholder involvement
Best management practices

fenced area at the bottom of the hill, far away from vineyards and being used for drinking water production, the contamination is most likely from diffuse sources. Our results were used to raise awareness on groundwater contamination from PPPs among farmers in the study area; moreover a waterproof platform for sprayers washing, equipped with wastewater recovery and disposal system, able to avoid point-source contamination, was implemented in a local demonstration farm. Several demonstration activities were then organised with the farmers of the entire Valley in order to show its functionality and promote its diffuse use.

1. Introduction

Groundwater plays a substantial role in water supply, in ecosystem functioning and human well-being (WWAP, 2015). In countries such as Austria, Germany, Italy or Denmark, more than 70% of the population's water supply comes from groundwater (Martínez-Navarrete et al., 2011). Groundwater resources are subject to increasing pressures, from both point - and diffuse - pollution sources. The main pressure factors are water pollution, water abstraction and droughts, due to climate change (Brouwer et al., 2018). In Europe, 25% of groundwater has poor chemical status (EEA, 2018). In particular, agricultural non-point source pollution has been increasingly recognized as a primary contributor to water quality impairment and as a key water quality problem worldwide (Tan et al., 2011; Kourakos et al., 2012). Many authors do not associate point pollution with agriculture, except with livestock farms and manure depots (e.g. Balderacchi et al., 2013; Parris, 2011). The overall growth of agricultural production has been achieved mainly through intensive use of inputs, such as pesticides. In particular, Italy vineyard productivity requires several pesticide treatments especially against pathogens as fungi and insects (Vischetti et al., 2008). Fungicides account for the largest share of pesticide treatments in most vineyards, with an average of 12–15, up to 25–30 applications in the most problematic conditions (Pertot et al., 2017). With the coming into force of the European directive 2009/128/EC (The European Parliament and the Council of the European Union, 2009a), the sustainable use of Plant Protection Products (PPPs) becomes a duty for all the European Member States (Suciu et al., 2011). Particular attention is accorded to PPP contamination of groundwater. In fact, PPPs can reach groundwater indirectly as a result of drift and run-off into adjacent or non-target environments (as non-point sources) or more directly via leaching from application sites or PPP handling procedures (point sources). The directive 2006/118/EC of the European Parliament and of the council of 12 December 2006 establishes specific measures to prevent and control groundwater pollution. The groundwater quality standard of active substances in pesticides, including their relevant metabolites, degradation and reaction products, is 0.1 μg/L for each individual pesticide and 0.5 μg/L for their sum (The European Parliament and the Council of the European Union, Annex 1, 2006/118/EC). This value was also included in the EU Regulation 1107/2009/EC (formerly 91/414/EEC), concerning the placing in the market of PPPs. The regulation establishes rules concerning authorization, placing on the market, use and control of PPPs. The directive 2009/128/EC and the regulation1107/2009/EC (The European Parliament and the Council of the European Union, 2009b) represent a challenge for water quality management and environmental risk assessment, environmental fate and exposure. Monitoring studies are very useful for regulatory purposes to verify whether the concentration of chemicals exceeds predetermined trigger values (e.g. 0.1 μg/L). However, they do not provide information on the origin of contamination (point and non-point source pollution, Di Guardo and Finizio, 2016). Furthermore, to date, little guidance has been provided on study designs of monitoring studies. SETAC EMAG-Pest GW, a group of regulatory, academic, and industry scientists, was created in 2015 to establish scientific recommendations for conducting such studies (Gimsing et al., 2019). "*The need to tailor study designs to objectives, exposure assessment options, compound properties and site characteristics complicates the development of standardised study designs*." (direct quotation from Gimsing et al., 2019). As a foundation for groundwater leaching assessments, FOCUS (FOrum for the Co-ordination of pesticide fate models and their Use) models are used in the pre-registration process to evaluate the environmental fate (groundwater, surface water, soil, sediment, and air) of pesticides. Unfortunately, the FOCUS Tier 1–3 simulations use standard scenarios and various refinements (Capri et al., 2005). At Tier 4, monitoring data can be used. This framework is intentionally simplified and, thus, has a number of constraints in the context, or application to, of either a site-specific evaluation or an evaluation of the full range of leaching conditions encountered on an EU level (e.g. leaching karstic soils etc.). The EFSA PPR Panel criticised the quality criteria in the FOCUS Tier 4 as too imprecise and the knowledge on groundwater hydrology at the European level as insufficient to demonstrate a safe use of pesticides at EU level (EFSA, 2013; European Commission, 2014).

As defined by the Water Framework directive (WFD) 2000/60/EC, "Groundwater" means all water that is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil (The European Parliament and the Council of the European Union, 2000). The protection goal implicit in the FOCUS groundwater modelling for EU registration is an overall vulnerability at the 90th percentile considering both spatial and temporal vulnerability for the yearly average pesticide concentration in groundwater, located at least one metre below the ground surface (EFSA, 2013). However, the representativity of monitoring data should be assessed combining pedoclimatic vulnerability and groundwater hydrology (Gimsing et al., 2019).

Recent monitoring studies (Zambito Marsala et al., 2020) in hilly vineyards in north-west of Italy, Province of Piacenza, settled in the EU project WaterProtect, show presence of PPPs used for grapevine cultivation in 15 out of 26 groundwater wells monitored, at values above the Environment Quality Standard (EQS) for groundwater (0.1 μg/L). Herrero-Hernández et al. (2013) reported similar results in groundwater of Spanish vineyards. Indeed, concentrations above 0.1 μg/L were detected for 37 of the 47 compounds studied, and in several cases recorded values of over 18 μg/L. The results reveal the presence of pesticides in most of the samples investigated. In 64% of groundwaters and 62% of surface waters, the sum of compounds detected was higher than 0.5 μg/L. Rabiet et al. (2010) for an agricultural catchment devoted to vineyard and located about 70 km north of Lyon, France, show PPPs presence in surface water for several months after PPPs application and the results pointed out pesticides potential to persist in soils and shallow groundwater. The study of Zambito Marsala et al. (2020) represents the first evaluation of PPPs occurrence in groundwater of Tidone Valley and the authors highlighted the significant influence of the sampling time, slope of the soil surrounding the wells, wells depth and wells location on the concentration of five PPPs. Furthermore, the authors suggested the need for a deeper analysis of territorial context, including hydrology studies and farmer behavior during PPPs storage and handling, and for an urgent introduction of best management practices and mitigation measures to promote a sustainable use of PPPs in viticulture. In this context, the objective of the present work is to evaluate the groundwater contamination sources by PPPs in one of the three catchments of the area monitored by Zambito Marsala et al. (2020), by collecting and integrating monitoring data, sub-surface water movement data and territorial characteristics. For sub-surface water movement, the hydrological three-dimensional catchment-scale model

CRITERIA 3D was used, while as territorial characteristics, the pedoclimatic conditions, the acquifer conceptual model, farm management and farmers' behavior during PPPs storage and handling, were taken into account.

2. Materials and methods

2.1. Study area

The area under study is part of the catchment of the stream Carona-Boriacco (Fig. 1), located in Tidone Valley, on the hydrographic right of the Po river in north-west of Italy and covers 7 km^2 and 375 ha of hilly vineyards. The territory is characterised by an elevation between 100 and 350 m above sea level and clay and clay-silty type of soils (Table 1, Table S1) (Zamboni, 2006). Already in 1987, when the detailed soil classification of the Val Tidone vineyards began, four main soil types were identified: *Case Basse* Silty Clay (Soil taxonomy: Calcic Haplusterts fine, mixed, active, mesic), *Monte Po* Silty Clay Loam(Soil taxonomy: Typic Ustorthents fine silty, mixed, superactive, calcareous, mesic), *Vicobarone* Clay (Soil taxonomy: Vertic Haplustepts fine, mixed, superactive, mesic) and *Montalbo* Clay (Soil taxonomy: Typic Ustorthents fine, mixed, active, calcareous, mesic) (https://geo.regione.emilia-romagna.it/cartpedo/).

2.2. Stakeholders involvement

As stated by Zambito Marsala et al. (2020), for the development of the sampling network and the characterization of the territorial agricultural and fertilization practices in the Italian Action Lab of WaterProtect project, two survey campaigns were conducted between August 2017 and June 2018, by the use of ad hoc questionnaires involving 175 farmers in Tidone Valley. The farmers involved were from five municipalities: Ziano Piacentino, 50.3%, Alta Val Tidone, 16%, Castel San Giovanni, 9.7%, Pianello Val Tidone, 6.9%, Borgonovo Val Tidone, 4.6%, and other regions and municipalities, 12.5%. For farmer involvement an “active engagement” methodology was adopted, through bilateral and multi-actor conversations and selecting strategic places and timing, and in this respect the support of farmers' organization Cantina Sociale Vicobarone, of farmers' unions Coldiretti, Confagricoltura and CIA, and of farmers' consultancy organization Consorzio Fitosanitario Provinciale, was fundamental (Calliera et al., 2020, submitted for this special issue).

At the end of the sampling campaigns and involving three farmers from the study area, a third survey campaign was conducted. The survey had the purpose of assessing farm management and PPPs use in farms, starting from type of cultivation system up to the operations following PPP treatments, i.e. the management of wastewater containing PPPs, equipment washing and waste disposal. The farmers involved are the owners of 4 of the 6 sampling groundwater wells and their farms covers 30.4% of the entire vineyards surface in the study area.

2.3. Groundwater monitoring

Six groundwater wells (WP11, WP13, WP25,WP26, WP28 and WP32) part of the network developed by Zambito Marsala et al. (2020, published in this VSI) and selected based on an hydrological upstream – downstream criteria, were monitored for the content of 15 PPPs (three insecticides, Chlorantraniliprole, Chlorpyrifos and Chlorpyrifos methyl used on grapevine against Eupoecilia ambiguella,

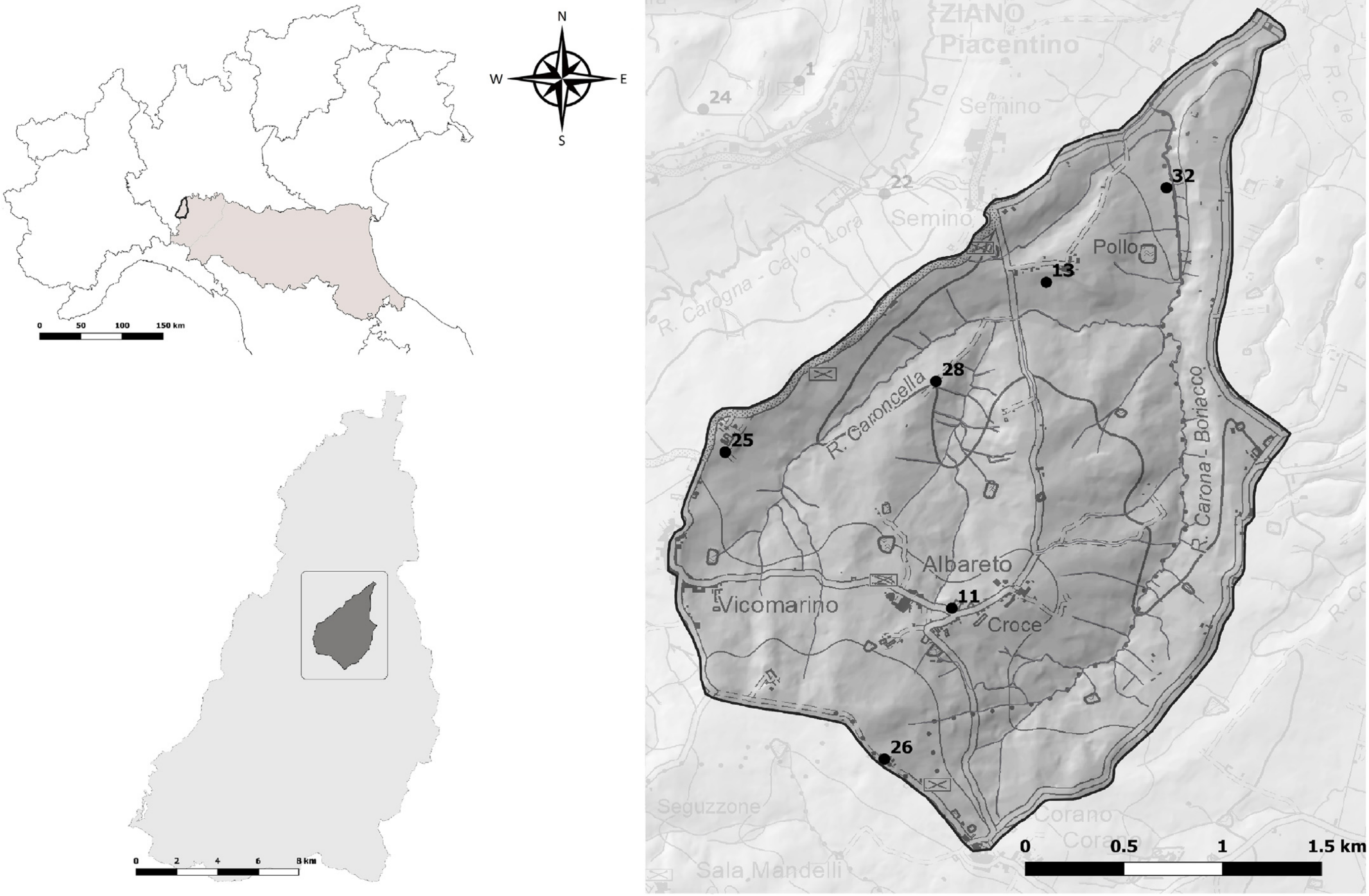

Fig. 1. Study area, as sub-area of the WaterProtect Action Lab (described by Zambito Marsala et al., 2020), located in Emilia - Romagna Region, north-west of Italy.

Table 1
Soil and groundwater wells' characteristics.

Well	Location	*Vallicola*	Depth (m)	Static level Nov 2017 (m)	Static level July 2018 (m)	Static level Sept 2018 (m)	Soil code	Soil Description	Soil Slope (°)
WP11	Albareto	Rio Bardonazzo	5.7	−3.72	−2.97	−3.19	VCB	VICOBARONE argillosi	5.4
WP13	Pollo	Rio Caroncella/ Bardonazzo	5.4	−3.75	−3.10	−3.00	VCB	VICOBARONE argillosi	7.8
WP25	Costola	Rio Caroncella	11.2	−2.80	−3.12	−2.90	MNB1	MONTALBO argillosi	7.6
WP26	Corano	Rio Carona	8.8	−0.68	−3.57	−4.88	SMD	SALA MANDELLI	1.7
WP28	Marano	Rio Bardonazzo	5	−1.23	−2.10	−1.90	MNB1	MONTALBO argillosi	2.4
WP32	Carona	Rio Carona-Boriacco	15	−6.80	−8.97	−10.50	VCB	VICOBARONE argillosi	1.7

seven fungicides Cyflufenamid, Cyprodinil, Dimethomorf, 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 authorised for grapevine cultivation but commonly used for cereals in conventional farming) between November 2017 and September 2018. The analytical and sampling procedures are described in Zambito Marsala et al. (2020). The development of the sampling network was a long and complex process, and took place between November 2017 and May 2018. For this reason, the first sampling campaign corresponds to November 2017 for wells WP11 and WP 13 and to May 2018 for wells WP25, WP26, WP 28, WP32. Well characteristics are listed in Table 1. Groundwater considered is surface phreatic water (shallow aquifer), fed by precipitation and, near the watercourses, by the hydrological relationship. Indeed, well WP 32, which is used for drinking water extraction and is located in the alluvial deposits of Stream Carona-Boriacco, is mainly recharged by the stream through streambed and partially by the subsurface inflow, while five wells (WP 11, WP13, WP25, WP26 and WP28) are recharged by rainwater and subsurface inflow.

2.4. Aquifer's conceptual model

Based on hydrology studies of the regional environmental agency ARPAE (Regione Emilia-Romagna, 2010; Farina et al., 2014), a wide permanent shallow aquifer - as requested by WFD for the definition of a groundwater body - does not exist in the study area.

The silty-clayed sediment, the soil slope between 0 and 20°, the thickness lower than 3 m and the substrate morphology, are the main parameters that government the groundwater movement in the shallow phreatic aquifers of the study area. There isn't a recharge groundwater area able to sustain a perennial groundwater flow, but when groundwater flow exists, is due to rainfall infiltration in the subsurface. Only into the alluvial porous deposits in the valley bottom the groundwaters flow are mainly dependent by the Stream Carona-Boriacco water level.

In the scheme of the versant from the crest to valley bottom of the study area (Fig. 2) are defined three zones where are different types of the local storage of groundwater: Type A, located in the valley crests where the slope is low (<3°) and recharge is only by rainfall inputs (wells 26 and 28); Type B, located in a middle zone of valley versant where the slope is the medium (>5°) and recharge is by rainfall inputs and by subsurface flows from Type A zones (wells 25, 11 and 13); Type C, located in the valley bottom where the slope is low (<3°) and recharge has already been described (well 32).

The variability of the water table (Table 1) is less in the wells of Type B than in the other two types, because the water table depending only rainfall input in the first and mainly water body Stream Carona-Boriacco in the second. Furthermore in the zones of Type B the substrate morphology determines the presence of a local depressions allows at groundwaters the permanence/stagnation (storage and accumulation) during dry periods. These areas are located where the large-diameter perennial wells are present, as the six groundwater stations of monitoring network.

2.5. Sub-surface water movement assessment

CRITERIA-3D is a physically based, three-dimensional catchment-scale model of surface and subsurface soil water balance developed by ARPAE (Bittelli et al., 2010). The model is based on the integrated finite

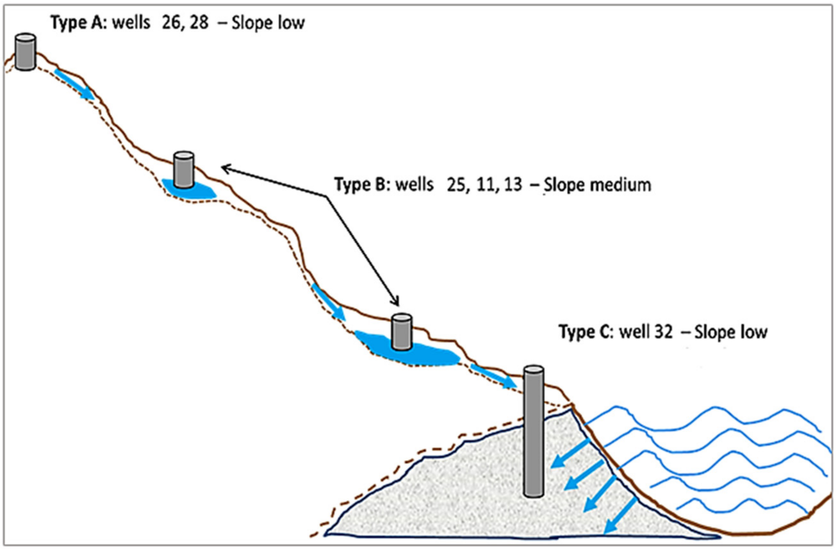

Fig. 2. Conceptual model of shallow aquifer (CMA).

difference (also called cell-centered finite volume scheme) method and accounts for saturated water flow, unsaturated water flow and surface runoff; the model is coupled with interpolation schemes for mapping the meteorological input variables (Antolini et al., 2015), and a topography-dependent solar radiation model. Spatial interpolation uses as input data from a monitoring network providing hourly data of temperature, precipitation, relative humidity, wind speed and solar irradiance, and takes into account topography dependencies by means of a DEM (Digital Elevation Model). A soil map is also needed as input with parameters for hydraulic properties and parameters. The soil hydraulic properties are computed using the modified Van Genuchten-Mualem model proposed by Ippisch et al. (2006). The model was validated both in its 1D version (Tomei et al., 2007) and 3D version (Bittelli et al., 2010). The model is freely available at the following link: https://github.com/ARPA-SIMC/CRITERIA3D.

CRITERIA-3D has already been coupled in previous works with phenology and plant growth models specific for grapevine (Bois et al., 2014). The phenology models (Bindi et al., 1997; Caffarra and Eccel, 2011) simulate the main development stages for grapevine and are computed at a daily time step. Plant growth is computed by simulating the photosynthetic process at hourly time step through the Farquhar equation, following the implementation of Magnani et al. (2009). The model estimates biomass accumulation and water uptake, while water stress acts in the process by reducing stomatal conductance (Lebon et al., 2003). The parameters used for scenario development and subsurface water movement simulations are shown in Tables S1, S2 and S3 of supplementary material.

Three model outputs, Cumulated Water Drainage (CD, water vertically flowing out from the soil profile bottom), Cumulated Water Inflow (CWI, water laterally flowing into the soil profile) in the soil profile surrounding the groundwater wells, and soil Degree Of Saturation (DOS) were obtained and integrated with monitoring, agricultural practices and farm management data in order to evaluate the sources of groundwater contamination by PPPs.

2.6. Statistical analysis

The normal distribution of the monitoring data was characterised by using UNIVARIATE procedure (SAS Inst. Inc., Cary, NC; release 8.0) by using the 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 the table, the data were presented in their original scale, whereas pooled error terms (i.e., root means square error or √MSE) referred to log normal transformed data (Petrie and Watson, 2006). The experimental design corresponded to a completely randomized block design. A generalized linear model (GLM procedure) was applied to log transformed data and the main tested effects in the model were the wells ($n = 6$) and the block sampling period ($n = 3$, November 2017, July 2018 and September 2018). Significance was declared for a $P < 0.05$ (Table 2).

3. Results and discussion

3.1. Surveys results

The results of the two surveys conducted between August 2017 and June 2018, involving 175 farmers of Tidone Valley, and described in details by Calliera et al. (2020, under submission in this special issue) and Zambito Marsala et al. (2020) show a moderate to low level of adoption of best management practices (BMPs) and mitigation measures (MMs) capable to prevent water contamination by PPPs. In some cases, the existing practices and measures are used in an incorrect way, as in the case of vegetated filter strip (VFS) at edge-of-field, which are present in 52% of farms but in a high percentage are used for vehicles' passage. Furthermore, suggested good agricultural practices, such as specific VFS at landscape level (to avoid diffuse contamination), or correct management of wastewater resulting from the internal and external machine cleaning (to avoid point source contamination) are discredited by farmers for several reasons, such as *not always compatible with farmers' work organization and landscape situations, their impact is not ensured, farmers need more information, or are not economically feasible* (Calliera et al., 2020, under submission in this special issue).

Regarding the study area and considering the results of the third survey, it was observed that just one of the three farms follows the guidelines of integrated pest management and implemented VFS at field edge while in two of the three farms the vineyard grass cover is the only practice adopted to avoid water contamination due to run-off. Furthermore, in order to avoid water contamination due to drift, two of the three farms adopted systems for regulating the direction of the air flow in combination with anti-drift nozzles. However, no other measures, for example a plant barrier or an insect/hail net, are adopted.

Concerning wastewater management, none of the three farms adopts an individual farm or co-operative wastewater management system, such as dedicated areas for sprayer washing, equipped with wastewater recovery and disposal systems.. The internal remaining mixture is further distributed in the field, after dilution, but the water resulting from the external washing of the sprayers is not collected. No farm has a collecting system for washing water and/or residual mixture and the washing of sprayers is done simply outdoors. No further information was provided by the farmers. Furthermore, the wells WP 11, WP 13, WP 25, WP 26 and WP 28 are present in the farms and WP 28 is e used for PPPs mixtures and sprayers washing.

Table 2
Effect of the sampling time (November 2017; July 2018; September 2018) and the well on PPPs concentration in groundwater (μg/L).

PPP	Period			Well						√MSE[a]	P model[a]	
	2017-Nov	2018-July	2018-Sept	11	13	25	26	28	32		Period	Well
Chlorantraniliprole	0.007	0.005	0.02	n.r.[b]	n.r.[b]	n.r.[b]	n.r.[b]	0.05	n.r.[b]	0.4	0.4	<0.0001
Dimetomorph	0.004	0.02	n.r.[b]	n.r.[b]	n.r.[b]	n.r.[b]	0.004	0.04	n.r.[b]	0.8	0.4	0.2
Fluopicolide	0.02	0.20	0.05	n.r.[b]	0.30	n.r.[b]	0.20	0.03	n.r.[b]	1.4	0.3	0.01
Metalaxyl-M	0.04	0.30	0.01	0.006	0.04	0.004	0.01	0.60	0.02	1.5	0.0009	0.008
Penconazole	0.01	0.09	0.02	0.002	0.04	0.007	0.02	0.20	n.r[c]	1.3	0.03	0.007
S-metolachlor	0.03	0.008	0.001	n.r[c]	n.r.[c]	0.003	0.005	0.06	n.r[c]	1.3	0.08	0.08
Tetraconazole	n.r.[b]	0.09	0.008	n.r.[b]	n.r.[b]	n.r.[b]	n.r.[b]	0.20	n.r.[b]	1.1	0.4	0.07
ΣPPPs	0.10	0.70	0.10	0.02	0.40	0.02	0.20	1.20	0.03	3.8	0.005	0.0002

These values correspond to the half of the limit of detection. According to Zambito Marsala et al. (2020) the LOQ of the substances Chlorantraniliprole, Dimetomorph, Fluopicolide and Tetraconazole is 0.02 μg/L; the LOQ of Metalaxyl-M is 0.0008 μg/L; the LOQ of Penconazole and S-metolachlor is 0.004 μg/L. 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.

[a] The values reported are in $\log_e$.

[b] n.r. = 0.003.

[c] n.r = 0.0006.

3.2. Groundwater monitoring

The monitoring results of the three sampling campaigns show the sum of 15 PPPs below the EQS (0.5 μg/L) in wells WP 25, WP 26, WP 11, and WP 32 with the highest value registered in September 2018 in well WP26, 0.3 μg/L. Fluopicolide, Metalaxyl-M, Penconazole and S-Metolachlor were the most frequently detected substances. Wells WP 28 and WP 13 were characterised by greatest contamination, with values for ΣPPPs higher than EQS in July 2018 (2.8 μg/L, well WP 28 and 0.99 μg/L, well WP 13). In well WP 32, a well-used for drinking water abstraction, the only PPP revealed was Metalaxyl-M, in July 2018, at values below EQS (0.1 μg/L). Sampling time was shown to have a significant influence on PPPs concentrations in groundwater, with significantly higher value for Σ7PPPs in July 2018. This could be explained by the fact that almost 95% of pesticide treatments for grape protection have been already carried out by July (expert judgment). However, Metalaxyl-M was the only PPP present in all the wells at values higher than limit of quantification (LOQ) while the second most found PPP was Penconazole. For statistical analysis, 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). Comparing our results with those of Herrero-Hernández et al. (2013) reported for the groundwater of Spanish vineyards, four of the forty-seven PPPs analysed in the Spanish study are present in this study: Chlorpyrifos, Cyprodinil, Dimethomorf and Penconazole, while for S-metolachlor and Metalaxyl – M, analysed in the present study, the enantiomers Metalaxyl and Metolachlor were screened for in Spanish groundwater. Metalaxyl, Penconazole, Dimethomorf and Metolachlor were found in 50%, 46%, <5% and <15%, respectively, of Spanish groundwater samples, with the highest concentration of Metalaxyl and Penconazole, as in the present study. Furthermore, Herrero-Hernández et al. (2013) reported an influence of well depth on PPPs concentrations in groundwater, with the shallow wells being the most contaminated. This is in agreement with our results, as wells WP 13 and WP28, resulted the most contaminated, and are also the most superficial, with a depth bellow 5.5 m. However, in the recent study of Herrero-Hernández et al. (2020) in a Spanish vineyard region included in the Denomination of Origin Jumilla reported lower frequencies of fungicides in water samples than the other groups of pesticides. This may be due to their unusual or low application in that area, with climatic conditions that do not favour the onset of fungal diseases. Some of the compounds studied were detected even in wells reaching down to 400 m.

3.3. Sub-surface water movement and contamination sources evaluation

The results of the model simulations, showing CD and CWI and DOS for the soil surrounding the six groundwater wells, are presented in the Figs. 3, 4 and 5. In general, the cumulated water movement (CD and CWI) in the soil surrounding the six groundwater wells is low, with values between near zero and maximum 15 mm during the entire period, mainly due to the clayey soils present in the study sub-area. These values, together with the slope and well position, at the top, bottom or middle of the hill, allowed a quite clear distinction between the six wells. Three types “A”, “B” and “C” were hypothesized (Fig. 2). Wells WP 26 and WP 28 are of type “A”, located on hilltop and with low slope. Water movement in the surrounding soils is almost negligible (Fig. 3) and the recharge of the aquifer is only through rainfall. Furthermore, the water level (WL) in the well is consistent with soil saturation level, maximum when the WL is highest. For well WP 26 the ΣPPPs in groundwater (μg/L) was higher in July and September compared to May, while for well WP 28 the highest concentrations were observed in July. However, the increase cannot be due to water movement as between May and September no water drainage or lateral movement were registered (Fig. 3). The PPPs found in well WP 28 above EQS in July were Dimetomorph, Metalaxyl-M, Penconazole and Tetraconazole, while in well WP 26 was Fluopicolide. Therefore, for Well WP 26, even though there is no water entering the aquifer, concentrations are increasing in time and this is dominated by Fluopicolide, which is a fairly persistent substance (EFSA, 2009). As contamination cannot be from leaching, it must be point source and when in the aquifer, Fluopicolide does not degrade. For well WP28, again, even though there is no water entering the aquifer, there is an increase of concentrations in July and this is dominated by Metalaxyl-M and Penconazole, which are not persistent substances. Penconazole was also found in September, at a value one quarter of the level detected in July, but remaining above EQS. Therefore, as Penconazole is a PPP with a fast degradation rate in water (EFSA, 2008), most probably, it was used after July and this is in agreement with the fungal disease in the area in August (expert statement). Also in this case, there is point-source entry followed by chemical transformation in the aquifer. Possible point sources are losses during pesticides mixture preparation, containers cleaning or inappropriate discharge of water resulted from sprayer cleaning. Indeed, the water of well WP 28 is used for PPPs mixtures preparation, dilution, and sprayer washing and the well is located in the middle of the vineyard. Furthermore, none of the specific BMPs and MMs are adopted in the farm to prevent water point source contamination by PPPs. However, the monitoring data is available just for the period May–September, which corresponds to the PPPs distribution period. Monitoring data in the period of non-use, would have been useful to sustain the hypostases of point-source contamination. Unfortunately, the development of the sampling network, containing the 26 wells and described by Zambito Marsala et al. (2020) was a long process, mainly due to the miss of trust of the wells' owners. Indeed, just for wells WP 11 and WP13, selected at the beginning of the selection process, in November 2017, was possible to have data from PPP non-use period (November–March).

Wells WP 25, WP 11 and WP 13, considered of “type” B, are located in areas with medium slope, in the middle of the hill, and their water is most probably (based on the aquifer's conceptual model) supplied by meteoric recharge and by significant underground hypodermic flow, determining its accumulation and stagnation even in dry periods. As shown in Fig. 4, WL is maintained and does not decrease. For both wells WP 25 and WP 11 the ΣPPPs in groundwater (μg/L) were below EQS during all three sampling campaigns, while for well WP 13 values higher than EQS (0.5 total and 0.1 individual μg/L) were registered in July 2018. The most detected PPPs were Fluopicolide, Metalaxyl – M and Penconazole, with values above EQS (0.1 μg/L) for the first two in WP 13. Based on PPPs characteristics, discussed above, and considering the higher water movement registered in the soil surrounding these wells, their contamination is most probably due to both diffuse and point sources. Indeed, the subsurface inflow from up-hill could transport chemical residues to these wells (diffuse contamination) but at the same time could dilute the existing concentrations and as outflow transport residues downhill, to downstream wells. Moreover, wells WP 11 and WP 25 are part of the same farm but well WP 11 is in the middle of the farm while WP 25 is in the middle of the vineyards and the water of both wells is not used for PPPs treatments or sprayer washing and these operations are made far away. However, a dedicated area for sprayers washing, equipped with wastewater recovery and disposal systems is not present in the farm. The well WP 13 is located in the middle of vineyards, but no information about its use and vineyard/farm management is available, as the owner does not manage the surrounding vineyards anymore and the new manager did not accept to collaborate.

Water movements are more consistent in the soil surrounding the well WP 32, type “C”, (Fig. 5), which is at the bottom of the hill and of the entire valley, with a low slope and river recharge through the riverbed and partially from hypodermic flow (subsurface flow), originating from the slope. The only PPP present in the groundwater was Metalaxyl

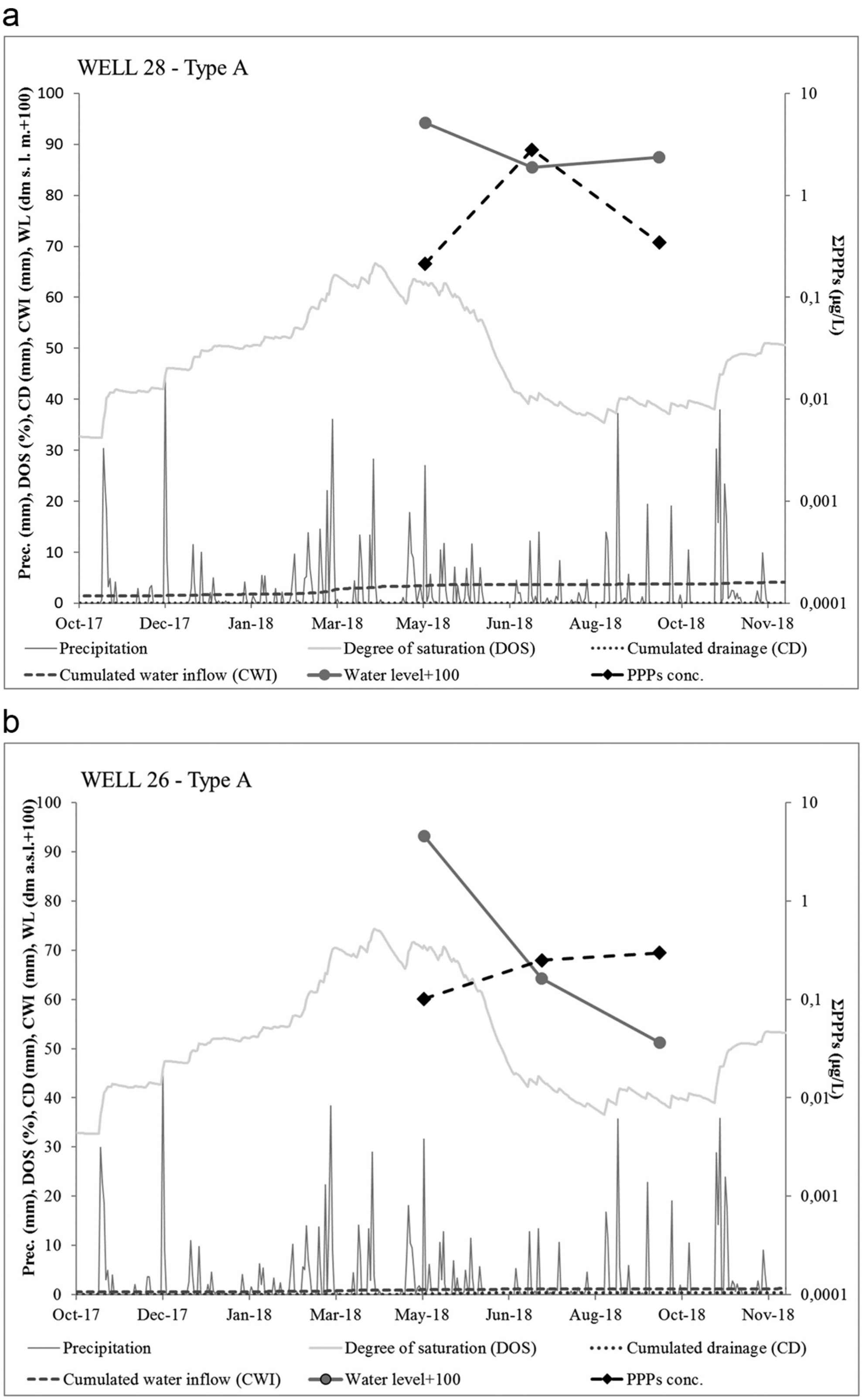

Fig. 3. Integration of modelling outputs with precipitation data and PPPs concentration in wells of type "A"; a) well WP 26 and b) well WP 28.

- M, in July 2018. Most probably, the contamination source is diffuse, driven by lateral transport. As in case of type B wells, the subsurface inflow from up-hill could have transported chemical residues to this well (diffuse contamination) from upstream contaminated wells. Indeed, WP 13 and WP 28 are upstream wells (Fig. 1.), having the highest Metalaxyl- M concentrations in July 2018, the only time in which Metalaxyl – M was found in well WP32. Furthermore, the well is located in a fenced/protected enclosure where it is utilised as a source for drinking water, where point contamination is impossible. However, in September 2018 Metalaxyl – M was no longer found in groundwater,

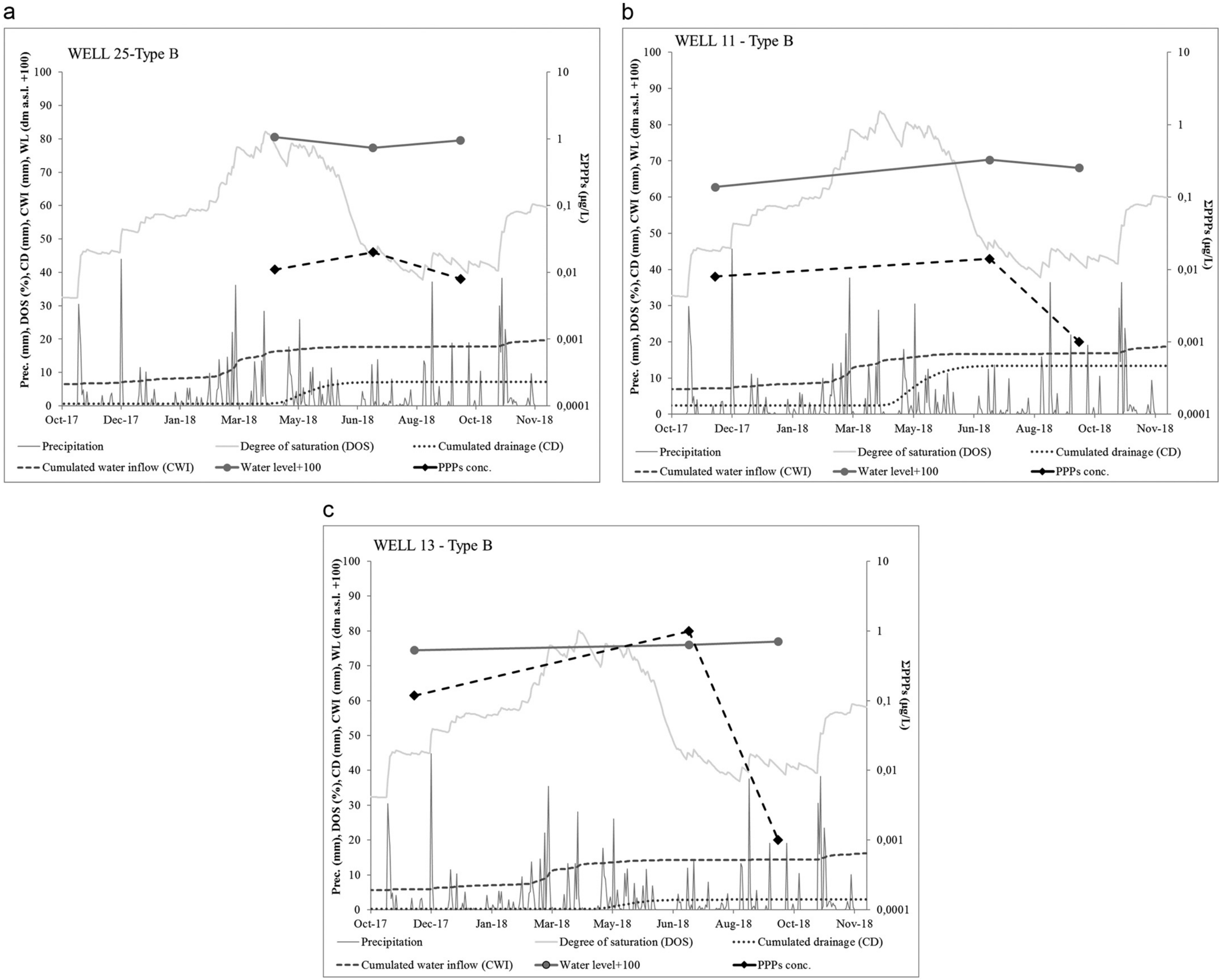

Fig. 4. Integration of modelling outputs with precipitation data and PPPs concentration in wells of type "B"; a) well WP 25, b) well WP 11 and c) well WP 13.

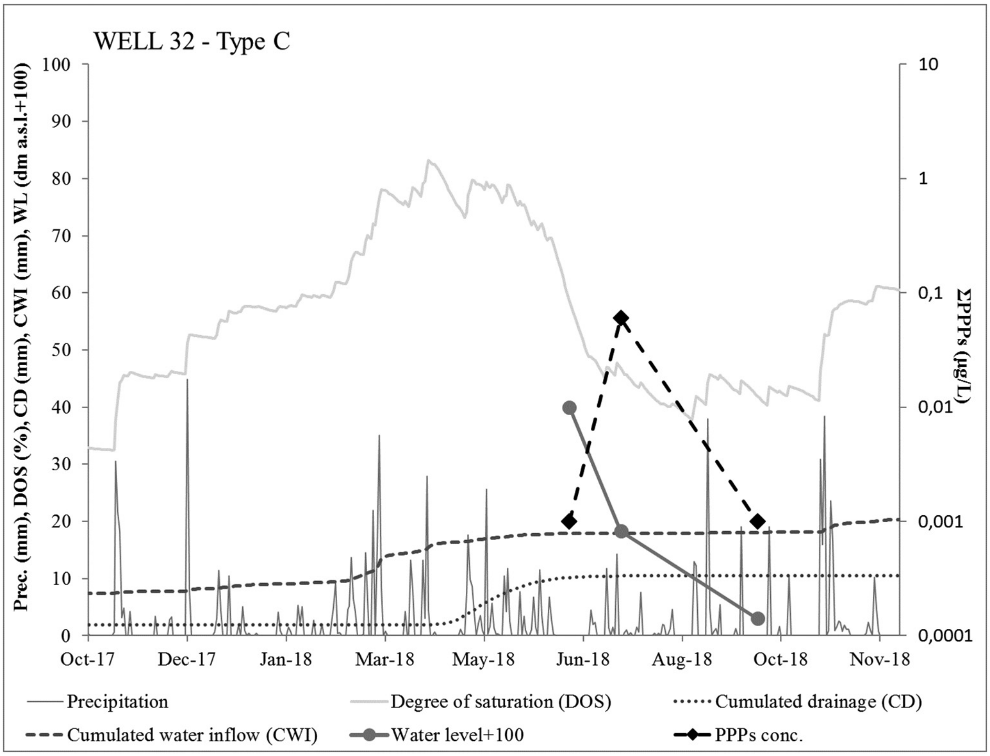

Fig. 5. Integration of modelling outputs with precipitation data and PPPs concentration in well 32, type "C".

probably due to its chemical transformation (not persistent PPP) and well dilution through the riverbed.

As a final point, the obtained results underlined the type A wells as the most exposed to PPP contamination and the type C as the less exposed, while type B wells are somewhere in the middle. This can be explained by the conservative conditions of the type A wells: use for PPPs mixtures and sprayer washing (well WP 28, for WP 26 no information is available), positioned in the middle of the vineyards, at the top hill, with low slope clayey surrounding soils and no subsurface inflow able to "wash" it. Therefore, when contaminated by point sources, the chemicals either degrade or in case of intense rainfalls are transported downhill by outflow. On the contrary, the position of type C well far away from agricultural crops, with a low slope and river recharge through the riverbed and just partially from subsurface inflow makes it less exposed. Indeed, the subsurface inflow could transport chemicals from uphill and contaminate it but due to river recharge, its water is continuously "washed off".

4. Conclusions

As main conclusion of the present work, it can be stated that the occurrence of PPPs in groundwater in areas with intensive agricultural activities cannot be related just to chemical environmental fate properties or pedoclimatic conditions, but also to end-user behavior. Indeed, the approach proposed in this work, which collected and integrated monitoring data, sub-surface water movement data and territorial characteristics, including farm management and farmer's behavior, is shown to be suitable for a first identification of the most probable contamination source of groundwater by PPPs used in viticulture. Indeed, for wells located on hilltop vineyards, with low slope and no water movement in the surrounding soil, that are utilised for PPP's mixture preparation and sprayer washing, the contamination is most likely from point sources. On the contrary, for wells located in a fenced area at the bottom of the hill, far away from vineyards and being used for drinking water production, the contamination is most likely from diffuse sources. However, additional hydrological data, both modelling and field, and monitoring data, with a higher frequency and for a longer period, would allow a more complete assessment. In the study area, the obtained results were used to raise awareness among farmers and one of the three farms involved in the third survey become a demonstration farm where a dedicated waterproof platform for sprayer washing, equipped with wastewater recovery and disposal system was implemented.. Several demonstration activities were then organised with the farmers of the entire Action Lab of WaterProtect Project in order to show its functionality and promote a diffuse use in Tidone Valley. Finally, the proposed approach could be used to assess possible effects of climate change and even transferred to other similar territorial realities. In our specific case, considering the particularity of the small shallow aquifers where the wells are located, an increase of atmospheric temperature and decrease of precipitations could determinate a concentration rise of PPPs in the groundwater of the wells. Furthermore, intensive rainfall events, that occurred frequently in recent summers, could result in an interaction between these shallow aquifers, due to lateral water movement in the first layer of the soil, posing a risk of contamination of the protected drinking water wells.

CRediT authorship contribution statement

Nicoleta Suciu: Investigation, Resources, Data curation, Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Project administration. **Camilla Farolfi:** Data curation, Methodology, Writing - review & editing. **Roberta Zambito Marsala:** Investigation, Data curation, Methodology, Writing - review & editing. **Elisabetta Russo:** Resources, Data curation, Conceptualization, Methodology, Validation, Writing - review & editing. **Marcello De Crema:** Methodology, Investigation, Writing - review & editing. **Emanuela Peroncini:** Methodology, Investigation, Writing - review & editing. **Fausto Tomei:** Conceptualization, Methodology, Validation, Writing - review & editing. **Gabriele Antolini:** Conceptualization, Methodology, Validation, Writing - review & editing. **Marco Marcaccio:** Conceptualization, Methodology, Validation, Writing - review & editing. **Vittorio**

Marletto: Conceptualization, Methodology, Validation, Writing - review & editing. **Ruggero Colla:** Methodology, Investigation, Visualization. **Antonio Gallo:** Data curation, Validation, Writing - review & editing, Visualization. **Ettore Capri:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Funding acquisition.

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.

Acknowledgements

This research is part of the WaterProtect project and has received funding from the European Union's Horizon 2020 Research and Innovation Program under grant agreement No. 727450. The Catholic University trough the Project ECORESILIENTE also supported the research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141495.

References

Antolini, G., Auteri, L., Pavan, V., Tomei, F., Tomozeiu, R., Marletto, V., 2015. A daily high-resolution gridded climatic data set for Emilia-Romagna, Italy, during 1961–2010. Int. J. Climatol. 36, 1970–1986. https://doi.org/10.1002/joc.4473.

Balderacchi, M., Benoit, P., Cambier, P., Eklo, O.M., Gargini, A., Gemitzi, A., Gurel, M., Kløve, B., Nakic, Z., Predaa, E., Ruzicic, S., Wachniew, P., Trevisan, M., 2013. Groundwater pollution and quality monitoring approaches at the European level. Crit. Rev. Environ. Sci. Technol. 43 (4), 323–408. https://doi.org/10.1080/10643389.2011.604259.

Bindi, M., Miglietta, F., Gozzini, B., Orlandini, S., Seghi, L., 1997. A simple model for simulation of growth and development in grapevine (Vitis vinifera L.). I. Model description. Vitis 36 (2), 67–71. https://doi.org/10.5073/vitis.1997.36.67-71.

Bittelli, M., Tomei, F., Pistocchi, A., Flury, M., Boll, J., Brooks, E.S., Antolini, G., 2010. Development and testing of a physically based, three-dimensional model of surface and subsurface hydrology. Advances in Water Resource 33, 106–122. https://doi.org/10.1016/j.advwatres.2009.10.013.

Bois, B., Volta, A., Rega, M., Caffarra, A., Costa, F., Antolini, G., Tomei, F., Galizia, S., Nascimben, J., Crestini, D., Baret, F., Neri, M., Bertozzi, C., Lughi, G., Roffilli, M., Botarelli, L., Bauer-Marschallinger, B., Hasenauer, S., Campagnolo, S., Dellavalle, D., Brossaud, F., Grosso, V., Marletto, V., 2014. GIS, mechanistic modelling and ontology: a performing mix for precision and sustainable viticulture. Proc. of 37h World Congress of Vine and Wine, Mendoza, Argentina, pp. 292–304.

Brouwer, R., Ordens, C.M., Pinto, R., Condesso de Melo, M.T., 2018. Economic valuation of groundwater protection using a groundwater quality ladder based on chemical threshold levels. Ecol. Indic. 88, 292–304. https://doi.org/10.1016/j.ecolind.2018.01.041.

Caffarra, A., Eccel, E., 2011. Projecting the impacts of climate change on the phenology of grapevine in a mountain area. Grape and Wine Research 17, 52–61. https://doi.org/10.1111/j.1755-0238.2010.00118.x.

Calliera, M., Capri, E., Zambito Marsala, R., Russo, E., Bisagni, M., Colla, R., Suciu, N., 2020. The Role of Risk Communication and Stakeholders Involvement in the Adoption of Best Management Practices and for a Sustainable Use of Pesticides in Hilly Vineyards (Submitted to this VSI).

Capri, E., Balderacchi, M., Yon, D., Reeves, G., 2005. Deposition and dissipation of chlorpyrifos in surface water following vineyard applications in northern Italy. Environ. Toxicol. Chem. 24, 852–860. https://doi.org/10.1897/04-151R.1.

Croghan, C., Egeghy, P.P., 2003. METHODS OF DEALING WITH VALUES BELOW THE LIMIT OF DETECTION USING SAS. Presented at Southeastern SAS User Group, St. Petersburg, FL (September 22–24).

Di Guardo, A., Finizio, A., 2016. A moni-modelling approach to manage groundwater risk to pesticide leaching at regional scale. Sci. Total Environ. 545–546, 200–209. https://doi.org/10.1016/j.scitotenv.2015.12.056.

EFSA, 2008. Conclusion regarding the peer review of the pesticide risk assessment of the active substance Penconazole. EFSA J. https://doi.org/10.2903/j.efsa.2008.175r.

EFSA, 2009. Conclusion on pesticide peer review regarding the risk assessment of the active substance fluopicolide. EFSA J. https://doi.org/10.2903/j.efsa.2009.299r.

EFSA Panel on Plant Protection Products and their Residues (PPR), 2013. Scientific opinion on the report of the FOCUS groundwater working group (FOCUS, 2009): assessment of higher tiers. EFSA J. 11, 3291. https://doi.org/10.2903/j.efsa.2013.3291.

EPA, Guidance for Data Quality Assessment, 2000. Practical methods for data analysis. https://19january2017snapshot.epa.gov/sites/production/files/2015-06/documents/g9-final.pdf.

European Commission (EC), 2014. Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU. Report of the FOCUS Ground Water Work Group. EC Document Reference Sanco/13144/2010 Version 3 (513 pp).

European Environmental Agency (EEA), 2018. European Waters Assessment of Status and Pressure 2018. EEA Report, 7/2018. vol. 2018. Publications Office of the European Union, Luxembourg. https://doi.org/10.2800/303664.

European Parliament and the Council of the European Union, 2000. Directive of the European Parliament and of the Council of 23 October 200 Establishing a Framework for Community Action in the Field of Water Policy, 2000/60/EC.

European Parliament and the Council of the European Union, 2009a. Directive of the European Parliament and of the Council of 21 October 2009 Establishing a Framework for Community Action to Achieve the Sustainable Use of Pesticides. 2009/128/EC.

European Parliament and the Council of the European Union, 2009b. Regulation (EC) of the European Parliament and of the Council of 21 October 2009 Concerning the Placing of Plant Protection Products on the Market and Repealing Council Directives 79/117/EEC and 91/414/EEC, No 1107/2009.

Farina, M., Marcaccio, M., Zavatti, A. (Eds.), 2014. Esperienze e prospettive nel monitoraggio delle acque sotterranee. Il contributo dell'Emilia-Romagna. Pitagora Editrice, Bologna (560 pp. (ISBN 88-371-1859-7).

Gimsing, A.L., Agert, J., Baran, N., Arnaud, B., Ferrari, F., Gibson, R., Hammond, L., Helger, F., Jones, L.R., König, W., Kreuger, J., van der Linden, T., Liss, D., Loiseau, L., Massey, A., Miles, B., Monrozies, L., Newcombe, A., Poot, A., Reeves, G.L., Reichenberger, S., Rosenbom, A.E., Staudenmaier, H., Sur, R., Schwen, A., Stemmer, M., Tüting, W., Ulrich, U., 2019. Conducting groundwater monitoring studies in Europe for pesticide active substances and their metabolites in the context of Regulation (EC) 1107/2009. Journal of Consumer Protection and Food Safety 14, 1–93. https://doi.org/10.1007/s00003-019-01211-x.

Herrero-Hernández, E., Andrades, M.S., Álvarez-Martín, A., Pose-Juan, E., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2013. Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region. J. Hydrol. 486, 234–245. https://doi.org/10.1016/j.jhydrol.2013.01.025.

Herrero-Hernández, E., Simon-Egea, A.B., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Andrades, M.S., 2020. Monitoring and environmental risk assessment of pesticide residues and some of their degradation products in natural waters of the Spanish vineyard region included in the Denomination of Origin Jumilla. Environ. Pollut. 264, 114666. https://doi.org/10.1016/j.envpol.2020.114666.

Ippisch, O., Vogel, H.J., Bastian, P., 2006. Validity limits for the van Genuchten–Mualem model and implications for parameter estimation and numerical simulation. Adv. Water Resour. 29, 1780–1789.

Kourakos, G., Klein, F., Cortis, A., Harter, T., 2012. A groundwater nonpoint source pollution modeling framework to evaluate long-term dynamics of pollutant exceedance probabilities in wells and other discharge locations. Water Resour. Res. 48. https://doi.org/10.1029/2011WR010813.

Lebon, E., Dumas, V., Pieri, P., Schultz, H.R., 2003. Modelling the seasonal dynamics of the soil water balance of vineyards. Funct. Plant Biol. 30 (6), 699–710. https://doi.org/10.1071/FP02222.

Magnani, F., Nolè, A., Ripullone, F., Grace, J., 2009. Growth patterns of Pinus sylvestris across Europe: a functional analysis using the HYDRALL model. IForest 2 (October), 162–171. https://doi.org/10.3832/ifor0516-002.

Martínez-Navarrete, C., Jiménez-Madrid, A., Sánchez-Navarro, I., Carrasco-Cantos, F., Moreno-Merino, L., 2011. Conceptual framework for protecting groundwater quality. International Journal of Water Resources Development 27 (1), 227–243. https://doi.org/10.1080/07900627.2010.532476.

Ogden, T.L., 2010. Handling results below the level of detection. The Annals of Occupational Hygiene 54-3, 255–256. https://doi.org/10.1093/annhyg/mep099.

Parris, K., 2011. Impact of agriculture on water pollution in OECD countries: recent trends and future prospects. International Journal of Water Resources Development 27 (1), 33–52. https://doi.org/10.1080/07900627.2010.531898.

Pertot, I., Caffi, T., Rossi, V., Mugnai, L., Hoffmann, C., Grando, M.S., Gary, C., Lafond, D., Duso, C., Thiery, D., Mazzoni, V., Anfora, G., 2017. A critical review of plant protection tools for reducing pesticide use on grapevine and new perspectives for the implementation of IPM in viticulture. Crop Prot. 97, 70–84. https://doi.org/10.1016/j.cropro.2016.11.025.

Petrie, A., Watson, P.F., 2006. Statistics for veterinary and animal science. Second edition. Blackwell Publishing Ltd., Oxford, UK.

Rabiet, M., Margoum, C., Gouy, V., Carluer, N., Coquery, M., 2010. Assessing pesticide concentrations and fluxes in the stream of a smallvineyard catchment – effect of sampling frequency. Environ. Pollut. 158, 737–748. https://doi.org/10.1016/j.envpol.2009.10.014.

Regione Emilia-Romagna, 2010. Approvazione delle attività della Regione Emilia-Romagna riguardanti l'implementazione della Direttiva 2000/60/CE ai fini della redazione e adozione dei Piani di Gestione dei Distretti idrografici Padano, Appennino settentrionale e Appennino centrale. Delibera di Giunta della Regione Emilia-Romagna n. 350 del 8/02/2010 (in Italian). Available on. http://ambiente.regione.emilia-romagna.it/it/acque/approfondimenti/normativa/DGR_350_2010_All2.pdf. (Accessed 25 May 2020). .

Suciu, A.N., Ferrari, T., Ferrari, F., Trevisan, M., Capri, E., 2011. Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards. Environ. Sci. Pollut. Res. 18, 1374–1383. https://doi.org/10.1007/s11356-011-0494-4.

Tan, Q., Huang, G.H., Cai, Y.P., 2011. Radial interval chance-constrained programming for agricultural non-point source water pollution control under uncertainty. Agric. Water Manag. 98 (10), 1595–1606. https://doi.org/10.1016/j.agwat.2011.05.013.

Tomei, F., Antolini, G., Bittelli, M., Marletto, V., Pasquali, A., Van Soetendael, M., 2007. Validazione del modello di Bilancio idrico CRITERIA. Italian Journal of Agrometerology 1 (AIAM, 10° Convegno nazionale di Agrometeorologia: Quaderno degli Abstract).

Vischetti, C., Cardinali, A., Monaci, E., Nicelli, M., Ferrari, F., Trevisan, M., Capri, E., 2008. Measures to reduce pesticide spray drift in a small aquatic ecosystem in vineyard estate. Sci. Total Environ. 389 (2–3), 497–502. https://doi.org/10.1016/j.scitotenv.2007.09.019.

WWAP (United Nations World Water Assessment Programme), 2015. The United Nations World Water Development Report 2015: Water for a Sustainable World. UNESCO, Paris.

Zambito Marsala, R., Capri, E., Russo, E., Bisagni, M., Colla, R., Lucini, L., Gallo, A., Suciu, N., 2020. A first evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2020.139730.

Zamboni, M., 2006. Le zonazioni viticole in Emilia-Romagna. Bollettino dell'Associazione Italiana Pedologi (AIP), Il Suolo, Convegno Suolo e Vino (numero 37-39).