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Glyphosate, glufosinate ammonium, and AMPA occurrences and sources in groundwater of hilly vineyards

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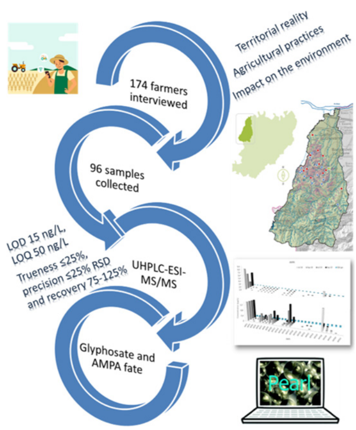
HIGHLIGHTS

- Glyphosate was detected in 40 % groundwater samples, 41 % of which were above EQS_{GW}.
- AMPA was detected in 55 % groundwater samples, with 56 % having values above EQS_{GW}.
- Glufosinate ammonium has never been detected in the groundwater of Tidone Valley.
- Diffuse and point sources are responsible for PPPs groundwater contamination.
- The use of glyphosate for non-agricultural weed control contributed to pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate [N-(phosphonomethyl) glycine] and glufosinate ammonium [ammonium dl-homoalanin-4-(methyl) phosphinate] are broad-spectrum, nonselective, post-emergence herbicides extensively used in various applications for weed control in both agricultural and non-crop areas. Aminomethylphosphonic acid (AMPA) is the major degradation product of glyphosate found in plants, water, and soil. Due to glyphosate's presumed low mobility, its monitoring in European water was limited. Recently both glyphosate and AMPA have been detected in several groundwater samples in Europe, U.S, Canada, Argentina, and China. Understanding the sources of these substances in water, especially in groundwater used for drinking, becomes a priority. In the present work the occurrences and the main drives of glyphosate, AMPA, and glufosinate ammonium in the groundwater of hilly vineyards located in the North-West of Italy were evaluated. Groundwater monitoring results showed frequent detection and concentrations above EQS_{GW} for glyphosate and AMPA, while glufosinate ammonium was never detected. More frequent occurrences and higher concentrations were detected in the samples collected from wells located in the farmyards, most of them being used for irrigation and/or preparation of PPPs mixtures. Indeed, AMPA was the only compound detected in one groundwater well used for drinking, at values bellow EQS_{GW}/DWQS. Such monitoring results were not expected as the modelling estimations under local pedoclimatic conditions indicated no risk of leaching to groundwater. However, the modelling

Abbreviations: AMPA, aminomethylphosphonic acid; ARPAE, Agenzia Regionale per la Prevenzione, l'Ambiente e l'Energia dell'Emilia-Romagna; DWQS, drinking water quality standards; EQS_{GW}, Environment Quality Standard for groundwater; FOCUS, FOrum for the Co-ordination of pesticide fate models and their Use; LOD, limit of detection; LOQ, limit of quantification; PPPs, plant protection products.

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performance and output may have been influenced by the non-consideration of important specific processes. Integrating monitoring and modelling results with information concerning the agricultural practices adopted and the wells use and location, possible contamination drivers were identified. These include the non-agricultural use of glyphosate in the farmyard, the point source contamination of wells and the possible transport with the subsurface lateral inflow of water from up-hill vineyard. This study strengthens the position of SETAC EMAG-Pest GW group concerning the necessity of spatial and temporal contextualisation of groundwater monitoring for a better understanding of its contamination drivers by PPPs.

1. Introduction

Glyphosate [N-(phosphonomethyl) glycine] and glufosinate ammonium [ammonium dl-homoalanin-4-(methyl) phosphinate] are broad-spectrum, nonselective, post-emergence herbicides extensively used in various applications for weed control in aquatic systems and vegetation control in non-crop areas (Barker and Dayan, 2019). Aminomethylphosphonic acid (AMPA) is the major degradation product of glyphosate found in plants, water, and soil (Van Stempvoort et al., 2014). Furthermore, glyphosate is one of the most widely used herbicides in European agriculture, representing 33 % (46,527 t) of total herbicide sales in the EU 28 + 3 countries (EU28 + Norway, Switzerland and Turkey, data collected between 2013 and 2017). 90 % of total national glyphosate sales (by volume) is used by the agricultural sector (Antier et al., 2020). Glufosinate ammonium was banned for use in Europe in 2018 (https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/active-substances/?event=as.details&as_id=79).

Degradation and mobility in soil of these substances have been extensively studied. As a result of many studies and reports glyphosate showed low leachability to groundwater. Glyphosate has a strong tendency to sorb to soil particles and to undergo degradation by microorganisms (Borggaard and Gimsing, 2008; Meftaul et al., 2020; Meftaul et al., 2021). Its relevant metabolite AMPA is considered more persistent in soil (Mamy et al., 2016), even if there is some evidence that both may leach through the macropores in the soil profile (Laitinen et al., 2006; Meftaul et al., 2021). Recently, Maggi et al. (2020) after a comprehensive analysis of glyphosate and AMPA potential environmental contamination hazard at global scale highlighted that a low contamination occurs in nearly all croplands where glyphosate is used. Glyphosate was found to be a persistent contaminant at relatively low values in about 30 % of global croplands but AMPA was found to be persistent in about 93 % of croplands. Due to the difficulty of analysis even by liquid chromatography, concentrations of glyphosate in European groundwater have been reported occasionally and its monitoring was limited. Recently both glyphosate and AMPA have been detected in several groundwater samples in Europe (EEA, 2020), U.S (Battaglin et al., 2014), Canada (Van Stempvoort et al., 2016), Argentina (Demonte et al., 2018; Okada et al., 2018) and China (Geng et al., 2021). The maximum concentrations in groundwater ranged from <0.02 to 11 μg/L for glyphosate and <0.05 to 6.5 μg/L for AMPA. Glufosinate ammonium was never found in groundwater samples in Europe, China, and Argentina (EEA, 2020; Geng et al., 2021, Demonte et al., 2018). In Italy, maximum glyphosate and AMPA concentrations of nearly 1 and 2 μg/L, respectively, were measured in groundwater samples of Po Valley (Paris et al., 2016). As numerous recent toxicological studies reported negative effects of glyphosate, its metabolite AMPA, and glufosinate ammonium to mammalian and aquatic organisms (Geetha, 2021), with glyphosate and glufosinate ammonium showing developmental toxicity and (EFSA, 2005; EFSA, 2015) AMPA being genotoxic (Mañas et al., 2009), understanding the sources of these substances in water, especially in groundwater used for drinking, becomes a priority. This will help implementing successful measures to mitigate this phenomenon or to develop targeted management and policy decisions. While agricultural applications are limited to crops, the use of these substances in urban environments is more diversified. Nevertheless, very little is known about the influence of land use and the impact of crop type on surface and groundwater contamination by glyphosate, AMPA, and glufosinate ammonium (Medalie et al., 2020).

In this context, the main objective of this study is to improve the understanding of the influence of mixed urban and agricultural land use on groundwater quality and to evaluate the occurrences and the main drives of glyphosate, AMPA, and glufosinate ammonium in the groundwater of hilly vineyards in North-West of Italy. In particular, the study aims (i) investigating the use of glyphosate and glufosinate ammonium on the territory by ad-hoc questionnaires, (ii) assessing glyphosate, AMPA, and glufosinate ammonium leaching to groundwater by use of approved EU fate models and (iii) integrating monitoring and modelling results with territorial information for the identification of contamination drivers.

2. Materials and methods

2.1. Problem formulation

As previously mentioned, several studies on glyphosate and AMPA mobility in soil evidenced that both may leach through the macropores in the soil profile (Laitinen et al., 2006; Meftaul et al., 2021). Since soil particles or colloidal transport of strongly adsorbed pesticides through macropores (preferential flow) cannot be prevented, a slight increase of the low glyphosate leaching potential, in soils where matrix flow is a significant process, may be present. Furthermore, additional experimental and numerical studies indicated that glyphosate and AMPA mobility is dependent on the soil physicochemical properties, with different sorption mechanisms being involved. Indeed, several authors reported that glyphosate sorbs on soil through its phosphonic acid moiety and that sorption increases with decreasing the pH of the solution and increasing the Al and Fe ions presence at the exchange soil surface (Borggaard and Gimsing, 2008). Therefore, considering this state of knowledge with respect to glyphosate end AMPA mobility and leaching, their occurrences in groundwater can be explained by several causes/hypothesis such as point source contamination, favourable soil physicochemical properties, macropore flow: (shallow groundwater), inflow of surface water or bank filtrate (Milan et al., 2022).

With the goal to evaluate the occurrences and the main drives of glyphosate, AMPA, and glufosinate ammonium in the groundwater of a hilly vineyards in Tidone Valley, a stepwise procedure was developed:

1- In the first step all the available information from the study area were collected (i.e. existence and use of groundwater wells in the farm/vineyard; adoption of IPM or organic farming approaches; use and handling of PPPs; number of PPPs application in vineyard; use and type of herbicides; participation to training courses, etc.) and analysed for the development of a suitable groundwater sampling network and the characterization of the territorial agricultural practices.
2- In a second step, the previously collected information were integrated with groundwater monitoring results and modelling fate results (FOCUS PEARL 4.4.4 model was used under real pedoclimatic conditions), for the final identification of the main contamination drivers. Indeed, the evaluation of the main drivers governing groundwater contamination is difficult to be performed by monitoring on a large scale due to the wide range of crops present and the diversified pedoclimatic conditions and agricultural practices adopted. Therefore, modelling is an effective screening tool used to estimate the PPPs' potential to reach groundwater (Geng et al., 2021).

2.2. Study area and development of the sampling network

The study area is in Tidone Valley, Province of Piacenza, Emilia Romagna Region, north-west of Italy (Fig. 1) and is described in detail by Zambito Marsala et al. (2020), Suciu et al. (2020) and Calliera et al. (2021). Shortly, the area covers 206.72 km^2 and includes part of the Tidone Torrent catchment and the catchments of the two streams Lora-Carogna and Carona-Boriacco. It is a hilly zone with an elevation level between 100 m and 350 m above sea level and characterized by clay and clay-silty type of soils (Zamboni, 2006). and 2941 ha of vineyard in 2016 (ISTAT, 2016: http://dati.istat.it/Index.aspx?DataSetCode=DCSP_COLTIVAZ).

As described in detail by Zambito Marsala et al. (2020), a sampling network of 26 wells was developed by selecting existing groundwater wells and following an upstream-downstream criterion: the upstream well should be the one not contaminated while the downstream well should collect all the residues of the treatments due to run-off at the soil surface and transport to surface water body and drainage to groundwater. The wells selected were coded from WP01 to WP32 and included: three wells used for drinking water and part of the network of the Regional Environmental Agency (ARPAE) and the water supply company (IRETI) and 23 wells used for irrigation and the preparation of PPP mixture and sprayers washing. The latter are located either in the middle of vineyards or in the farmyards and have depths between 2 m and 34 m (Fig. 1, Table 1).

For the development of the sampling network and the characterization of the territorial agricultural and fertilization practices, including the use of glyphosate and glufosinate ammonium herbicides, a survey campaign was conducted between August and November 2017. An ad hoc questionnaire was developed and 174 farmers from the study area were involved (Calliera et al., 2020).

2.3. Groundwater sampling and chemicals determination

Between July 2018 and September 2019, a total of 97 groundwater samples were collected. Four sampling campaigns were carried out: July and September 2018 and July and September 2019. The sampling time was chosen based on grapevine treatments, after pesticides and fertilizers spraying. The samples were filled into 1500 mL plastic bottles after well flush out and kept at −28 °C until analysis.

Glyphosate, AMPA, and glufosinate ammonium analysis in groundwater were performed by the private laboratory Tentamus Agriparadigma (https://www.agriparadigma.it/) following an internal protocol developed based on the requirements of SANTE/12682/2019 Guidelines (SANTE, 2019; https://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727). Tentamus Agriparadigma has the accreditation for the execution of chemical, microbiological, and product analysis, listed in the official Accredia list, following UNI CEI EN ISO/IEC 17025: 2018. Shortly, the

Table 1
Network wells description.

Well	Municipality	Upstream/downstream	*Vallicola*[a]	Depth (m)
WP01	Ziano	Downstream	Rio Gatto	2
WP03	Ziano	Upstream	Rio del Volto	6.0
WP04	Ziano	Downstream	Rio Lora	–
WP05	Ziano	Downstream	Rio Valle	3.0
WP06	Ziano	Upstream	Rio Valle	7.0
WP07	Ziano	Upstream	Rio Battilana	34.0
WP08	Castel San Giovanni	Downstream	Rio Battilana	30.1
WP09	Ziano	Downstream	Rio Guarone	6.2
WP10	Ziano	Upstream	Rio Guarone	9.0
WP11	Ziano	Upstream	Rio Bardonazzo	5.7
WP13	Ziano	Downstream	Rio Caroncella/Bardonazzo	5.4
WP14	Ziano	Upstream	Rio Montalbo	4.5
WP15	Ziano	Downstream	Rio Montalbo	4.6
WP17	Pianello Val Tidone	Upstream	Rio Lisone	11.5
WP18	Pianello Val Tidone	Downstream	Rio Lisone	3.5
WP19	Alta Val Tidone	Action lab upstream/drinking water	Rio Gualdora	0.0
WP20	Castel San Giovanni	Action lab downstream	Rio Ganaghello	117.0
WP21	Pianello Val Tidone	Drinking water	Torrente Tidone	11.0
WP22	Ziano	Upstream	Rio Lora	5.4
WP24	Ziano	Upstream	Rio Gatto	3.7
WP25	Ziano	Upstream	Rio Caroncella	11.2
WP26	Borgonovo Val Tidone	Upstream	Rio Carona	8.8
WP28	Ziano	Downstream	Rio Bardonazzo	5.0
WP29	Ziano	Upstream	Rio del Volto	2.9
WP30	Ziano	Downstream	Rio del Volto	7.8
WP32	Ziano	Downstream/drinking water	Rio Carona	15.0

[a] Stream crossed by tributaries of *Tidone Torrent*.

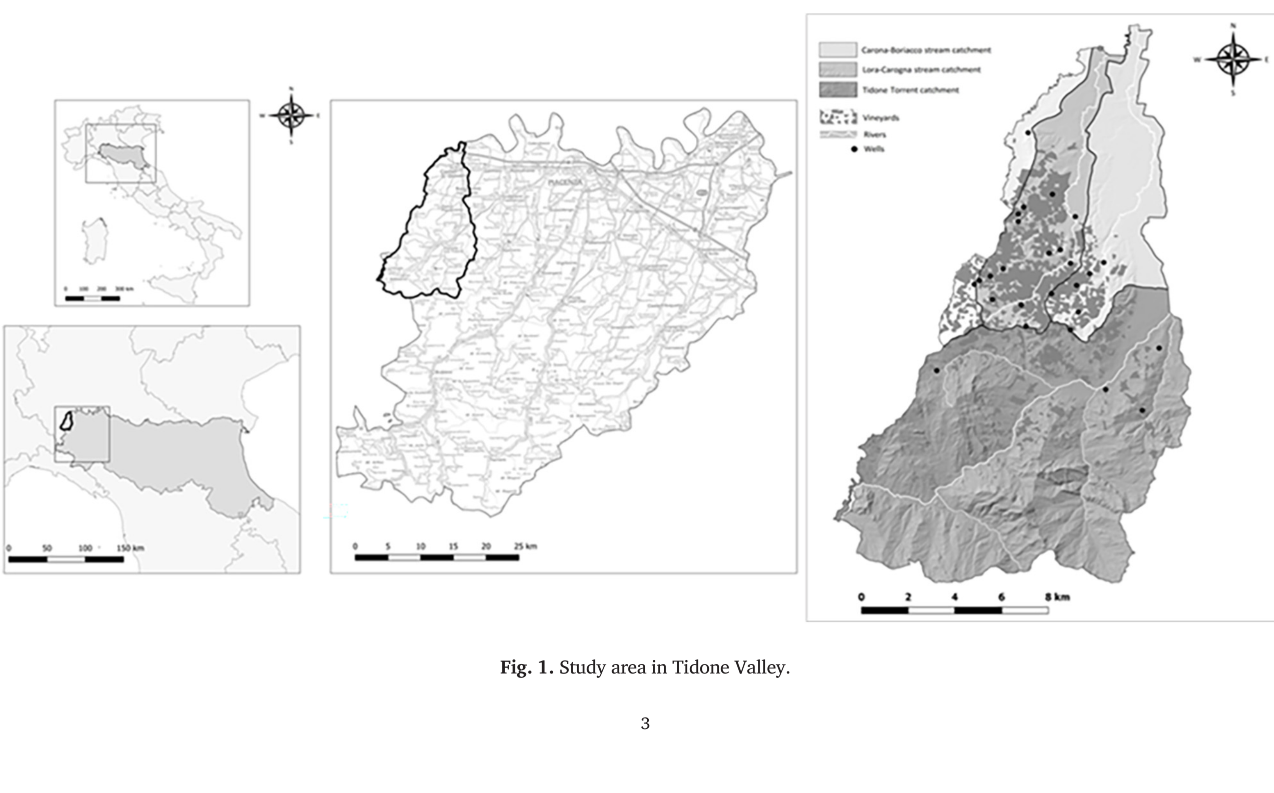

Fig. 1. Study area in Tidone Valley.

groundwater samples were centrifuged, filtered through 0.22 μm membrane, and 1 mL of water was derivatized by adding 0.1 mL 5 % borate buffer (pH 9) followed by 0.1 mL 9-fluorenyl methyl chloroformate (FMOC-Cl) reagent (10,000 mg/L) and allowing the reaction to take place for 4 h at room temperature. After that, samples were centrifuged again and analysed by UHPLC-ESI-MS/MS. The mass spectrometers used for the analysis were two SCIEX Triple Quad 5500 and one SCIEX Triple Quad 6500+. The chromatographic separation was achieved on a Waters ACQUITY UPLC HSS T3 Column, 100 Å, 1.8 μm, 2.1 mm × 100 mm column using ultrapure water with 10%methanol, 0.5 % ammonium formiate (1 M) and 0.1 % formic acid (phase A), and methanol with 0.5 % ammonium formiate (1 M) and 0.1 % formic acid (phase B). Mobile phase flow was 0.4 mL/min and the injection volume was 10 μL. Glyphosate (99.7 % purity), AMPA (99.4 % purity), and glufosinate ammonium (99.6 % purity) standards were purchased from Merck KGaA (Darmstadt, Germany) and analysis standard solution were performed in water: acetonitrile (90:10 v/v). All the reagents were of LC-MS/MS grade.

2.3.1. Validation study

The linearity of the method was evaluated by analyzing six standard solutions for all three analytes in the range of 50–2000 ng/L.

Precision (repeatability, expressed as the relative standard deviation in %) and recoveries were determined within the day by analyzing fortified samples in sextuplicate. This experiment was performed at two spiking levels: 50 ng/L and 500 ng/L.

The limits of detection (LOD), defined as the lowest concentration that the analytical process can reliably differentiate from background levels, were obtained when the less sensitive signal was at least three times the average of background noise in the chromatogram at the lowest analyte concentration assayed. The limits of quantification (LOQ) were established as the lowest concentration assayed and validated, which gave satisfactory Trueness (≤25 %), precision (≤25 % RSD) and recovery (75–125 %) (Dlgs 31, 2001).

The specificity of the method was evaluated by analyzing a blank procedure, a processed blank sample, and a blank sample spiked at the lowest fortification level assayed (LOQ), 50 ng/L. Under these conditions, the response obtained for both the blank procedure and the blank samples should not exceed 10 % of the response corresponding to the LOQ.

2.4. Fate model application

The FOCUS PEARL model - Pesticide Emission Assessment at Regional and Local scales, as pesticide registration tool used in the review process according to Council Directive 1107/2009 (EU, 2009), carries out the predicted environmental concentrations (PECs) of pesticides in groundwater and topsoil and provides an evaluation of the main drivers for pesticide leaching to groundwater (Van den Berg et al., 2016). In this study the FOCUS PEARL version 4.4.4 was used. The simulation of water flow and heat transport in the soil-plant systems is realized by using the SWAP (Soil Water Atmosphere Plant) model. This hydrological model is combined with the pesticide model PEARL into one software package. A detailed description of processes for pesticides in the soil-plant system and the emission of these substances is given by Van den Berg et al. (2016). For the assessment of risk leaching, the FOCUS Groundwater Scenarios have been developed. In this study, the Piacenza Vines Scenario was modified considering the daily local weather data (January 2017 – December 2020) and soil characteristics of Val Tidone. All the input data were provided by the Regional Environmental Agency, ARPAE (Fig. 2, Tables S1, S2). Irrigation, tillage, and deposition were not considered. Glyphosate, its transformation in AMPA, and glufosinate ammonium were implemented in PEARL (AMPA as metabolite) and considered as applied at soil surface at the maximum dosage allowed in the labeling of the technical formulations. The parameters values were taken for the PPDB database (http://sitem.herts.ac.uk/aeru/ppdb/).

2.5. Data analysis

The percentage of AMPA (P_{AMPA}) and $Ratio_{AMPA}$ were calculated following the approach proposed by Geng et al. (2021), which considers:

$$P_{AMPA} = \frac{C_{AMPA}/M_{AMPA}}{C_{AMPA}/M_{AMPA} + C_{glyphosate}/M_{glyphosate}} \times 100\%$$

$$Ratio_{AMPA} = \frac{C_{AMPA}}{C_{AMPA} + C_{glyphosate}} \times 100\%$$

where C_{AMPA} and $C_{Glyphosate}$ are their concentrations in the positive water samples (ng/L), C_{AMPA} or $C_{Glyphosate}$ was set to 0 ng/L when below the LOD, C_{AMPA}, or $C_{Glyphosate}$ was set to 30 ng/L when between the LOD and the LOQ. M_{AMPA} and $M_{Glyphosate}$ are their molar mass (g/mol). P_{AMPA} and $Ratio_{AMPA}$ were not calculated when both glyphosate and AMPA were not detected (<16 ng/L); P_{AMPA} provides insight into the fate of glyphosate and AMPA in the aquatic environment. When $P_{AMPA} \geq 0.5$, indicating the molar concentration $C_{AMPA,\,mol} \geq C_{glyphosate,\,mol}$ under-aged glyphosate treatment; when $P_{AMPA} < 0.5$, implying the molar concentration $C_{AMPA,\,mol} <$

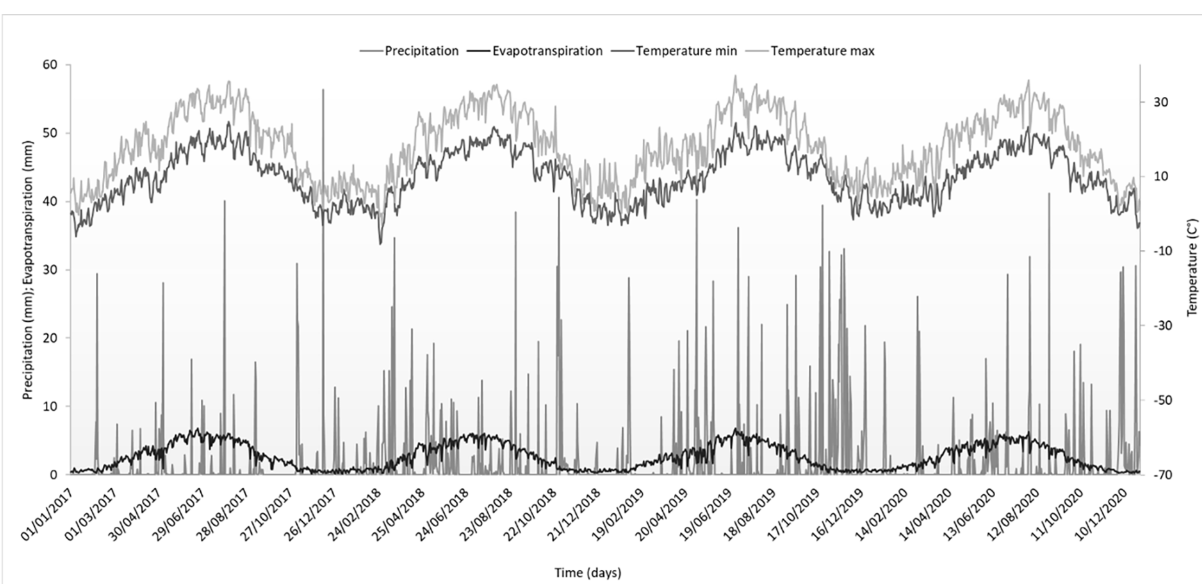

Fig. 2. Climatic parameters of Tidone Valley between January 2017 and December 2020.

$C_{glyphosate,\ mol}$ under freshly glyphosate treatment. The relationship between glyphosate and AMPA concentration in groundwater was assessed by use of Wilcoxon test in Excel program.

3. Results and discussion

3.1. Survey campaign results

The results of the survey conducted between August and November 2017, which involved 174 farmers from Val Tidone and is described in detail by Calliera et al. (2021) and Zambito Marsala et al. (2020), show that 77 % of farmers apply PPPs to grapevine <10 times a year and 85 % of them reported using fungicides, 70 % insecticides, and only 28 % herbicides. Of these, 84 % said they use glyphosate at least once a year, while the remaining 16 % use water/acetic acid or do not know as PPPs are applied by a specialised company. None of the farmers reported using glufosinate ammonium (still approved for use at that date). By checking the ISTAT data on PPPs sales in 2017 in the province of Piacenza (http://dati.istat.it), it was observed that 55.1 % were fungicides, 16.3 % were insecticides, 25.3 % were herbicides and 3.3 % were of biological origin. Therefore, integrating the results of the survey with the ISTAT data it can be stated that grapevine is a crop with moderate use of herbicides and higher use of fungicides and insecticides.

3.2. Analytical method validation

Good selectivity and separation were achieved in 4 min for glyphosate, AMPA, and glufosinate ammonium with FMOC derivatization under Waters C18-T3 100 × 2 mm 1.8 μ column coupled with MS-friendly eluents (Figs. S1–S4).

3.2.1. Limits of quantitation (LOQs) and limits of detection (LODs)

With signal-to-noise ratios of at least 10 and 3 on the less sensitive MRM, the LOQs and LODs were determined to be 50 and 16 ng/L for all three analytes. The highly sensitive mass spectrometer (e.g. SCIEX 6500+) can provide excellent identification and quantification performance. For each analyte the specificity was guaranteed by the recording of the chromatographic trace of 2 MRM transitions and by compliance with the two conditions: ion ratio +/− 30 % of theoretical and retention times and peak shape overlapping (Fig. S1). In literature, under FMOC-Cl pre-column derivatization and solid-phase extraction enrichment, the reported LODs, and LOQs were 0.2–200 ng/L and 0.7–600 ng/L for glyphosate, 0.1–100 ng/L and 0.5–200 ng/L for AMPA, 0.5–12 ng/L and 0.9–100 ng/L for glufosinate ammonium (Demonte et al., 2018; Küsters and Gerhartz, 2010; Sanchís et al., 2012). When compared to them, the obtained LODs and LOQs resulted in the same range. The sensitivity obtained was suitable for the quantification of glyphosate, AMPA, and glufosinate ammonium background levels in the groundwater of Tidone Valley.

3.2.2. Calibration curves, accuracy, and precision

The coefficient of determination ($R^2 \geq 0.9993$) demonstrated good linear regressions for all targets in the groundwater matrix. The calibration curves ranged from 50 to 2000 ng/L for glyphosate, AMPA, and glufosinate ammonium. The samples of blank groundwater matrix were spiked at two levels, 50 and 500 ng/L, with a total of six replicates at each level. The accuracy (recovery) was calculated according to: *accuracy (recovery) = concentration/theoretical concentration*100 %.* An accuracy of 100 % points out that the calculated value is the same as the theoretical value. Trueness is another way to express accuracy and the COUNCIL DIRECTIVE 98/83/EC requires it for the quality of water intended for human consumption. It is calculated as absolute difference between the true value and what found, in percentage trueness % = |100 - recovery%. |The precision, defined as the relative standard deviation (RSD) of recovery, was also determined. Under the two fortification levels (50 and 500 ng/L), the calculated average recovery for glyphosate, AMPA, and glufosinate ammonium were 78 %–79 %, 91 %–103 %, and 84 %–86 % with RSD of 3.8 %–5.4 %, 9.3 %–12.8 %, and 2.8 %, respectively. The results indicate acceptable Trueness (3 % -22 %), accuracy (78 %–103 %) and precision (≤12.8 %) at both fortification levels according to Legislative Decree 31 of 02/02/2001 "Implementation of Directive 98/83/EC relating to the quality of water intended for human consumption" (Dlgs 31, 2001). After ≥120 injections on the column, excellent column stability and reproducibility were observed without obvious retention time shift (within 0.07 min) or target peak shape deterioration. The validated method provides an effective, easy, and reliable method to determine the levels of glyphosate, AMPA, and glufosinate ammonium in groundwater, at values below EQS_{GW}.

3.3. Occurrence of the analytes in groundwater and their main drivers

The detection frequencies of the three analytes in the groundwater samples were different among analytes and sampling campaigns (Figs. 3 and 4).

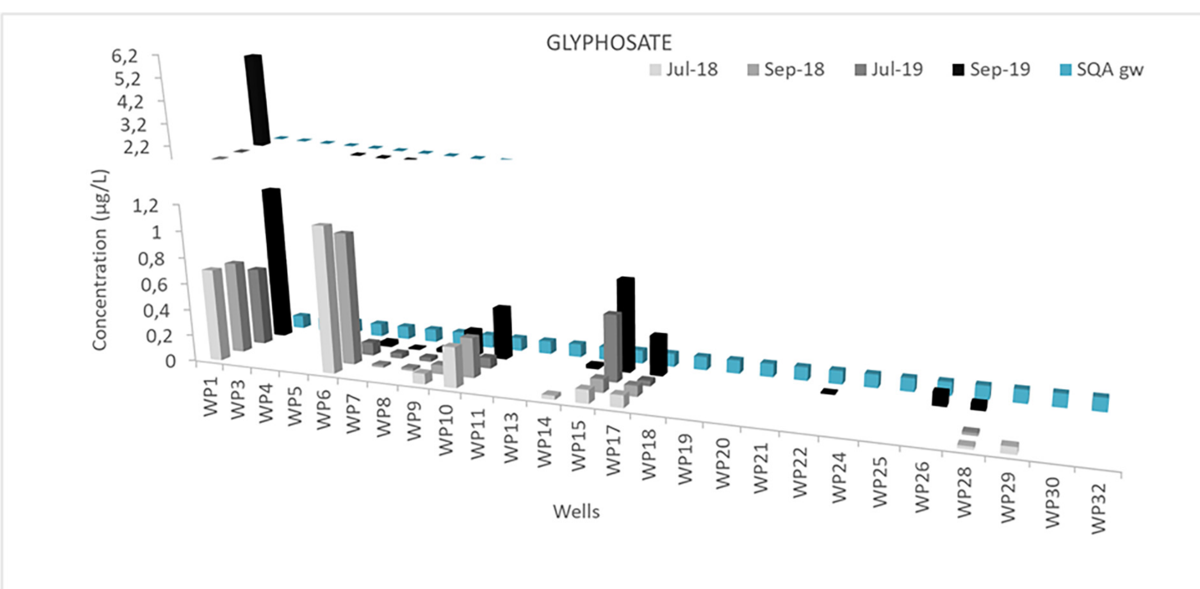

Fig. 3. Glyphosate concentrations in groundwater of Tidone Valley.

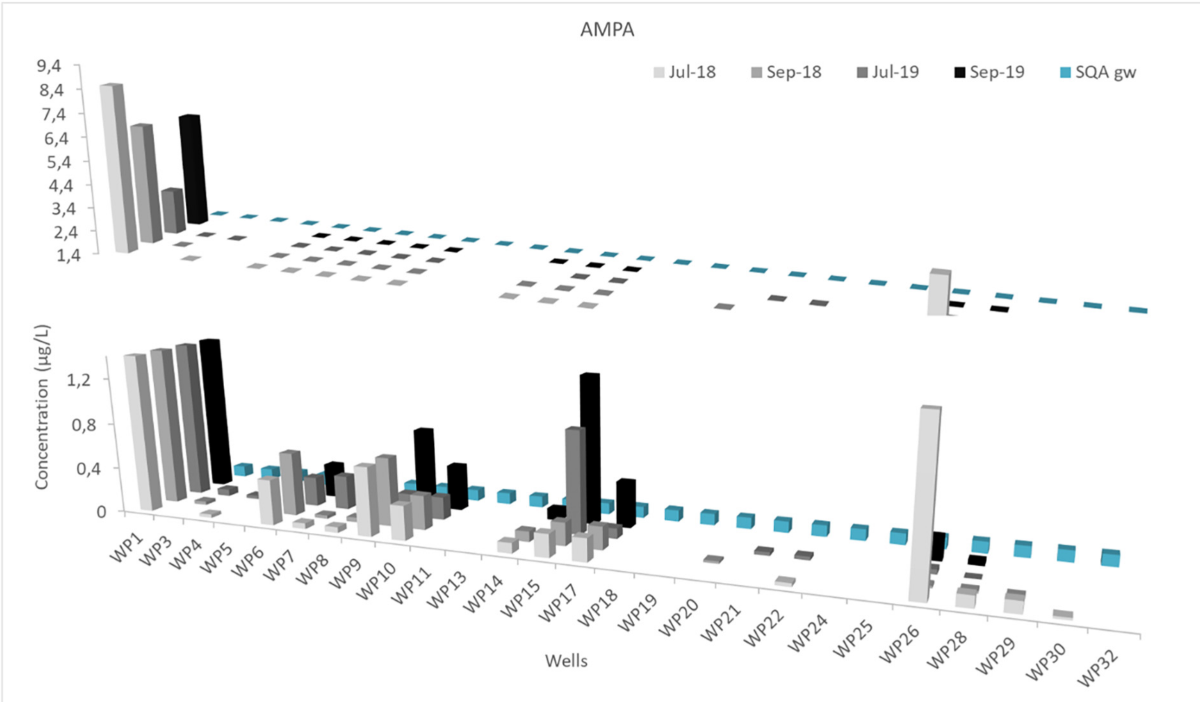

Fig. 4. AMPA concentrations in groundwater of Tidone Valley.

In general, glyphosate was detected at values between <50 and 5500 ng/L in 40 ± 10 % of groundwater samples collected from July 2018 to September 2019, of which 41 ± 11 % were above EQS $_{GW}$. Its metabolite AMPA was detected at values between <50 and 8500 ng/L in 55 ± 2 % of groundwater samples collected during the same time frame, of which 56 ± 14 % were above EQS $_{GW}$. Glufosinate ammonium has never been found in the groundwater of Tidone Valley. This is in line with the non-use declared by the farmers during the surveys. Previous studies in China, Europe and South and North America found glyphosate in 1 to 66 % of groundwater samples analysed (Geng et al., 2021; Horth and Blackmore, 2009; Sanchís et al., 2012; Poiger et al., 2017; Battaglin et al., 2014; Van Stempvoort et al., 2016; Demonte et al., 2018; Okada et al., 2018) and AMPA in 0.8 to 96 % of groundwater samples (Geng et al., 2021; Horth and Blackmore, 2009; Battaglin et al., 2014; Van Stempvoort et al., 2016; Demonte et al., 2018; Okada et al., 2018). Like in the present study, AMPA showed higher occurrences than glyphosate and glufosinate ammonium was not detected in the groundwater in Europe, South and North America, and China. Furthermore, the positively detected concentration of glyphosate was significantly lower than its metabolite under paired Wilcoxon test ($p = 0.01$) during all four sampling campaigns and all wells with positive samples. Furthermore, Due to the weaker adsorption to particulates (Meftaul et al., 2021) and the stronger penetrability to microbial cell membranes (Aparicio et al., 2013), the degradation rate of glyphosate is higher than that of AMPA in soil, resulting in lower DT_{50} and persistence of glyphosate ($DT_{50\ soil\ field}$ 6.45 days) compared to AMPA ($DT_{50\ soil\ field}$ 419 days). Indeed, the median $Ratio_{AMPA}$ was 77 % with an interquartile range of 53–100 % and the median P_{AMPA} was 83 % with an interquartile range of 64–100 %. 38 samples had both glyphosate and AMPA, 15 samples had AMPA and no detectable glyphosate (100 % AMPA ratio), whereas one sample had glyphosate but no detectable AMPA, which yields a $Ratio_{AMPA}$ equal to zero. The P_{AMPA} values provide information on the source, fate, and transport of glyphosate in the environment with lower values suggesting recent or proximal input of glyphosate and higher values suggesting more residence time or distance between input and the measured occurrence. P_{AMPA} median value of 83 indicates that in the groundwater of Val Tidone glyphosate has a long residence time from the time of application. This is in line with the common use of glyphosate for grapevine, which is one treatment in early March (expert judgment). The obtained results are similar with the median $Ratio_{AMPA}$ in groundwater samples from USA (Battaglin et al., 2014) and from Argentina (Okada et al., 2018) while lower values were reported for groundwater samples from China (Geng et al., 2021).

Most of the occurrences of glyphosate and AMPA were in groundwater wells with shallow depth (<9 m), 10 out of 13 for glyphosate and 12 out of 17 for APMA. For one positive well, the depth is unknown. The same trend was observed for the values ≥ to $EQS_{GW;}$ glyphosate was found at values ≥ to EQS_{GW} in seven wells, of which six were shallow, whereas AMPA in 11 wells, of which nine were shallow. Furthermore, considering the territorial position of the monitored groundwater wells, it was observed that 57 % of the wells located in the farmyards have values of glyphosate ≥ to EQS_{GW} (4 out of 7) whereas just 16 % of the wells located in the vineyards have values of glyphosate ≥ to EQS_{GW} (3 out of 19) (Fig. 5). The same trend was observed for AMPA, with 86 % of the wells located in the farmyards (6 out of 7) and just 26 % of the wells located in the vineyards having values ≥ to EQS_{GW} (5 out of 19) (Fig. 6). This may indicate improper or non-agricultural use of glyphosate in the farmyard. In fact, for well 17, having a depth of 11.5 m and a water column of at least 6 m during all 4 monitoring campaigns, the contamination is due to the use of glyphosate during yard cleaning activities. The owner did not use glyphosate in the vineyards as he adopted the measure promoted by the Emilia-Romagna Region on the "vineyard without glyphosate". Concerning the drinking water wells, just AMPA was present in July 2019 in one of the three wells, at values bellow EQS_{GW}.

The frequent detection and high concentrations of glyphosate and AMPA in the groundwater of Tidone Valley were not expected as the modelling estimations under the local pedoclimatic conditions imply the no risk of leaching to groundwater. Indeed, the 80th percentile of the leaching concentration at 1 m dept. (the depth of groundwater layer in the FOCUS groundwater scenarios) was equal to zero (data not shown). For the most contaminated well, WP01, which has a depth of 2 m, a water column of at least 1.2 m during all 4 monitoring campaigns and it is located downstream a vineyard with a slope > 3°, the subsurface lateral

Fig. 5. Wells location and glyphosate concentration in groundwater. Note: in pink values above EQSGW, in green values bellow EQSGW. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

inflow of water from up-hill vineyard could have transported chemicals residues to this well determining its contamination. Suciu et al. (2020) reported similar contamination patterns for wells located at the bottom of hilly vineyards by integrating PPPs monitoring results with data simulating the three-dimensional movement of water in the subsurface soil. Even if in the PEARL 4.4.4 version the lateral infiltration into the unsaturated soil matrix and lateral infiltration into and exfiltration out of the saturated soil matrix are considered by the hydrological model SWAP, embedded in PEARL, these processes were not considered due to miss of specific required parameters (Van den Berg et al., 2016). This may have limited the simulation performance and influenced the outputs. For well WP15, located at the bottom of a hilly vineyard and individuated by Zambito Marsala et al. (2020) as the most contaminated by PPPs used in vineyard, the contamination may be due to the use of water for preparing the glyphosate mixture and washing the sprayers after application, making the well vulnerable to contamination from point sources (expert statement). Masia et al. (2014) reported a similar groundwater contamination pattern for glyphosate in the Lombardy region, underling the point source contamination originated from losses/uses of herbicide near farmhouses or the cleaning of sprayers and trucks in the proximity of the wells. However, similar modelling outputs were reported by Geng et al. (2021) for China, where eight scenario locations and five representative crops (apple, cotton, maize, wheat, and rice) were considered, and all 30 simulated Predicted Environmental Concentrations (PECs) for glyphosate were equal to 0 μg/L.

Fig. 6. Wells location and AMPA concentration in groundwater. Note: in pink values above EQSGW, in green values bellow EQSGW. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

Glyphosate is the most used herbicide in the Tidone Valley, 84 % of the farmers that declared to use herbicides in their vineyards, use it at least once a year. Between July 2018 and September 2019, the detection frequencies in groundwater were different among analytes and sampling campaigns. Glyphosate was detected (>LOD) in 40 ± 10 % of the groundwater samples collected, of which 41 ± 11 % at values > EQS_{GW} whereas AMPA was detected in 55 ± 2 % of the groundwater samples, of which 56 ± 14 % at values >EQS_{GW}. Glufosinate ammonium was never detected in the groundwater of Tidone Valley. The validated analytical method allowed the quantification of all three chemicals at values twice lower than the EQS_{GW}. Highest occurrences and concentrations were detected in wells from farmyards, if compared with wells from vineyard, and all positive wells, except one, were used for irrigation and preparation of PPPs mixtures. Indeed, AMPA was the only compound detected in groundwater used for drinking in July 2019, at values bellow EQS_{GW}/DWQS. Modelling simulations predicted opposite behaviors, with no leaching to groundwater under local pedoclimatic conditions, even if the simulations performance and outputs may have been limited/influenced by the no consideration of specific processes (lateral infiltration/exfiltration). Integrating monitoring and modelling results with information concerning the agricultural practices adopted and the wells use and location, possible contamination drivers were identified. These include the nonagricultural use of glyphosate in the farmyard, the point source contamination of wells and the possible transport with water through subsurface lateral inflow from up-hill vineyard. This study strengthens the position of SETAC EMAG-Pest GW group (Gimsing et al., 2019) concerning the necessity of spatial and temporal contextualization of groundwater monitoring and modelling for a better understanding of its contamination drivers by PPPs.

CRediT authorship contribution statement

Nicoleta Suciu: Writing – original draft, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Project administration, Visualization. **Elisabetta Russo:** Writing – review & editing, Conceptualization, Methodology, Resources. **Maura Calliera:** Conceptualization, Writing – review & editing. **Gian Piero Luciani:** Writing – review & editing, Methodology, Validation, Formal analysis. **Marco Trevisan:** Writing – review & editing, Methodology, Validation, Formal analysis. **Ettore Capri:** Writing – review & editing, Supervision, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known conflict of 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.2022.161171.

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