



Herbicides in river water across the northeastern Italy: occurrence and spatial patterns of glyphosate, aminomethylphosphonic acid, and glufosinate ammonium

Mauro Masiol¹ · Biagio Gianni² · Marco Prete²

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Abstract

Glyphosate and glufosinate ammonium are the active ingredients of commonly used herbicides. Active agricultural lands extend over a large part of the Veneto region (Eastern Po Valley, Italy) and glyphosate and glufosinate ammonium are widely used. Consequently, surface waters can be potentially contaminated. This study investigates the occurrence of glyphosate and glufosinate ammonium as well as aminomethylphosphonic acid (AMPA, the degradation product of glyphosate) in river water of Veneto. Eighty-six samples were collected in 2015 at multiple sampling points across the region. Samples were analyzed for the two target herbicides, AMPA as well as for other variables, including water temperature, pH, dissolved oxygen, conductivity, hardness, BOD, COD, inorganic ions, total nitrogen, total phosphorus, total suspended solids, arsenic, and lead. The average concentrations (all samples) were 0.17, 0.18, and 0.10 $\mu\text{g L}^{-1}$ for glyphosate, AMPA, and glufosinate ammonium, respectively. The European upper tolerable level for pesticides (annual average 0.1 $\mu\text{g L}^{-1}$) was often exceeded. Chemometric analysis was therefore applied to (i) investigate the relationships among water pollutants, (ii) detect the potential sources of water contamination, (iii) assess the effective water pollution of rivers by identifying river basins with anomalous pollution levels, and (iv) assess the spatial variability of detected sources. Factor analysis identified four factors interpreted as potential sources and processes (use of herbicides, leaching of fertilizers, urban/industrial discharges, and the biological activity on polluted or stagnant waters). A discriminant analysis revealed that the pollution from anthropogenic discharges is homogeneously present in surface water of Veneto, while biological activity and fertilizers present heterogeneous distributions. This study gives insights into the concentrations of herbicides in rivers flowing through a wide region that has heavy use of these chemicals in agriculture. The study also points out some hot-spots and suggests the future implementation of the current monitoring protocols and network.

Keywords Rivers · Herbicides · Glyphosate · Glufosinate ammonium · Aminomethylphosphonic acid · Veneto

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✉ Mauro Masiol
mauro.masiol@gmail.com

¹ Department of Public Health Sciences, University of Rochester Medical Center, 265 Crittenden Boulevard, CU 420644, Rochester, NY 14642, USA

² Dipartimento Regionale Laboratori, Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (ARPAV), 31100 Treviso, Italy

Introduction

The contamination of surface water is a serious environmental issue (Moore and Ramamoorthy 2012; Lapworth et al. 2012; Stuart et al. 2012; Meffe and de Bustamante 2014) often associated with many adverse effects on human health and aquatic life (e.g., Schinegger et al. 2012; Zareitalabad et al. 2013; Khan et al. 2014; Richardson and Kimura 2015; Morrissey et al. 2015). In Europe, the protection of surface waters is regulated under the European Water Framework Directive (EC 2000), which aimed to achieve good qualitative and quantitative status of all water bodies by 2015. However, its implementation has been—and still is—a major challenge for the Member States (Hering et al. 2010).

Since its commercial introduction in 1974, glyphosate (GLY, N-(phosphonomethyl)glycine) has become the main active ingredient of many common herbicides and weed-killing formulations. GLY is used in agriculture and silviculture, as well as along roadways and railways and in urban areas. GLY is a water-soluble ($> 10 \text{ g L}^{-1}$ at $25 \text{ }^\circ\text{C}$), highly effective broad-spectrum, postemergence, non-selective herbicide. Its success was largely boosted by (i) the absence of relevant harmful environmental effects except for target organisms; (ii) the introduction of transgenic glyphosate-resistant crops around mid-90s; and (iii) the apparent limited risk of leaching to groundwater due to its strong sorption in soil and a relatively fast microbial degradation to aminomethylphosphonic acid (AMPA), its primary metabolite (Baylis 2000; Cerdeira and Duke 2006; Duke and Powles 2008).

The use of GLY is controversial: its environmental implications, ecotoxicology, and potential carcinogenicity are still debated (see Section S11). Its soil half-life is highly variable (2 to 215 days; Giesy et al. 2000; Battaglin et al. 2014a, b), as its mobility in soil depends on properties such as pH, mineralogy, texture, amount and chemical composition of organic matter, and soil tillage and erosion (Sørensen et al. 2006; Laitinen et al. 2006; Borggaard and Gimsing 2008; Todorovic et al. 2014). The half-life of GLY in aquatic environments ranges from 2 to 91 days (Vera et al. 2010). AMPA has a lower water solubility (5.8 g L^{-1} at $25 \text{ }^\circ\text{C}$) and a longer soil half-life (60 to 240 days), while the aquatic half-life is comparable to GLY (Giesy et al. 2000; Bergstrom et al. 2011).

Glufosinate ammonium (GLU, (RS)-2-Amino-4-(hydroxy(methyl)phosphonyl)butanoic acid) is another widely used active ingredient of non-selective herbicides (Duke 2014), and it is mostly used as a pre-harvest desiccant. GLU is highly soluble in water (solubility, $\sim 1370 \text{ g L}^{-1}$) and has a half-life of ~ 1 week (range 3–42 days) (Siimes et al. 2006; Dinehart et al. 2009; Carpenter and Boutin 2010, and references therein). Similarly to GLY, the main sources of GLU in aquatic systems are related to surface runoff, spraying, and leaching from treated crops. Many studies pointed out its harmful effects on biota (e.g., Peltzer et al. 2013; Lajmanovich et al. 2014). Although toxicological studies indicated that GLU is harmful to human beings at acute doses (Mao et al. 2012), its chronic effects at low doses remain largely unclear (Calas et al. 2008).

In Italy, the use of GLY has recently increased from 1473 to 2090 tons (+ 22%) between 2002 and 2011. However, north-eastern regions of Italy have experienced even a faster trend: in Veneto (NE Italy, Fig. 1), the use of GLY has dramatically increased from 42 to 316 tons (+ 648%) in 2002/11 (APPA 2014). Although the use of GLU is more limited than GLY, its use across Italy has also increased from 46 tons in 2002 to 79 tons in 2009, when it was temporarily banned from the market in April 2010. However, the ban ended in April 2012, when

more than 40% of GLU sold in Italy was marketed in Veneto (APPA 2014). Since approx. 45% of the Veneto hosts active agricultural lands mostly requiring irrigation, the surface waters of Veneto are strongly exposed to these herbicides.

Despite the fast degradation in soils and the apparent low mobility, GLY adsorbed on soil particles may find its way into surface and ground waters due to leaching from crops and runoff. The use of GLY-based formulations near aquatic environments or spillage, volatilization, and atmospheric deposition after crop spraying are other potential pathways for water contamination. In addition, GLY has an extensive use in urban areas (Hanke et al. 2010): the pavement covering retards infiltration and promotes a rapid runoff to sewage systems. Combined sewer outflows are present in Veneto. This way, GLY residues and AMPA can be frequently found in sewer systems, in the environment (e.g., Battaglin et al. 2005, 2009, 2014a, b; Scribner et al. 2007; Crowe et al. 2011; Coupe et al. 2012; Glozier et al. 2012; Aparicio et al. 2013; Van Stempvoort et al. 2014; Struger et al. 2015; Poiger et al. 2017) and on food (Bøhn et al. 2014).

In 2015, ARPAV (the Environmental Protection Agency of Veneto region, Italy) started a monitoring program to assess the water quality in major rivers across the Veneto. This study investigates the concentrations and seasonality of GLY, AMPA, and GLU measured over 1 year (2015) as well as the levels of other water pollutants, nutrients, and other physicochemical variables in major rivers included in eight main drainage basins. The study, the first carried out in the NE Italy, aims to (i) detect the concentrations of herbicides on a seasonal basis, (ii) identify rivers or drainage basins with anomalous pollution levels, (iii) investigate the relationships among water pollutants, (iv) detect the potential sources of pollution, and (v) assess the spatial patterns of the potential sources of water contamination.

Materials and methods

The Veneto region

The Veneto (Fig. 1) covers an area of $\sim 18,000 \text{ km}^2$ and hosts a population of 4.9 million inhabitants. The northwestern part is mainly occupied by mountains (Alps), with a low population density mostly concentrated along narrow valleys (Fig. 1a). A wide southeastern alluvial plain accounts for most (56%) of the territory and is affected by heavy anthropogenic pressures due to the presence of major cities, industrial areas, and intensive farming (Fig. 1c). A belt of hilly environments is located between mountains and the lowland: it hosts rural environments and farming, mostly vineyards and orchards (Fig. 1c). The alluvial plain is composed of sandy to silty-clay materials deposited by major rivers: the northwestern plain is generally characterized by more permeable soils, while the central and

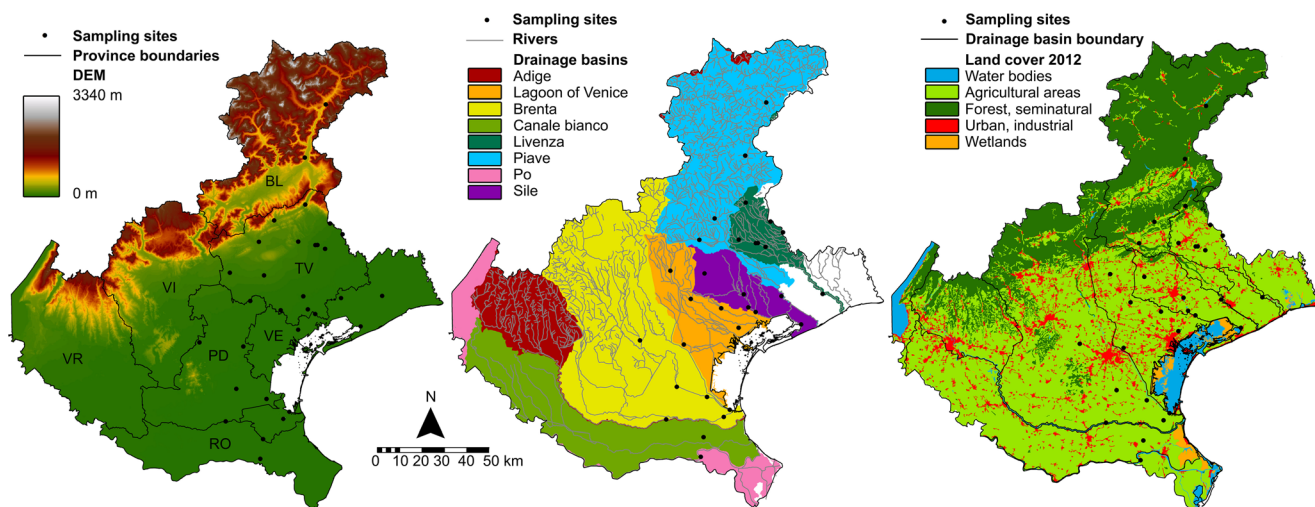


Fig. 1 Map of the Veneto Region: administrative borders and terrain relief (left); main rivers and drainage basins (center); land use and cover from CORINE Land Cover 2012 data (right) (EEA 2017). Provinces (left

map) are BL, Belluno; TV, Treviso; VI, Vicenza; VR, Verona; VE, Venice; PD, Padua; RO, Rovigo

southern plain host heavy soils and waterlogging with shallow groundwater levels (sometimes < 2 m). The two areas are separated by a belt of springs called “risorgive”, which generate several streams.

The mountain chains (Alps and Prealps) are mainly composed of sequences of sedimentary rocks (mainly limestone and dolomite) on metamorphic basements with magmatic extrusions. Springs of major rivers (e.g., Piave, Brenta, Adige) are located in the Alps, while other rivers flow (Livenza) or join tributaries (e.g., Brenta) flowing from karstic systems (Capraro et al. 2011). Other major rivers (e.g., Bacchiglione, Dese, Sile, Zero) born in the “risorgive” area from springs fed by aquifers catching water across the Prealps area. The soil permeability map is provided as supplementary material Figure S11. Soils in the plain areas are also characterized by low organic carbon content (Figure S11), especially where intensive agriculture is practiced. The low levels of soil organic matter limit the cation exchange capacity, lower the fertility, and increase the potential mobility of contaminants, including herbicides.

Sampling

Sites were selected along 24 major rivers or streams flowing across eight main drainage basins (Table 1), named Adige, Brenta, Canalbiano, Livenza, Piave, Po, Sile, and the drainage basin of the Lagoon of Venice (DBLV) (Fig. 1b). This latter basin needs special care: it hosts several streams and small rivers flowing directly into a large (~500 km² wide) coastal lagoon affected by high nutrient and pollutant levels, such as dissolved nitrogen and phosphorous (Facca et al. 2011; Zirino et al. 2016), heavy metals (As, Co, Cd, Cu, Fe, Pb, Zn, Ni, Cr), persistent organic pollutants (polychlorinated biphenyls, organochlorine pesticides), and polycyclic

aromatic hydrocarbons in top sediments (Zonta et al. 2007; Masiol et al. 2014; Khan et al. 2014). Three more samples were collected close to springs in the “risorgive” area. Each site was sampled during 1 year with different frequency (1–5 samples per site). Water was collected near the center of the river or, wherever not possible, at points having flowing water stream (i.e., no samples were collected on stagnant water conditions). Samples were stored in pre-cleaned HDPE bottles and in the dark at +4 °C to prevent sample degradation and photochemical reactions and were analyzed within 6 days (ISO 2014). During the sampling, water temperature was also measured, as well as pH (method APAT-CNR-IRSA-2060) and dissolved oxygen (method APAT-CNR-IRSA-4120).

Experimental

GLY, AMPA, and GLU were analyzed following the method ISO 16308:2014 (Hanke et al. 2008; ISO 2014). Briefly, the compounds are derivatized using 9-fluorenylmethylchloroformate (FMOC-Cl) in order to lower their polarity and increase the retention of compound in a separation on a reverse phase column as well as to improve the mass spectrometric detection. The derivatized sample was then purified by liquid/liquid extraction and concentrated by solid phase extraction (SPE). Methanol (≥99.9%, Sigma Aldrich) was used in SPE extraction. For each sample extraction, ~13 mL methanol is used. The analysis is performed by high-performance liquid chromatography coupled with tandem mass spectrometry via an electrospray source (HPLC–ESI–MS/MS; Hanke et al. 2008), using matrix-matched calibration. Calibration of the instrument was performed for every analytical batch; limit of quantification (LOQs, calculated according to the IUPAC Gold Book; IUPAC 2014) was 0.05 µg L⁻¹ (Table S11).

Table 1 Characteristics of the sampling sites and average (min-max) concentrations of target compounds. *GLY* glyphosate, *GLU* glufosinate ammonium, *AMPA* aminomethylphosphonic acid. Provinces (see Fig. 1) are BL, Belluno; TV, Treviso; VE, Venice; PD, Padua; RO, Rovigo. *LOQ* limit of quantification

Main drainage basin	Secondary drainage basin	River name	Site no.	Province	No. samples	GLY		AMPA		GLU	
						$\mu\text{g L}^{-1}$		$\mu\text{g L}^{-1}$		$\mu\text{g L}^{-1}$	
						Mean	(min-max)	Mean	(min-max)	Mean	(min-max)
Adige		Adige	206	PD	4	0.04	(<LOQ–0.1)	0.17	(<LOQ–0.23)	0.07	(<LOQ–0.22)
Brenta		Brenta	436	VE	3	0.29	(<LOQ–0.83)	0.13	(<LOQ–0.35)	0.13	(<LOQ–0.33)
Brenta	Bacchiglione	Bacchiglione	181	PD	3	<LOQ	–	<LOQ	–	<LOQ	–
Brenta	Bacchiglione	Cagnola	175	PD	2	<LOQ	–	<LOQ	–	<LOQ	–
Brenta	Bacchiglione	Tesinella	112	PD	3	0.04	(<LOQ–0.06)	<LOQ	–	<LOQ	–
Brenta	Gorzone	Gorzone	437	VE	2	<LOQ	–	<LOQ	–	<LOQ	–
Canalbianco		N. Adigetto	223	RO	4	0.40	(<LOQ–1.4)	0.36	(<LOQ–0.75)	0.18	(<LOQ–0.55)
Livenza	Monticano	Monticano	620;1147	TV	5	0.04	(<LOQ–0.1)	0.31	(<LOQ–0.83)	0.08	(<LOQ–0.3)
Livenza	Monticano	Cervada	621	TV	4	0.49	(0.07–1.3)	0.28	(0.07–0.56)	0.11	(<LOQ–0.3)
Livenza	Monticano	Crevada	6008	TV	1	0.45	(0.45–0.45)	<LOQ	–	0.30	(0.3–0.3)
Livenza		Livenza	72;453	TV, VE	4	0.34	(<LOQ–0.55)	0.42	(<LOQ–1.4)	0.05	(<LOQ–0.11)
Livenza		Meschio	23;236	TV	2	0.11	(<LOQ–0.2)	<LOQ	–	0.11	(<LOQ–0.2)
Piave		Anfella	409	BL	4	0.06	(<LOQ–0.1)	0.04	(<LOQ–0.07)	0.07	(<LOQ–0.22)
Piave		Piave	65	VE	5	0.17	(<LOQ–0.66)	0.28	(<LOQ–1.2)	0.06	(<LOQ–0.12)
Piave		Teva	6013	TV	2	0.31	(0.11–0.51)	0.77	(0.72–0.82)	0.42	(<LOQ–0.82)
Piave		Val di Frari	420	BL	4	0.06	(<LOQ–0.17)	<LOQ	–	0.05	(<LOQ–0.12)
Po		Po	227	RO	4	0.05	(<LOQ–0.08)	0.22	(<LOQ–0.54)	<LOQ	–
Sile		Bigonzo	6033	TV	4	0.32	(<LOQ–0.7)	0.16	(0.09–0.27)	0.08	(<LOQ–0.14)
Sile		C.U.A.I.	351	VE	3	0.10	(<LOQ–0.26)	0.06	(<LOQ–0.14)	<LOQ	–
Sile		Melma	333	TV	4	0.13	(<LOQ–0.37)	0.12	(<LOQ–0.26)	0.10	(<LOQ–0.26)
Sile		Sile	238;329	TV, VE	5	0.07	(<LOQ–0.25)	0.10	(<LOQ–0.25)	0.09	(<LOQ–0.25)
Lagoon of Venice		Musoncello	1127	TV	3	0.72	(<LOQ–2.1)	0.48	(<LOQ–1.4)	0.72	(<LOQ–2.1)
Lagoon of Venice		Tergola	117	PD	3	<LOQ	–	<LOQ	–	<LOQ	–
Lagoon of Venice		Zero	488	TV	5	0.04	(<LOQ–0.06)	0.03	(<LOQ–0.05)	0.03	(<LOQ–0.05)
Extra samples		“Risorgive”	NA	TV	3	<LOQ	–	0.05	(<LOQ–0.1)	0.05	(<LOQ–0.1)

Standards for spikes are dissolved in an aqueous matrix along with internal standards. Spikes are performed from these aqueous solutions. Once prepared, standards are kept at $-20\text{ }^{\circ}\text{C}$ for 6 months max (see ISO 5667-3:2012). Samples were spiked before the derivation step with labeled glyphosate (1,2 $^{13}\text{C}_2$, ^{15}N) and labeled AMPA (13C, ^{15}N). The range of acceptability for recoveries adopted by ARPAV lab range from 75 to 125%. The mean recoveries (in the concentration range of analyzed samples) were 103, 103, and 109% for GLY, GLU, and AMPA, respectively. Physicochemical characteristics of water and chemical species were also analyzed using well established analytical protocols (see SI Section 2 for standard methods used).

QA/QC and data handling

Method performance for GLY, AMPA, and GLU was tested by participation to LGC proficiency test AQ 492/2015 (LGC Aquacheck 2017) obtaining a satisfactory Z-score ($Z < 2$) among laboratories of European countries and confirming a good accuracy of the adopted analytical protocol. At least two water samples for each batch were spiked with target compounds and then included in the analytical procedure: recoveries were in the range of 80–100%. Precision was evaluated through analysis of replicated spiked water samples: results showed relative standard deviations $< 30\%$. In this study, all the samples analyzed for herbicides were used for descriptive statistics, but only samples also analyzed for the remaining

chemical and physical variables were further used for explorative analysis. Data below the LOQs (Table S11) were set as LOQ/2.

Chemometrics

The water samples were collected in rivers with different characteristics and/or affected by different anthropogenic pressures. Rivers also flow over different soil and rock types. This way, the chemical and physical characteristics of water may change according to the strength of natural/anthropogenic sources, the occurrence of biochemical processes in water, the soil characteristics, the flow rate, the closeness to point sources, the spatial distribution of diffuse sources, etc. A factor analysis (FA) was therefore performed to investigate the inter-variable relationships and to identify the most probable sources of water contamination or the ongoing biochemical processes. The principal aim of FA is to reduce the dimensionality of the dataset and to detect the main hidden processes/sources driving most of the variance of the original dataset.

Most of the species analyzed in this study are not normally distributed (Shapiro–Wilks test), with most of the variables exhibiting positive skewness. In addition, most variables have large differences in the units, i.e., the variables exhibits a striking difference in the amount of variability. For these reasons, non-parametric tests and correlations are used.

The Kruskal–Wallis analysis of variance by ranks was applied as a global non-parametric test for depicting statistically significant seasonal variations of analyzed variables. The null hypothesis is rejected for $p < 0.05$, meaning that concentrations are statistically different among seasons.

Since factor analysis is affected by data distribution and data scale (e.g., Reimann et al. 2002), a series of data transformations were applied to obtaining a robust dataset. Firstly, a Box–Cox transformation (Box and Cox 1964) was applied to approach normal distributions; thus, a standardization (mean zero and unit variance) was applied to scale the data and overcome differences in variation ranges.

In a second step, a discriminant analysis (DA) was applied to the factor score matrix to study the spatial distribution of identified factors, i.e., to verify whether the sites in a drainage basin are isolated or characterized by a general homogeneity of the sources/processes. DA is typically applied to detect variables which significantly explain differences between two or more groups (drainage basins, in this case). The results of the test of univariate equality of group means can classify variables (factors, in this case) as not discriminant or discriminant: high Wilks' Λ (> 0.9) and significance > 0.3 identify not discriminant variables, i.e., homogeneously present in all drainage basins. On the contrary, significances below 0.05 identify discriminant variables, i.e., having a heterogeneous distribution over the study area.

Results and discussion

The average concentrations across the Veneto (all seasons, all sites) were 0.17, 0.18, and 0.10 $\mu\text{g L}^{-1}$ for GLY, AMPA, and GLU, respectively (Table 1). The higher annual average concentrations of GLY were recorded on Musoncello (0.72 $\mu\text{g L}^{-1}$), followed by some sites along Livenza (Cervada, 0.49 $\mu\text{g L}^{-1}$; Livenza 0.45 $\mu\text{g L}^{-1}$) and Canalbianco (Nuovo Adigetto 0.4 $\mu\text{g L}^{-1}$), while AMPA was higher on Teva (0.77 $\mu\text{g L}^{-1}$), Musoncello (0.48 $\mu\text{g L}^{-1}$), and Livenza (0.55 $\mu\text{g L}^{-1}$). The river Musoncello was also affected by the higher annual concentrations of GLU (0.72 $\mu\text{g L}^{-1}$), followed by Teva (0.42 $\mu\text{g L}^{-1}$). Musoncello presents, therefore, the higher annual average concentrations of herbicides: it is affected by substantial loads from the urban sewer of Castelfranco Veneto (~33,000 inhabitants) and then flows through agricultural areas by also touching other towns (Resana). Finally, it joins the Dese River and, then, flows into the Lagoon of Venice. Therefore, further investigations and/or sampling campaigns are suggested for those polluted rivers in order to better monitor the sources of herbicides. In addition, more sites should be placed close to the outlets to quantify the load of herbicides flowing into the Lagoon of Venice.

In Europe, the upper tolerable level for all the pesticides in drinking water is administratively set to 0.1 $\mu\text{g L}^{-1}$ (EC 1998). This regulatory limit is applied to annual average concentrations. The threshold of 0.1 $\mu\text{g L}^{-1}$ was often exceeded in single samples (26, 37, and 22% of all analyzed samples, respectively); however, only 11, 14, and 7 sites breached the annual upper tolerable level computed over multiple samples for GLY, AMPA, and GLU, respectively.

The design of our sampling campaign is not sufficient to accurately represent seasonal concentrations or to identify peak concentrations at single rivers, which can be missed even with a weekly sampling interval (Mahler et al. 2016). The analysis of seasonal differences was therefore assessed for the whole set of data (Fig. 2): only water temperature, pH (Section S13), and concentrations of GLY and AMPA were statistically different (Table S12).

The herbicides were rarely detected during spring, while the higher median concentrations for GLY and AMPA were measured in summer, followed by autumn and winter. This pattern is likely related to the seasonality of crops. Glyphosate is typically applied after crops and weeds have emerged from the soil (Battaglin et al. 2014a), but it can be applied more than once during the growing season: this way, in Northern Italy crops and orchards are mostly treated in late-spring and summer when unwanted plants grow faster. However, herbicides are also applied to vineyards until mid-autumn (grape harvest). In addition, residues of herbicides may remain in the soil for weeks (half-life for GLY and GLU are 2–91 and 3–42 days, respectively); therefore, surface runoff and draining

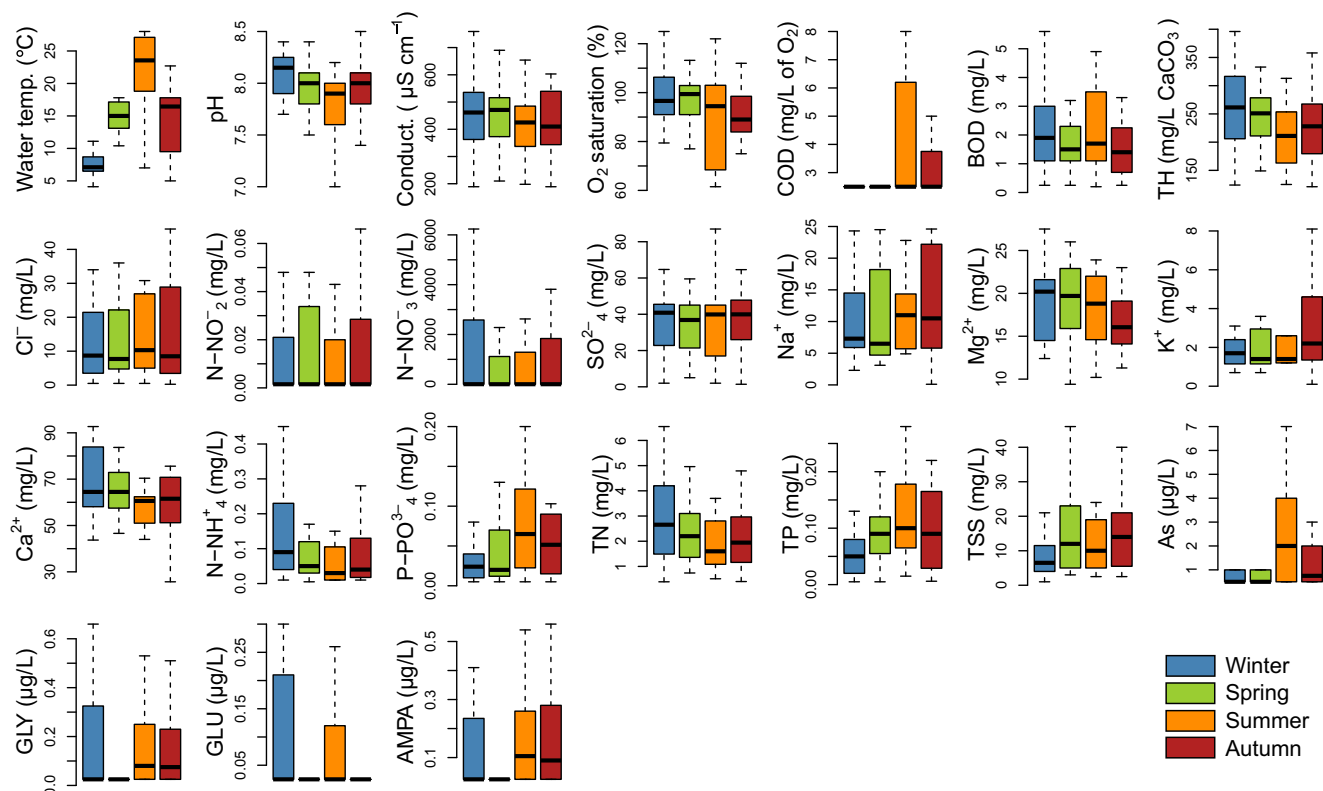


Fig. 2 Seasonal distributions of the analyzed variables. Data are aggregated to show data collected at all sites during the four seasons. Boxplot lines = medians, boxes = 25th–75th percentile ranges, whiskers = ± 1.5 *inter-quartile ranges. Outliers and extremes not

shown. *COD* chemical oxygen demand, *BOD* biochemical oxygen demand, *TH* total hardness, *TN* total Kjeldahl nitrogen, *TP* total phosphorus, *TSS* total suspended solids, *GLY* glyphosate, *GLU* glufosinate ammonium, *AMPA* aminomethylphosphonic acid

to groundwater may continue for months after treatment. Similar patterns were found in surface waters in Switzerland (Poiger et al. 2017) and rural/urban catchments in Canada (Struger et al. 2015).

Correlations among variables

GLY and GLU exhibit a moderate correlation (0.53) and are also well correlated with AMPA (0.64 and 0.44, respectively). However, they are not well correlated ($\rho < 0.4$) with any other variable (Table S13). AMPA is the main metabolite of GLY but is also formed by the degradation of phosphonic acids in detergents, such as EDTMP and DTPMP (Skark et al. 1998; Jaworska et al. 2002; Nowack 2003; Lesueur et al. 2005). Finally, AMPA degrades to inorganic phosphate, ammonium, and CO₂ (Borggaard and Gimsing 2008). Under this view, it may play a role in the levels of total phosphorus in aquatic systems (Vera et al. 2010). AMPA exhibits a strong correlation with GLY ($\rho = 0.64$), a poor correlation with orthophosphate ($\rho = 0.26$) and it is uncorrelated to TP (Table S13). This result suggests that GLY degradation is the dominant source of AMPA in river waters of Veneto. However, the lack of a clear correlation with P compounds may be masked by the strong input of P-containing species from other sources, e.g.,

fertilization and urban and industrial discharges. Correlations among other variables are discussed in Section S14.

Potential sources of river contamination

The transformed dataset (Box–Cox/standardized) was used as input for a Varimax-rotated FA. A first attempt was made by including all the species. However, a pre-selection of variables to be processed in FA was subsequently performed to ensure robust and reliable results and to exclude chemically redundant species: (i) some variables (chemical oxygen demand, Na⁺, K⁺, Pb) were excluded because their high percentage of missing data (> 25%); (ii) missing data for other variables were substituted with the variable median; (iii) hardness was preferred to Mg²⁺ and Ca²⁺ because of their high correlation and the lower number of missing data; (iv) total phosphorous and total Kjeldahl nitrogen (TKN) were excluded because their strong correlations with orthophosphates and the sum of N-species, respectively; (v) nitrite was excluded because the high associated uncertainty due to its relatively unstable oxidation state; (vi) dissolved O₂ was converted from percent saturation to water concentration by considering the correction factors for water conductivity, water temperature and barometric pressure (USGS DOTABLES; U.S. Geological Survey 2011); (vii) hydrogen ion activity [H⁺]

Table 2 Results of factor analysis (Varimax rotated solution). Variables with factor loadings (>0.6) are in italics; factor loadings less than 0.35 are not shown; variables are ordered for decreasing absolute loadings. Var

(%): percentage of variance explained by each factor; Cum. var. (%): cumulative variance

Factor 1 Fertilizers/salinity	Factor 2 Biological activity/arsenic	Factor 3 Herbicides	Factor 4 Urban/industrial discharges
<i>Hardness (0.85)</i>	<i>As (0.81)</i>	<i>GLY (0.85)</i>	<i>BOD (0.77)</i>
<i>Conductivity (0.81)</i>	<i>P-PO₄³⁻ (0.69)</i>	<i>GLU (0.83)</i>	<i>H⁺ activity (-0.73)</i>
<i>SO₄²⁻ (0.71)</i>	<i>TSS (0.67)</i>	<i>AMPA (0.77)</i>	Dissolved O ₂ (0.55)
<i>Cl⁻ (0.69)</i>	<i>Dissolved O₂ (-0.67)</i>		N-NH ₄ ⁺ (0.4)
<i>N-NO₃⁻ (0.67)</i>	Cl ⁻ (0.56)		
<i>N-NH₄⁺ (0.62)</i>	N-NH ₄ ⁺ (0.37)		
<i>P-PO₄³⁻ (0.41)</i>			
Var. = 23%	Var. = 19%	Var. = 15%	Var. = 12%
Cum. var. = 23%	Cum. var. = 42%	Cum. var. = 56%	Cum. var. = 69%

TSS total suspended solids, BOD biochemical oxygen demand

(mEq L⁻¹) was calculated from pH to obtain a linear variable. Four factors with eigenvalues > 1 were extracted, accounting for ~70% of total variance. A four-factor solution was also suggested by parallel analysis, a method for determining the number of components or factors to retain from FA (Hayton et al. 2004).

Along with the factor loadings (Table 2), an $n \times m$ factor score matrix is also extracted: it is composed of n cases (samples collected) and m new variables proportional to the daily source impact. The factor scores were then mapped on a seasonal basis (Figure S12): although a quantitative analysis is not possible due to the data transformation, the factor scores may be mapped to show the spatial/temporal gradients of extracted factors; they are, therefore, useful to qualitatively interpret the data.

Factor 1 (23% of variance) mainly represents the analyzed ions and, in particular, all the nutrients. It is primarily composed (loading > 0.6) of anions (chloride, sulfate, nitrate), ammonium and, secondarily (0.35 < loadings < 0.6), orthophosphate (Table 2). Consequently, the factor also exhibits high loading of hardness (directly linked to Ca and Mg) and water conductivity (0.83), which reflects the ionic activity. Ammonium, nitrate, and phosphate are the main components of NPK fertilizers; ammonium also derives from fertilizers made by ammonia, anhydrous ammonium nitrate as well as from urea. Nitrate may enter water bodies directly as the result of runoff of fertilizers containing nitrate, from atmospheric deposition and/or urban/industrial discharges. The oxidation of more reduced N-containing compounds, including nitrite, ammonia, and organic nitrogen compounds (e.g., amino acids, urea) is another source of nitrate: this process occurs in both soil and water following the biological activity of ammonia-oxidizing bacteria (e.g., Nitrosomonas) and the oxidation of nitrite driven by Nitrobacter and Nitrospira. Sulfate is a ubiquitous ion in natural waters and can be released by a variety of natural (e.g., dissolution of minerals) and anthropogenic (e.g., fertilizers, mine drainage, and urban and industrial runoff) sources. Chloride

can also derive from similar anthropogenic sources (wastewaters, fertilizers). In winter, chloride may also derive from the runoff of deicing salts in roads. The use of fertilizers is the most probable source, also according to some insights: (i) fertilizers are used throughout the year and factor scores are not statistically significant different among seasons (analysis of variance, ANOVA, at $p < 0.05$); (ii) maps of factor scores (Figure S12) show that high scores are recorded in the sites across the lowland, where crops are present; and (iii) although K⁺ was excluded from the FA due to the missing data, it shows high correlations with most of the ions, conductivity (Table S13) and with the factor scores for factor 1; (iv) potassium chloride and potassium sulfate are two main species in modern fertilizers.

Since an excessive loading of nutrients (considering all nitrogen species and phosphorus) is a major threat to water quality and may cause eutrophication (e.g., Cherry et al. 2008; Withers and Jarvie 2008; Carey and Migliaccio 2009), rivers showing high scores of factor 1 should be investigated in more detail to find the most impacting point and diffuse sources. Since eutrophication is a major threat for the Lagoon of Venice (e.g., Masiol et al. 2014; Zirino et al. 2016), rivers flowing through DBLV and having high scores for factor 1 deserve future investigations.

Factor 2 (19% of variance) is made up of arsenic, orthophosphate, total suspended solids and, secondarily, chloride and ammonium (Table 2). Under this view, it can be related to a pollution source and/or runoff. For example, phosphate may be released from various anthropogenic sources, including urban and industrial sewage discharges (e.g., Withers and Jarvie 2008), while arsenic may be linked to several anthropogenic point sources (e.g., Smedley and Kinniburgh 2002). However, high concentrations of arsenic can be also related to the high pedo-geochemical background concentrations, e.g., above 20 mg kg⁻¹ in the Brenta River basin (Giandon et al. 2000, 2004; Ungaro et al. 2008) and in groundwater (Carraro et al. 2013, 2015). The presence of total suspended solids (TSS) and

As in this factor may also indicate a possible load of crustal materials from runoff. Under this view, combined sewer outflows are present in Veneto, allowing the release of mixed urban and runoff discharge during overflow events. However, the temporal frequency of the sampling campaign has not allowed an analysis of the relation with rainfall depth or intensity. Consequently, the effect of runoff in this factor remains unclear.

Factor 2 also shows a strong negative loading with dissolved oxygen (−0.67), which is indicative of an ongoing aerobic activity. Low levels of dissolved oxygen are generally indicative of oligotrophic water conditions, which likely occurs during the warmer season, i.e., when higher water temperature and lower river flow rates are expected. Under this view, statistically significant (ANOVA at $p < 0.05$) inter-seasonal differences were found: the application of a multiple comparison post hoc test (Tukey HSD; Tukey 1949) reported significantly (95% confidence level) higher factor scores in summer and autumn than in winter. Such seasonal pattern confirms that the lower dissolved oxygen is likely driven by a stronger aerobic activity during the warmer season, as well as the more stagnant waters in summer due to low flow rates (ARPAV 2017). The high loading of TSS further confirms this hypothesis, as the turbidity and the presence of colloids generally increase in more stagnant waters. The poor correlation of factor 2 with biochemical oxygen demand (BOD) (0.23) further suggests that the amount of biodegradable organic material is not a limiting factor for the aerobic activity or may indicate that the biological activity has depleted most of the organic material (i.e., the source does not represent a fresh input to the river).

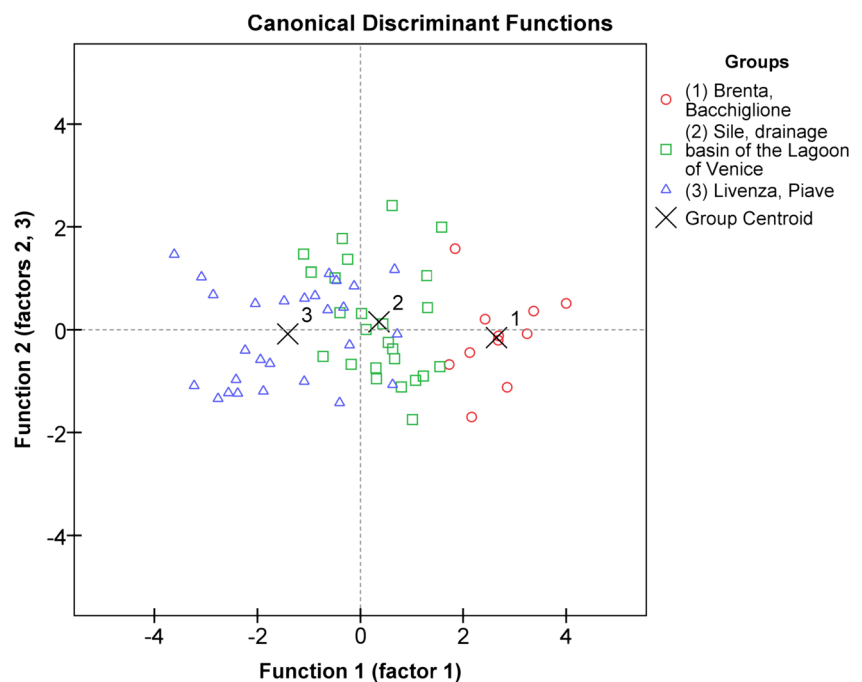
Factor 3 (15%) only links GLY, AMPA, and GLU (Table 2). The absence of high loadings with any other analyzed

species indicates that the contamination of herbicides is uncorrelated with other pollution sources. The higher scores are found in summer > autumn > winter, and sites in the province of Treviso (TV, Fig. 1) generally show the higher factor scores throughout the year. Relatively high scores are also recorded during summer in the two more northern sites (Piave drainage basin), which generally show the lower scores for the remaining factors (Figure SI2). These rivers (Anfella and Val di Frari) flow in mountain areas and, therefore, are not likely affected by a load of herbicides from agriculture or silviculture. These sites represent an anomaly that should be investigated in more detail.

Factor 4 (12%) links BOD, dissolved oxygen and, secondarily, ammonium; it also shows a negative correlation with the activity of H^+ (Table 2), i.e., it is linked to the more alkaline waters. No statistically significant inter-seasonal differences are found, i.e., it is almost constant all the year.

This factor depicts waters with high loads of organic matter (BOD), but it also represents waters with high primary production and/or affected by low aerobic activity (high loading of dissolved O_2). A possible interpretation is the fresh release of anthropogenic discharges of nutrients and effluents and the consequent increased photosynthetic activity. Figure SI2 shows pretty similar factor scores recorded during the year at the sites across the plain area of the region; however, a significant increase of the scores was found for the more northerly sites. This increase could be related to the expected boost of anthropogenic effluents (sometimes without efficient sewer systems) following to the summer touristic season in the mountain.

Fig. 3 Discriminant scores scatterplot. Group centroids are shown as gray crosses



Spatial distribution of sources

The factor scores were used in DA as independent variables; three areas including five drainage basins having similar characteristics were selected as grouping variable: (1) Brenta and Bacchiglione, i.e., rivers flowing in the center and southern part of Veneto; (2) DBLV and Sile, rivers mostly flowing from “risorgive” springs; (3) Piave and Livenza, rivers flowing in the northern part of Veneto with sources located in the Alps, but also having heavy contributions from “risorgive.” Samples collected in Po, Canalbianco, and Adige were excluded from DA due to the low number of sites and samples. The test of univariate equality of group means (Table S14) shows that only factor 4 is not discriminant, having the highest Wilks' Λ (0.98) and presenting a significance of 0.5. This result indicates that the pollution due to the fresh release of anthropogenic discharges (mostly attributable to urban or industrial sewage effluents) is homogeneously present in all the study area. Since the outputs from urban or industrial sewage effluents are expected to be constant through the year, this result confirms the interpretation of factor 4.

On the contrary, factors 1, 2, and 3 are highly discriminant (significance < 0.05), i.e., they present heterogeneous distributions over the three groups of rivers. Two discriminating functions (Table S14) were also extracted and interpreted by analyzing their correlations with the input variables (factors): the first function only presents weak correlations with factor 1 (fertilizers/salinity) and 2 (biological activity and arsenic), while the second one presents the largest absolute correlation with the factors 2 and 3 (herbicides). Figure 3 shows the bi-dimensional scatterplot of sample scores into the planes defined by the discriminant functions. The plot shows that the samples in the three groups of rivers are generally well differentiated under the discriminant function 1 (weakly correlated with factors 1 and 2), with higher scores for samples collected in the southern area (Brenta-Bacchiglione) and lower for the samples collected to the north (Piave-Livenza). On the contrary, group centroids are not well separated along the discriminant function 2.

Conclusions

This study is the first one investigating the occurrence of glyphosate, glufosinate ammonium, and AMPA in river water of the NE Italy. The main findings of this study can be summarized as follows:

1. The contamination of herbicides is a critical issue in Veneto: GLY, AMPA, and GLU frequently exceeded the European upper tolerable levels for pesticides (annual average $0.1 \mu\text{g L}^{-1}$) during 2015. However, this tolerable level is based on political consensus, not ecotoxicological significance and it is very low if compared to the maximum level of GLY permitted in the USA ($700 \mu\text{g L}^{-1}$) based on toxicity tests;

2. GLY and AMPA showed statistically different seasonal concentrations, with higher medians in summer and autumn and lower in spring. This seasonal pattern agrees with the use of herbicides in agriculture and silviculture;
3. The River Musoncello was affected by the higher annual average concentrations of GLY and GLU. This river catches substantial loads from urban sewer of some large towns and should be investigated in more detail in future studies;
4. The correlation and factor analyses pointed out the interspecies relationships. Four factors were extracted and interpreted as possible sources/processes affecting the water quality of rivers. Herbicides were identified by a single factor. Two more factors were linked to possible sources: the leaching of fertilizers and the urban/industrial discharges. Another factor was attributed to the biological activity on polluted or stagnant waters;
5. A discriminant analysis was performed on the factor scores and over 3 areas representative of 5 drainage basins. Results revealed that the anthropogenic discharges (mostly attributable to urban or industrial sewage effluents) are homogeneously present over all the study area, while biological activity and fertilizers present heterogeneous distributions. However, a clear spatial gradient was not detected.

This study shows that the extensive use of herbicides in Veneto affects the water quality of major rivers and poses the basis for further investigations. The study also gives important insights upon the most impacting pollution sources of river water. The large uncertainty raised by the current scientific literature on the possible adverse health effects of glyphosate and glufosinate ammonium does not make possible to assess a potential increased risk for human health. Reducing the use of herbicides across hydrologically contributing areas, close to streams and rivers potentially affected by fast runoff and/or soil erosion is, therefore, the most simple and effective approach to mitigate a diffuse herbicide pollution in Veneto.

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Compliance with ethical standards

Disclaimer The views and the conclusion expressed in this paper are exclusive of the authors and may not reflect those of ARPAV. This study is not intended to replace any official report and/or data released by ARPAV; these latter data should be considered as a reference for administrative and regulatory purposes.

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