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Ph.D. in Agro-Food System

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Impact and prevention of groundwater pollution by pesticides and nitrate in hilly vineyards: evaluation of contamination sources and development of best management practices and mitigation measures

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Academic Year 2019/2020

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“If there is magic on this planet, it is contained in water”

Loren Eiseley

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Thesis outline

Chapter 1

1. *General introduction and objectives*

Many anthropic activities, including the agricultural and food industries, give rise to environmental problems for which it is necessary to find solutions.

The presence of undesirable substances in water, soil and foodstuffs, indeed, can pose a risk to the health and hygiene of both men and animals. It is, therefore, essential to find methods in order to avoid pollutants from these matrices, so as to make them compatible with the maintenance of healthy environmental conditions. This work aims to assessing the groundwater quality of an area in which the quality of water was never studied, particularly investigating the occurrence of pesticides and nitrate in order to understand the grant of viticulture on water pollution. This study derives from the necessity to improve the water governance and to implement the best management practices and mitigation measures to prevent groundwater and environmental pollution.

This thesis is part of a broader project which aims to contribute to a better knowledge and understanding of how water governance is organized at catchment level and how the agricultural activities can be improved in order to limit their impact on groundwater. The Italian case study considers three catchments in Tidone Valley, northern Italy, characterized by an intensive viticulture production.

In particular the major purposes of this thesis are:

- Investigate the impact of viticulture on groundwater quality by pesticides and nitrate in Tidone Valley, an area where the quality of groundwater was never investigated before, through monitoring studies;
- Understand the groundwater contamination source by pesticides and nitrate through isotopic studies and by collecting and integrating monitoring data, sub-surface water movement data and territorial characteristics;
- Develop an engagement strategy to prevent groundwater contamination by pesticides involving all stakeholders with a role in water governance;
- Raise awareness concerning groundwater contamination issues and consequently the water benefits given by the adoption of the Best Management Practices to the farmers of the study area.

- Contribute to a better knowledge and understanding of how water governance is organized at catchment level and how the agricultural activities can be improved in order to limit their impact on drinking water.

2. *The context and background*

2.1 Environmental pollution by anthropogenic compounds

The earth system is entering a new epoch—the Anthropocene—which is characterized by significant global environmental impacts mainly driven by human activities (Steffen et al. 2011).

The ambition of mankind to improve life quality has great benefits for humanity but has also strongly affected the environment for centuries. According to the Nobel Prize chemist Paul Crutzen, our planet has entered the Anthropocene, a new epoch that is dominated by intense human activities causing global environmental changes (Crutzen, 2002). Nowadays, an incredibly large variety of compounds of anthropogenic origin is present in the environment all over the world and threatens environmental quality and human health (Hutzinger, 2013; Lewis and Maslin, 2015). Among these compounds, pesticides represent one of the few chemicals that are intentionally released at large scales into the environment (e.g. into agro-ecosystems to protect crops). As a result of their widespread use, in fact, pesticide residues together with chemical fertilizers such as nitrogen, are major environmental contaminants contributing to environmental pollution (Rathore and Nollet, 2012). This paradox has its origin in weighing up pesticide benefits against pesticide hazards (Storck, 2016).

2.2 Pesticides and chemical fertilizers

Any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or weed is a pesticide. Pesticides are mainly known as plant protection products (PPPs) but while the term 'pesticide' is something that prevents, destroys, or controls a harmful organism ('pest') or disease, or protects plant products during production, storage and transport, PPPs are 'pesticides' that protect crops or desirable or useful plants. They contain at least one active substance and have one of the following functions:

- protect plants or plant products against pests/diseases, before or after harvest
- influence the life processes of plants (such as substances influencing their growth, excluding nutrients)
- preserve plant products
- destroy or prevent growth of undesired plants or parts of plants.

The term 'pesticide' is often used interchangeably with 'plant protection product', however, pesticide is a broader term that also covers non plant/crop uses, for example biocides (https://ec.europa.eu/food/plant/pesticides_en). However in the text both the terms “PPPs” and "pesticides" are used.

PPPs can be classified according to their target, their mode or period of action, or their chemistry. More than 500 different pesticide formulations are being used in our environment, mostly in agriculture (Azevedo, 1998), although the control of biological public health hazards also continues to be an important field of application. Today, around 2.4 million tons of PPPs (active substances) are released into the environment worldwide each year (U.S. EPA, 2011), whereof 80% are used in agriculture (Enserink et al., 2013). PPPs can be distinguished with three majorly used groups: insecticides used against insects, herbicides used for growth control of various weeds, and fungicides effective to control fungal diseases (Gilden et al., 2010), which account for 30 % (insecticides), 40 % (herbicides) and 10 % (fungicides) of the global pesticide market (Enserink et al., 2013).

PPPs contribute to high agricultural yields and help in ensuring that good quality food is available at reasonable prices. However at the same time they can have negative effects on human health and the environment, which represent high costs for society.

In addition, the PPPs use can cause effects on non-target organisms, including human. Non-target pesticide poisoning has been identified as the cause of fish kills, reproductive failure in birds, and illness in humans (Rao et al., 1993). In fact, it has been estimated that less than 0.1% of the pesticide applied to crops actually reaches the target pest; the rest enters the environment, contaminating soil, water and air, where it can poison or otherwise adversely affect non-target organisms (Pimentel and Levitan, 1986). Indeed, often, measurements indicate the occurrence of PPPs on non-agricultural land as in groundwater. In particular, PPPs represent a potential threat to the quality of extracted groundwater when the water-supply area is used for agricultural activities (Gaus, 2000). In this regard, particular attention is paid for PPP contamination of surface and groundwater, and appropriate measures to reduce exposure of water bodies to nonpoint sources (spray drift, drain flow, and runoff) and point sources (pesticide handling procedures) should be adopted (Suciu et al., 2013; The European Parliament and the Council of the European Union. 2009).

However, if PPPs are applied under appropriate cropping and climatically conditions in prescribed amounts using modern techniques according to good farming practices, they can be effective in pest control with little adverse effects on the surrounding environment. Therefore, the European Community has developed a comprehensive regulatory framework in order to minimize negative effects as much as possible. For example, the enforcement of the European directive 2009/128/EC is determining for all the European Member States to develop National Plans aimed at setting quantitative objectives, targets, measures, timetables and indicators for reducing the risks and impacts of pesticide use on human health and the environment and at encouraging the development and introduction of integrated pest management.

Different international regulatory bodies such as the European Union (EU), the United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) established maximum allowed concentrations for PPPs in drinking water (Donato et al., 2015) that in most of the cases correspond to the Environmental Quality Standards for groundwater (EQSgw; equal to 0.1 μg/L and 0.5 μg/L, respectively for the single substance and for the sum of the substances), established by Directive 2006/118/EC (EC, 2006).

Another big issue is represented by the excessive use of chemical fertilizers (i.e. nitrogen-based fertilizers), which can lead to the nitrate contamination. In fact, in Italy, as in the rest of Europe, nitrate contamination in surface and groundwater is a widespread phenomenon especially in the North-Centre, where agriculture is the main nitrogen input (Balestrini et al., 2003). In particular, nitrogen fertilizers are applied extensively in agriculture to increase crop production, but excess nitrogen supplies can cause air, soil, and water pollution as well. Arguably one of the most widespread and damaging impacts of agricultural overapplication of nitrogen fertilizers is the degradation of groundwater quality and contamination of drinking water supplies, which can pose immediate risks to human health (Schroeder et al., 2004).

Indeed, groundwater contamination by nitrate and other nutrients is a major problem throughout the world, often occurring as the result of anthropogenic activities, lack of management, and over-exploitation of groundwater resources. In the last few decades in the majority of the Italian regions, the nitrate concentrations in groundwater have dramatically increased, mainly as a consequence of the large-scale agricultural application of manure and fertilizers (Pisciotta et al., 2015).

Nitrate is the primary form of inorganic nitrogen within the soil, which is essential for the growth and development of healthy crops. It has been shown in vivo that nitrite derived from nitrate can form N-nitroso compounds with amines and amides, which may have carcinogenic properties (Van Maanen et al., 1996). The EU Directive 91/676/EEC, which protects waters against pollution caused by nitrates from agricultural sources, sets the acceptable threshold of nitrate concentration in groundwater at 50 mg/l as nitrate. The EU Directive 2006/118/EC also attempts to protect groundwater against pollution and deterioration by suggesting that Member States establish quality standards, develop methodologies for assessing and monitoring groundwater quality, and implement measures supporting groundwater protection, including changes to farming and forestry practices (Wick et al., 2012).

The prevention, control and combat of groundwater pollution are addressed in various European Union (EU) and national legislative acts, since groundwater is considered a valuable natural source. The EU Water Framework Directive (2000/60/EC, 2000), WFD, and its daughter Directive on the Protection of groundwater against Pollution (2006/118/EC, 2006), GWD, establish criteria for the definition of groundwater status (quality and quantity). Moreover, the Nitrates Directive (91/676/EEC, 1991) is an integral part of the WFD and it was drawn up with the specific purpose to reduce water pollution caused by nitrate from agricultural sources and prevent further such pollution. In this regard, EU members are required to identify waters affected by nitrate pollution, designate nitrate vulnerable zones (NVZs) and several spatial analysis techniques were adopted to identify them. Italy formally acknowledged this directive in 1999 and in 2006 with the Italian Legislative Decree 152/06, 2006, Italian Legislative Decree 152/99, 1999. This national regulation suggests a parametric system based on empirical relationships between the soil or sub-soil characteristics and Nitrogen leaching risk.

2.3 Environmental risk assessment of PPPs

PPPs use in agriculture can cause undesirable effects on humans and the natural environment, and one of the objectives of integrated agriculture is the elimination or reduction of possible sources of environmental pollution such as PPPs. To achieve this objective, farmers need a method to assist them in estimating the environmental impact of PPP use (Van der Werf, 1996). The environmental impact of a PPP depends on its dispersion in the environment and on its toxicological properties.

In the European Union (EU), a statutory PPP authorization process is the prerequisite for the market permission of a pesticide. After the invention of a new pesticide, its behavior in the environment and its potential hazards for non-target organisms are investigated during an environmental risk assessment procedure at EU and national level prior to its authorization. Only active substances that are registered on the EU's list of approved active substances and subsequently authorized as PPPs by each EU Member State are released into the environment (Storck, 2016). Despite these efforts to minimize environmental risks, the safe use of PPPs appears to be one of the biggest challenges of sustainable agriculture, because pesticide residues remain one of the most widespread pollutant groups worldwide (Rathore and Nollet, 2012).

The PPP risk analysis process, therefore, is well regulated in the EU in order to avoid risks for human health and environment in the use phase, information on how these substances are employed and on socio-behavioral factors that can influence the exposure have to be considered (Calliera et al., 2015).

Over the last decades, agriculture and crop management practices have shown deep changes, to allow the extension of cropped areas ensuring an efficient control of pest populations and diseases. PPPs are part of these management practices, and the catalogue of products available to farmers has followed a parallel evolution to match farmers' expectations regarding efficacy and safety, but also the expectations of the public. The regulatory framework ruling the placing on the market of PPPs, as well as aspects of their use reflect these changes and shape the conditions of their use on a sustainable way. EC Regulation No. 1107/2009 bases the placing of pesticide products on the market on the demonstration that their use complies with defined protection goals guaranteeing a high level of safety for humans and the environment. Directive 2009/128/EC also called the "Sustainable Use Directive" extend the set of measures that, from the training and certification of users to the control of application machines and the development of effective alternative methods, should improve the safety level over the whole process (Alix and Capri, 2018).

In addition, although PPPs are already regulated in Europe under Directive 91/414/EEC, there is particular increasing concern about the pollution of ground and surface water caused by point sources of PPPs, such as tank filling, spillages, faulty equipment, washing, waste disposal, and direct contamination (Fait et al., 2007). The European Union (EU) strategy for sustainable development, revised in 2006, indicated sustainable consumption and production as key challenges for the future. From the regulatory point of view in the development of environmental and human health policies, this requires deciding which economic sectors, products and resources should be subject to political regulatory intervention. In agriculture, PPPs control, for which the perception of risk is substantial as they are deliberately released into the environment, and the sustainability of their use, is one of the most important aspects. To achieve more sustainable use of PPPs, in 2009 the European Parliament and the Council approved Directive 128 for the sustainable use of pesticides which provides measures to establish and reduce the overall risk that PPPs pose to human health and to the environment during their use. According to this Directive, EU Member States have to establish National Action Plans to set objectives, targets and measures to reduce risks and impacts of pesticide use on human health and the environment and to encourage integrated pest management. Training has a strategic role to achieve all the objectives that the Directive sets for the EU Member States, who must ensure that all professional users, distributors and advisers have access to 'appropriate training by bodies designated by the competent authorities' (Calliera et al., 2013).

2.4 Sustainable use of PPPs

Sustainability in agriculture is an important goal for many farmers and agronomists (Medrano et al., 2014).
The Sustainable Use Directive (SUD; 2009/128/EC) is a Community action aiming at the sustainable use of chemicals like PPPs. It aims at improving use and handling of pesticides, and mitigating human and environmental exposure. Focus areas of the SUD including training pesticide users, inspection of PPP applicators, and ensuring local processes and infrastructures are in place to manage waste and remnants. The SUD addresses poor use and handling of pesticides on farm to prevent "point source" contamination, e.g., spills or waste water from rinsing pesticide application equipment. That is why Member States' National Action Plans also include measures that promote good agricultural practices, tailored to local conditions, to help with preventing "diffuse source" contamination from the field, e.g., runoff (Singh et al., 2018). As with the Water Framework Directive (2000/60/EC), the implementation of the SUD is challenged. Indeed, the implementation across Member States is reported to be inconsistent and the measures implemented not sufficient to deliver improvements in the sustainable use of PPPs. However, the execution of suitable remedial measures facilitates to reduced incidents of pesticide toxicity and other health issues linked to usage of PPPs.
The rational usage of pesticides (RUP), is a term invented in the label of a book written by Brent and Atkin (1987). RUP (Fig 1) mainly emphasized on the sub-set of integrated crop management (ICM), which efforts to moderate the harmful influences of PPP usage through better specificity and accuracy in PPP usage with space as well as time of the products themselves. The advantages of RUP are enhanced by a mixing of all three, and the promising advantages including decreased expenses (for pesticides as well as labour), decreased environmental influence (by additional efficient application of sprays and usage of the selective compounds

including biopesticides), and better safety (Boardman, 1986; Mancini et al., 2008; Abhilash and Singh, 2009; Gupta et al., 2010).

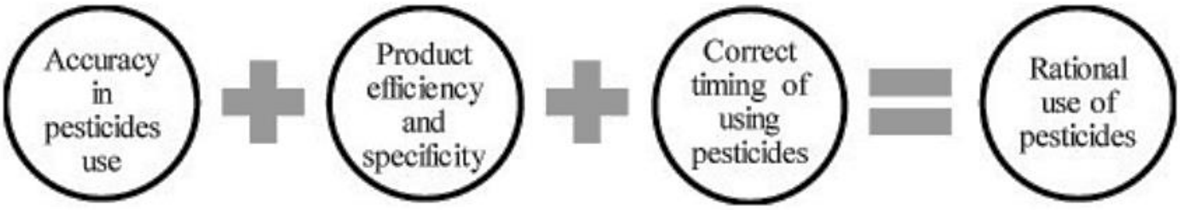

Fig. 1. Benefits of the ‘rational use of pesticides’ to decrease effects of pesticides on the environment (Rani et al., 2020).

Moreover, various types of remediation techniques are being used to overcome the PPP problems from the contaminated environment. At first, by spreading awareness in the society, some problems due to PPPs can be prevented at the source of their application. Indeed, different stakeholders such as environmental protection organizations, academia, research organizations, farmers, health officials, pesticides manufacturers, and government authorities have to come forward to find some suitable solution to this problem. A close collaboration of these people will definitely reduce the risks of pesticide toxicity on the living creatures as well as on the environment. It is our moral duty to take necessary steps for the efficient management of PPPs by making strict laws for pesticide uses and its toxicity regulations. The quantity of pesticides should be developed with precision and accuracy along with better safety profile so that their negative impact on the environment and human beings can be reduced.

This point will be deeply discussed in chapter 4.

2.5 Chemical fertilizers and PPPs: role in groundwater contamination

Agriculture has been an important practice to sustain the life-support systems of human civilizations since ancient times. Modern agriculture has included several innovative ideas to enhance crop production such as the applications of chemical fertilizers and PPPs in farming. Addition of chemical fertilizers and PPPs has become the fundamental part of today's agricultural systems to fulfill the huge demand of food grains of the whole world. However, excessive application of agrochemicals is deteriorating the quality of soil as well as groundwater due to the addition of nitrogen, phosphorous, and persistent pesticides. Groundwater contamination, in fact, poses several human health problems as it is the main source of safe drinking water (Srivastav, 2020).

Most problems related to water quality are caused as well as by intensive agriculture, also by industrial production, mining and untreated urban runoff and wastewater. Expansion of industrial agriculture, indeed, has led to increases in fertilizer applications. These and other industrial water pollutants create environmental and health risks: for example, excessive loads of nitrogen, which represents the most common chemical contaminant in the world's freshwater resources (WWAP, 2009), contribute to the eutrophication of freshwater and coastal marine ecosystems, creating 'dead zones' and erosion of natural habitats (WWAP, 2013).

Over the past several decades, ever-growing demands for – and misuse of – water resources have increased the risks of pollution and severe water stress in many parts of the world. Although the central and irreplaceable roles that water occupies in all dimensions of sustainable development have become progressively recognized, the management of water resources and the provision of water-related services remains far too low on the scales of public perception and of governmental priorities. As a result, water often becomes a limiting factor, rather than an enabler, to social welfare, economic development and healthy ecosystems (WWAP, 2015).

Moreover, agricultural water quality has been identified as a major environmental issue in Organization for Economic Co-operation and Development (OECD) countries, and as a topic for policy analysis, is an issue of relevance across all OECD countries. The primary agricultural sector is mainly responsible for nitrate, phosphorus, PPP, soil sediment, salt, and pathogen pollution of water from crop and livestock activities, but it can also play a role under certain farm practices in terms of improving water quality through a water purification function (Parris, 2011). In the European Union, 38% of water bodies are significantly under pressure from agricultural pollution (WWAP, 2015) and this causes greater awareness and growing concern on the part of the population towards agricultural practices related to aquatic ecosystems.

Following the growing food demand in relation to population growth and changes in dietary patterns, agricultural pressures on water quality, also coming from livestock and animal husbandry, have intensified.

The degradation of water quality can also have serious direct consequences on the aquatic ecosystem, on biodiversity, on fishing and on productivity in general.

Management of the nitrogen cycle has been identified as a major challenge across most of the region, and improving the handling of nutrients in agriculture plays a key role in addressing the related problems.

Water quality in rural areas is largely depending on farming practices. Despite numerous efforts to reduce nutrient and pesticide concentrations in surface water and groundwater and regulation (Nitrates Directive (91/676), Water Framework Directive (2000/60), Groundwater Daughter Directive (2006/118), Directive on Environmental Quality Standards (2008/105), Sustainable Use Directive (2009/128)), many water bodies are not in good status for nitrates and hot spots of contamination for phosphorous and PPPs persist. The stagnation of the water quality is not only due to a long-term storage of the agrochemicals in soil and groundwater systems but also to the lack of implementation of good agricultural practices and mitigation measures that prevent the chemicals to enter the water system. Over the past two to three decades, our understanding of the functioning of the water system and the effect of farming practices and mitigation measures has increased tremendously, but somehow we fail to convert that knowledge into actual implementation at a scale which is necessary to create real improvement of water quality. We think that a paradigm shift from purely top-down regulation and enforcement to local actor engagement is needed to revert the trend (Belmans et al., 2018). In this regard, implementation of sustainable agricultural practices and mitigation measures can prevent the groundwater contamination from these agrochemicals along with high crop yield as well as safeguards to the environmental ecosystems. Moreover, it also promotes the use of biologically originated fertilizers and PPPs via giving equal importance to the local/traditional knowledge and innovative farming techniques (Srivastav, 2020).

Therefore, in the chapter 4 of this thesis is presented a multi-actor approach to engage actors at the scale of water system catchment or a so-called action lab. Within an action lab, key actors are involved in setting up new governance strategies including participatory monitoring approaches, best management practices, and collaborative software applications to facilitate the process of implementation of mitigation measures.

2.6 The importance of groundwater

Groundwater is a major source of drinking water all over Europe, and thus the state of groundwater in terms of quality and quantity is of vital importance (EEA, 1999).

Groundwater constitutes about 30% of the world's freshwater resources. This represents 97% of the freshwater that is potentially available for human use, taking into account that 70% of freshwater resources are frozen (Morris et al., 2003).

Despite this relatively small proportion, its role is important for two reasons: on the one hand, groundwater is well suited for the supply of drinking water due to its usually high quality. On the other hand, groundwater basins are important long-term storage reservoirs, which in semi-arid and arid countries often constitute the only perennial water resource (Kinzelbach et al., 2003).

Moreover, groundwater is extensively used worldwide for domestic, industrial, and agricultural purposes, and both urban and rural areas rely on groundwater resources to meet their water demands (Postigo et al., 2015; Swartjes et al., 2020, Singh et al., 2015).

Worldwide, 2.5 billion people depend solely on groundwater resources to satisfy their basic daily water needs, and hundreds of millions of farmers rely on groundwater to sustain their livelihoods and contribute to the food security of so many others (WWAP, 2012). Groundwater reportedly provides drinking water to at least 50% of the global population and accounts for 43% of all water used for irrigation (Groundwater Governance). Groundwater also sustains the baseflows of rivers and important aquatic ecosystems. Uncertainty over the availability of groundwater resources and their replenishment rates pose a serious challenge to their management and in particular to their ability to serve as a buffer to offset periods of surface water scarcity (Van der Gun, 2012).

Groundwater supplies are diminishing, with an estimated 20% of the world’s aquifers being over-exploited (Gleeson et al., 2012), leading to serious consequences such as land subsidence and saltwater intrusion in coastal areas (USGS, 2013).

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 (Brouwer et al., 2018) as water pollution, water abstraction and droughts, due to climate change. In

Europe, 25 % of groundwater has poor chemical status (EEA, 2018), and particularly, 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 (Kourakos et al., 2012). Nowadays, within a generation, a global water crisis has developed, due to poor resource management since the scientific evidence has been clear, that water withdrawals exceed natural rates of renewal. For groundwater, indeed, it is vital that finite amounts of any renewable resource can be recognized and quantified (Edmunds, 2003).

European Environmental Agency identifies 29% of 35% of diffuse pollution in agriculture and 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, as PPPs and nitrogen-based fertilizers.

As mentioned before, PPPs in drinking water are currently regulated by the Drinking Water Directive using a maximum allowable concentration of 0.1 μg/L. This standard (a surrogate zero) was consistent with the precautionary principle when it was originally set in 1980 and remained consistent when retained in 1998. However, given developments in EU pesticide and water policy, international experience in regulating pesticides, and an increasing knowledge of pesticide toxicity, it can be argued that the level of epistemic uncertainty faced by regulators has substantially decreased (Dolan et al., 2014).

Based on what has been argued, it can be concluded that a constant monitoring of the most vulnerable ecosystems to contamination, represents a primary importance.

2.7 Groundwater monitoring

Groundwater monitoring is considered a higher tier assessment in the regulatory groundwater assessment of PPPs in the European Union (EU Commission, 2014). In fact, in order to determine if groundwater is adequately protected against leaching of active substances and their metabolites used in PPPs, groundwater monitoring is considered a fundamental approach. The recently published report “Conducting Ground Water Monitoring Studies in Europe for Pesticide Active Substances and their Metabolites in the Context of Regulation (EC) 1107/2009” was prepared by advisory group SETAC EMAG-Pest GW, and provides recommendations on study design and study procedures, with specific emphasis on vulnerability assessment and mapping of monitoring sites. Vulnerability, in the context of groundwater monitoring for pesticides, usually refers to the vulnerability of groundwater to leaching of these compounds from the topsoil. Understanding groundwater vulnerability is crucial for the design and interpretation of groundwater monitoring studies.

In the European Union, placing a PPP on the market is regulated by Regulation (EC) No. 1107/2009 and its associated implementing Regulations (i.e., 546/2011 on uniform principles, plus 283/2013 and 284/2013 on data requirements). Regulation 284/2013 requires estimating concentrations in groundwater (PECgw) of the active substance and all metabolites identified as part of the residue definition for risk assessment with respect to groundwater. Therefore, monitoring is useful for determining whether groundwater is being adequately protected against leaching of active substances and their metabolites (biotic or abiotic degradation products) under relevant field conditions and it is considered the highest tier of assessment also in the FOCUS groundwater assessment scheme for assessing potential impacts of active substances and their metabolites (FOCUS, 2009; European Commission 2014).

Decree no. 152/1999, for example, introduced the ‘integrated system for monitoring and control’ of water resources for quality and quantity. This monitoring system is based upon the DPSIR model (Determinant-Pressure-Status-Impact-Response, i.e. the analysis of driving forces that can assert pressure on the state of water bodies) and it is very important in order to plan actions as part of the Water Protection Plan.

In Italy, in 2007, the situation was as follows: 48% (1,014) of monitored sites falled into quality class 1 (very good) and 2 (good), 32% falled into class 3 (sufficient) and the remaining 20% of sites were of poor quality (Fig. 2) (Balzarolo et al., 2011).

A study of a groundwater monitoring in an area situated in the North-West of Italy is reported in chapter 2.1 and it represents a first evaluation of groundwater quality by PPPs occurrence.

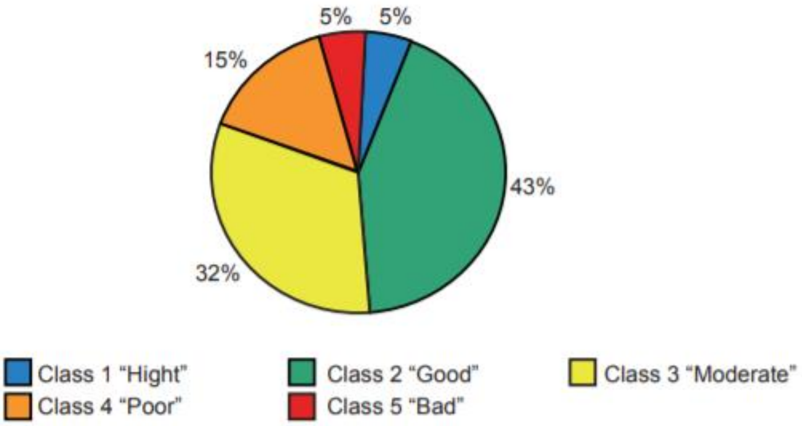

Fig. 2. Percentage distribution of the classes of the Ecological Status Watercourses quality index. (ISPRA, 2009)

2.8 Pesticides fate and the ways of water contamination

The greatest concern regarding human exposure to pesticides is their presence in water (Younes and Galal-Gorchev, 2000) especially that used for drinking.

All pesticides in groundwater, and most residues present in surface water enter via the soil. There are two main routes by which pesticides enter the soil: spray drift to soil during foliage treatment plus wash-off from treated foliage (Rial-Otero et al., 2003) and release from granulates applied directly to the soil (López-Pérez et al., 2006) (Fig. 3).

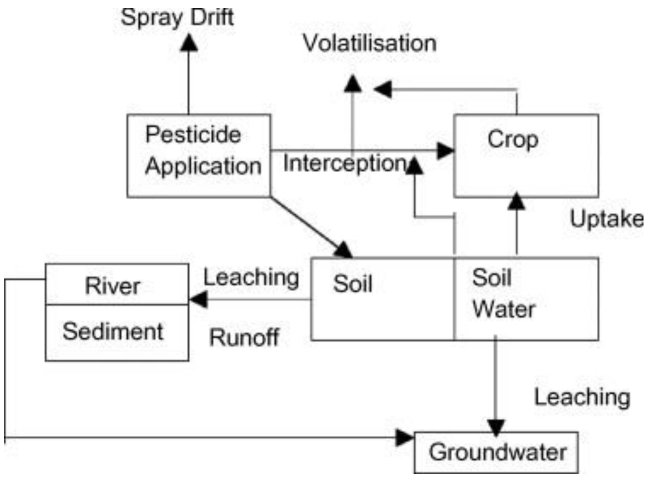

Fig. 3. Pathways of a pesticide applied to a crop. Ideally, at least one includes its contact with the targeted pest (Arias-Estévez et al., 2008).

Groundwater resources in particular, are subject to increasing pressures from both point and diffuse pollution sources (Brouwer et al., 2018). Diffuse sources, particularly from agriculture (35 %), and point sources (14 %) are the main pressures on groundwater chemical status (EEA, 2018).

Diffuse agricultural pollution poses significant pressure on 38% of the European union's (EU) water bodies. the EU water blueprint also identifies the need to tackle diffuse pollution using different approaches to accommodate the wide range of agricultural systems (WWDR, 2015).

Diffuse pollution can be caused by a variety of activities that have no specific point of discharge. Agriculture is a key source of diffuse pollution, but urban land, forestry, atmospheric deposition and rural dwellings can also be important sources (EEA, 2020).

Non-point source pollution generally results from land runoff, precipitation, atmospheric deposition, drainage, seepage or hydrologic modification and, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. As runoff from precipitation moves, it picks up and transports pollutants resulting from nature and human activity, ultimately depositing them into rivers, lakes, wetlands, and groundwater (Lam et al., 2011).

In addition, agricultural diffuse pollution has been increasingly recognized as a primary contributor to water quality impairment and as a key water quality problem worldwide (Kourakos et al., 2012).

This kind of source pollution can includes:

- Excess fertilizers, herbicides and insecticides from agricultural lands and residential areas
- Oil, grease and toxic chemicals from urban runoff and energy production
- Sediment from improperly managed construction sites, crop and forest lands, and eroding streambanks
- Salt from irrigation practices and acid drainage from abandoned mines
- Bacteria and nutrients from livestock, pet wastes and faulty septic systems
- Atmospheric deposition and hydro modification

By its very nature, the management of diffuse pollution is complex and requires the careful analysis and understanding of various natural and anthropogenic processes. As the name suggests, non-point source areas can be difficult to characterize due to spatial and temporal heterogeneity (Rao et al., 2009). States report that nonpoint source pollution is the leading remaining cause of water quality problems. The effects of nonpoint source pollutants on specific waters vary and may not always be fully assessed. However, we know that these pollutants have harmful effects on drinking water supplies, recreation, fisheries and wildlife (EEA, 2017).

On the other hand there is the point sources contamination, which is mainly linked to the filling and cleaning area on the farm. Indeed, the most direct losses are related with spillages resulting from the filling operation, spray excess and technical rest volumes in the tank, leakages of the spray equipment, pump and booms, rinsing water from cleaning the internal tank to avoid carry over effects onto the following crop, water from external cleaning of spray equipment, etc. (Isensee and Sadeghi, 1996). The term "point source" means any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged. This term does not include agricultural storm water discharges and return flows from irrigated agriculture (EEA, 2017). For this reason, identify the source of contamination allows to effectively preventing or reducing groundwater contamination and this is an important component in groundwater management (Wang et al., 2012). This kind of study was elaborated and will be discussed in chapter 2.2.

In conclusion, additional technological and infrastructural solutions are required to reduce the direct pesticide releases. Some possible solutions could include (i) the existence of a filling and loading area on the farmyard to minimize the release of pesticides (Rose 2001), (ii) the cleaning process of the spray equipment in the field (Balsari, 2003), and (iii) waste water treatment systems to separate and/or degrade the contaminants from the water fraction (De La Rocque, 2004; Osaer et al., 2001).

Furthermore, 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.

2.9 The sustainability in the contest of viticulture

Viticulture represents a long-term commitment. As perennial crops, grapevines must be natured over years and even decades. Sustainable practices are therefore essential for any vineyard, because concerns about pruning and crop loads pale in comparison to those regarding whether or not there will be enough water, whether the soil will remain fertile enough to support vines, and whether the climate will even allow grapes to survive in the near future (Gerling et al., 2015).

Since ancient times, viticulture has been developing in two opposite trends: quality and quantity. The origin of this paradox can be found in the Greek and Roman period and raises from the interaction between technical and cultural factors (Corino et al., 2001).

To progress, it is necessary to improve the agronomic knowledge and general understanding of viticulture and it's environment. (Corino, L., Calo, A. 2001).

Sustainability plays a key role in the wine industry, as shown by the attention paid at several levels by the academia, institutions and associations. In particular, the Italian wine industry is strongly committed to sustainability: the stakeholders' interest in the topic is constantly growing and a wide number of sustainability programs have been launched in recent years, by both private businesses and consortium. One of the essential sustainability objective for the vineyard is the improving Water Use Efficiency (WUE) in grapevines, especially under the increasing aridity induced by global climate change. Indeed, water is critical for viticulture sustainability since grape production, quality and economic viability are largely dependent on water availability. The total water consumption of vineyards, 300 to 700 mm, is generally higher than the annual average precipitation in many viticulture areas, which induces a risk for sustainability of vineyards. Increased sustainability of water resources for vineyards can be achieved using agronomical technology. Indeed, agronomical practices focus on increasing green water use by increasing soil water storage capacity, reducing direct soil water loss, or limiting early transpiration losses (Medrano et al., 2014).

Furthermore, although the wine industry be less "dirty" than other sectors, as for example the chemical one (Barber et al., 2009), wine producers and vine growers have been increasingly engaged in sustainability driven by different forces, first of all the environmental concerns. The wine industry, indeed, has to face several environmental issues and challenges. The literature reports several environmental sustainable practices and these aspects are often mentioned as relevant: soil management, water management, wastewater, biodiversity, solid waste energy use, air quality, and agrochemical use (Ohmart, 2008).

Water must also be managed responsibly by minimizing consumption and reducing run-off of contaminated wastewater. Moreover, wineries must manage the landscape, to protect the health and safety of workers, as well as minimize its impact on the community (from chemical spray drifts, odor, and noises) (Gabzdylova et al., 2009; Barber et al., 2009).

The global wine industry also faces institutional and stakeholders' pressures. The pressures from governments and environmental groups, the growing interest from consumers for green products and the higher commitment to export in countries with a strong attention for "sustainable products" are among the "institutional drivers" to sustainability (Sinha et al., 2010; Marshall et al., 2005). Finally, managers' personal values, entrepreneurs' personal motivations, and employees' environmental attitudes can be considered as important drivers to guide the wine industry towards sustainability, given the fact that the sector is mainly made by small-medium companies, and there is a frequent coincidence between the ownership and the management (Marshall et al., 2005).

The term "sustainability" also has to be interpreted from a social and economic point of view: only an equal consideration of the ecological, economic and social dimensions of sustainability can lead to the achievement of (among the others) "changing unsustainable patterns of production and consumption and protecting and managing the natural resource base of economic and social development" (United Nations , 2005). Therefore, the three interdependent and mutually reinforcing pillars of sustainability must always be jointly considered in order to define viticulture as "sustainable", promoting aspects such as, the health and safety of workers, the Company's contribution to the rural and local development, and the economic viability and profitability of the measures taken.

2.10 Best Management Practices for a sustainable agriculture

As aforementioned, some studies have found that pollutants such as chemical fertilizers and PPPs, resulting from various agricultural practices, lead to the degradation, as well as the environment also of surface and groundwater (Donoso et al. 1999; Zalidis et al. 2002). Agriculture has been identified as the major contributor of diffuse source pollution of water resources (Humenik et al. 1987; Duda 1993; Behrendt et al. 1999; Lam et al. 2010). Therefore, application of Best Management Practices (BMPs) is a useful method to eliminate or minimize pollution resulting from agricultural activities in order to achieve good ecological and chemical conditions of water quality standard regulated by the European Framework Directive (EC 2000).

BMPs are methods, measures, or practices designed to promote environmental, social and economic sustainability from the agricultural sector to mitigate the air, soil and water pollution in a sustainable way (Martinho, 2019). They include structural and non-structural controls as well as operation and maintenance procedures. The practices can be in varying combinations to prevent or control pollution from a particular non-point or point source (Logan, 1990). Point and non-point source pollution, indeed, are become a serious problem causing the impairment of water quality in many European countries.

Research on water quality degradation caused by point and diffuse source pollution plays an important role in protecting the environment sustainably and implementation of BMPs is challenged by integration of environmental, economic, and institutional criteria. Assessment of environmental issues in watersheds relates to social benefits such as achieving the goal of maximum productions, minimum yield reduction, and unchanged farming habits. Establishment cost and environmental effectiveness of BMPs are often crucial factors in selecting and adopting BMPs (Arabi et al. 2004). Identifying optimal combination of BMPs requires systematic approaches that allow decision makers to quickly assess trade-off among environmental and economic criteria.

Conclusions

Although contaminants like PPPs and nitrates are regulated in Europe, there is increasing concern about the pollution of environment, particularly of groundwater which is highly affected by the improper usage of chemicals in the fields. In fact, nowadays, the intensive agricultural activities and the unsustainable use of PPPs and fertilizers, can potentially cause pollution of the groundwater. In this regard, monitoring studies are fundamental in order to investigate groundwater quality and thus to find the better solutions for a sustainable water management. Furthermore, to achieve this purpose, the implementation of Best Management Practices and mitigation measures is essential.

From the assessment of status, and from the assessment of pressures and impacts, it is evident that the driving forces behind the achievement or non-achievement of good water status are activities insectors such as agriculture, energy or transport. This integration throughout the river basin is enhanced, for example, by better cooperation between competent authorities, increased involvement of stakeholders and early participation of the public. Sustainable water management is a critical element of the green economy because healthy and resilient ecosystems provide the services needed to sustain human well-being and, thus, our economy. Therefore, we need to ensure that economic sectors, such as agriculture energy and transport, also adopt management practices that can keep water ecosystems healthy and resilient. The WFD is an important policy to achieve this. The good status objective under the WFD defines these boundaries of sustainability. Managing water in a green economy means using water in a sustainable way in all sectors and ensuring that ecosystems have both the quantity and the quality of water needed to function. It also means fostering a more integrated and ecosystem-based approach that involves all relevant economic sectors as well as society as a whole (EEA, 2018).

It is therefore of paramount importance to develop new integrated strategies to preserve natural groundwater quality, to protect it from further contamination and to promote new, sustainable management practices at the local and regional level. If groundwater resources are carefully managed, they can make a significant contribution towards meeting water demands, agricultural needs and adapting to global climate change (WWAP 2012).

To conclude, the prevention of contamination is the primary strategy of water quality management, and the implementation of best management practices is mandatory to prevent water and environmental pollution.

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Chapter 2

Assessment of groundwater contamination by plant protection products and pollution source

Groundwater monitoring is essential to the prevention of pollution from contaminants like PPPs. However, in order to take the necessary measures to avoid water contamination, it is essential to study the possible sources of contamination.

Chapter 2.1 examines the occurrence of fifteen PPPs in groundwater of an area characterized by an intensive viticulture activity in order to have a full picture of the general impact that vineyard may have on groundwater. The peculiarity of the study area, over the huge vineyard, is that the groundwater contamination was never investigated before.

Chapter 2.2 represents the second part of this study and evaluates the groundwater contamination sources by PPPs in a smaller part of the study area, by collecting and integrating monitoring data obtained in the study of the chapter 1, sub-surface water movement data and territorial characteristics.

This chapter also shows how the several demonstration activities organized with the farmers of the entire Valley to prevent the point-source and diffuse contamination have been successful as demonstrated in chapter 4.

Chapter 2.1

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

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Abstract

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

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

The results of three monitoring campaigns revealed the occurrence of seven PPPs at a level higher than EQS for groundwater (0.1 µg/L) in 30% of the wells. The main pesticides detected were Chlorantraniliprole, Dimetomorph, Fluopicolide, Metalaxyl-M, Penconazole, and Tetraconazole, all commonly used in viticulture, together with S-metolachlor, authorized for cereal cropping. Statistical analysis revealed a significant influence of the sampling time, slope of the soil surrounding the wells, wells depth and wells location on the concentration of five PPPs. Therefore, the results obtained show that the improper use of PPPs for grapevine cultivation may cause groundwater contamination and suggest the need for a deeper analysis of territorial reality, including hydrology studies and farmer behavior and for an urgent introduction of best management practices and mitigation measures to promote a sustainable use of PPPs in viticulture.

Keywords

Groundwater pollution, Grapevine, Multi-actor approach, plant protection product

Abbreviations

ARPAE Regional Agency for Prevention, Environment and Energy

AUSL health local agency

EQS Environmental Quality Standard

GLM generalized linear model

GUS groundwater ubiquity score

HPLC-MS/MS high performance liquid chromatography tandem mass spectrometry

PPP plant protection product

UPLC-QTOF-MS ultra performance liquid chromatography quadrupole time of flight mass spectrometry

ANOVA analysis of variance

1. Introduction

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

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

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

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

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

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

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

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

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

2. *Materials and methods*

2.1 Study area

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

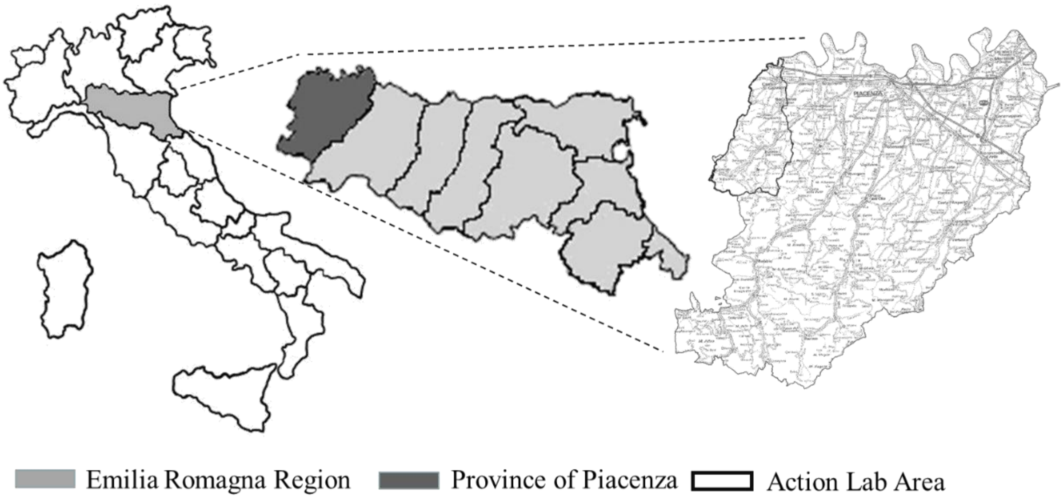


Fig 1. The Action Lab area, an intensive viticulture region in North-Western Italy.

2.2 Development of the sampling network

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

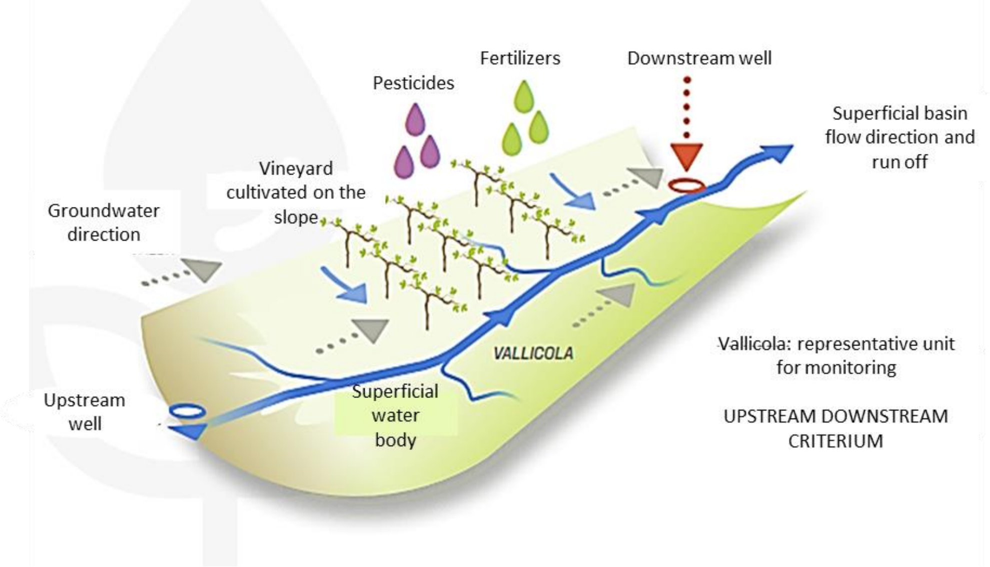


Fig 2. Upstream-downstream criterium. Representation of the criterium for wells selection, with groundwater flow considered from south-west to north-east.

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

Table 1. Network wells description.

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

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

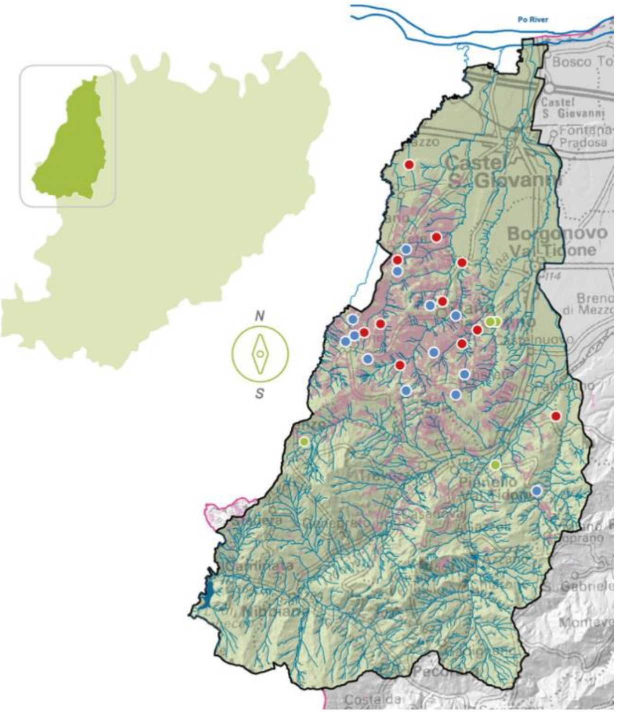


Fig. 3. Map of the wells network. Blue - upstream wells, red – downstream wells, green - drinking water wells. In pink the area with grapevine cultivation.

2.3 Development of PPPs list to be monitored

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

2.3.1 Stakeholders consultation

The scope of stakeholder consultation was to collect information about PPPs with high volume of use by farmers, high probability to be find in groundwater, based on existing PPP occurrence data in groundwater and surface water of the entire province and high toxicity. In order to reach the scope, survey campaigns were carried out and six stakeholder categories involved: farmers (175, farmers, 97 of them are members of the local Social Winery Vicobarone), farmers associations (Confagricoltura, Coldiretti and CIA), environmental local agency (ARPAE), reclamation authority (Consorzio di Bonifica di Piacenza), water supplier company (IRETI) and local Health Agency (AUSL).

2.3.2 Untargeted analysis

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

2.3.3 Expert judgement

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

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

2.4 Reagents and standards

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

2.5 Groundwater sampling and instrumental analysis

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

A method based on solid phase extraction from groundwater, suitable for the selected PPPs, and their analysis through HPLC-MS/MS, was then developed following the Guidelines for the detection of Residues for post-registration control and monitoring, proposed by European Commission (https://ec.europa.eu/food/plant/pesticides/approval_active_substances/guidance_documents_en; https://esdac.jrc.ec.europa.eu/projects/focus-dg-sante) (EC, 2010).

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

For the analysis of the extracts, a 1200 series liquid chromatograph system equipped with quaternary pump, electrospray ionization system and coupled to a G6410A triple quadrupole mass spectrometer detector (all from Agilent technologies, Santa Clara, CA, USA) was used. The chromatographic separation was achieved on a EC-C18 column (4.6 x 100 mm, 2.7 µm, Agilent technologies, Milan, Italy) using ultra-pure water with 0.1% formic acid (phase A) and 0.1% formic acid in methanol (phase B) as mobile phases. Injection volume was 20 µL, run time was 30 min and the flow rate was 0.2 mL/min. The proposed method was validated by evaluating linearity, matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability). The linearity was evaluated through the coefficient of determination (R2) of the analytical curves at concentration levels between 1 and 2500 µg L-1. The solutions for instrumental calibration were prepared in methanol. Matrix effect was calculated comparing the slope of curves prepared in solvent and in the blank extract. Precision was evaluated in terms of repeatability and intermediate precision, by estimating the relative standard deviation (RSD) of the recovery percentage for each spiked level. The LOD and LOQ were calculated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1. The complete description of the analytical method and the results of recovery test are presented in the supplementary material.

2.6 Statistical analysis

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

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

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

3. *Results and discussion*

3.1 PPPs selection for groundwater monitoring

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

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

The outcomes of stakeholders and expert judgement consultation produced a list of twenty one PPPs, with high interest for the local stakeholders and high use on the territory (Table 5S and 6S in the supplementary materials). In particular, farmers and other stakeholders indicated seven herbicides (Acetolachlor, Flufenacet, Isopropalin, Metsulfuron-methyl, S-metolachlor, Terbuthylazine and Tribenuron-methyl), two insecticides

(Chlorantraniliprole and Parathion-methyl) and two fungicides (Benomyl and Fluopicolide), whereas the expert judgement consultation indicated three insecticides (Chlorpyrifos, Chlorpyrifos-methyl and Thiamethoxam) and six fungicides (Cyflufenamid, Cyprodinil, Mancozeb, Metiram, Penconazole and Tetraconazole) as high used pesticides on the study area. Tables 5S and 6S in the supplementary material show their physicochemical properties and GUS Index.

For what concern the physicochemical properties of the pesticides previously detected/indicated by the stakeholders, the dissipation of a substance is usually expressed through the DT50 and contributes, in combination with the Koc, to the leaching potential through the GUS index: GUS = log (DT50) x [4 - log (Koc)]. This is an empirical index and represents a potential indicator since environmental conditions are not considered. GUS values higher than 2.8 indicate that the leaching of the substance is probable, while this is not likely to happen with GUS values less than 1.8. Intermediate values point indicates a limited leaching potential. The partition coefficient Koc is expressed on the basis of the organic carbon content of the sediment. This parameter gives indications on the chemical compound's ability to bind to the soil according to its characteristics. The higher value represents the stronger tendency to be tied to the ground, while the lower value represents the greater tendency to move with percolation water. The half-life of the pesticides in the soil (soil DT50), expressed in days, indicates the time in which the substance is halved compared to the initial concentration: greater is the value, more persistent is the substance in the soil. For this last parameter, three different values are provided: laboratory, field and typical. The typical value is that reported in the literature and it is often the average of all field and laboratory studies. (Vassiliou 2016).

Therefore, merging all the information obtained from the untargeted analysis, the outcomes of stakeholders and expert judgement consultation, the physicochemical properties (Koc, DT50 and water solubility) and finally the GUS Index, the pesticides list showed in Table 2 was selected. Higher priority was given to the PPPs authorized for grape cultivation and with high number of treatments, following the integrated pest Management guidelines of Emilia - Romagna Region. It consists in three insecticides (Chlorantraniliprole, Chlorpyrifos and Chlorpyrifos methyl), used on grapevine against Eupoecilia ambiguella, seven fungicides (Cyflufenamid, Cyprodinil, 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. Indeed, the selected herbicides were included in the final list (Table 2) in order to assess a possible inappropriate use for grapevine cultivation or a possible impact of cereals cultivation. The ISTAT data, elaborated by AAAF (Gruppo di lavoro Fitofarmaci) group, concerning the active ingredients quantity sold in Emilia Romagna Region in 2012 (no other recent data available) confirm the high use of Chlorpyrifos, S-Metolachlor, Dimetomorph, Chlorpyrifos-methyl, Cyprodinil, Metalaxyl-M, Chlorantraniliprole, Fluopicolide, Penconazole, Flufenacet, Tetraconazole, Metsulfuron-methyl and Cyflufenamid, with values ranging between 16 kg (Cyflufenamid) and 117069 Kg (Chlorpyrifos) (http://www.appa.provincia.tn.it/fitofarmaci/programmazione_dei_controlli_ambientali/Criteri_vendita_prodotti_fitosanitari/pagina123.html).

Table 2. List of PPPs to be monitored.

Compound name	Type	GUS index[1]	K_{oc}[1] (mL/g)	DT50[1] (days)	Water solubility[1] (mg/L)
Chlorpyrifos	Insecticide	1.04	5509	27.6	1.05
Chlorpyrifos-methyl	Insecticide	0.92	4645	12	2.74
Chlorantraniliprole	Insecticide	4.22	362	204	0.88
Cyflufenamid	Fungicide	1.85	1592	25.3	0.52
Cyprodinil	Fungicide	1.11	2277	45	13
Dimethomorph	Fungicide	2.56	348	44	28.95
Flufenacet	Herbicide	2.02	401	39	51
Fluopicolide	Fungicide	3.63	321.1	138.8	2.8
Isopropalin	Herbicide	0.00	10000	100[2]	0.11
Metalaxyl-M	Fungicide	1.71	78.9	14.1	26000
Metsulfuron-methyl	Herbicide	3.99	12	13.3	2790
Penconazole	Fungicide	1.36	2205	90	73
S-metolachlor	Herbicide	1.91	226.1	21	480
Tetraconazole	Fungicide	1.81	1152	430	156.6
Tribenuron-methyl	Herbicide	2.4	35	3.6	2483

[1] Lewis K.A., Tzilivakis, J., Warner, D. and Green (2016) An international database for pesticide risk assessments and management. International Journal of Human and Ecological Risk Assessment.

[2] Typical value in the above database

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

Methyl, S-metolachlor and Tribenuron-Methyl. Cyprodinil, Dimetomorph, Flufenacet and Penconazole have a moderately persistence in soil.

3.2 PPPs occurrence in groundwater

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

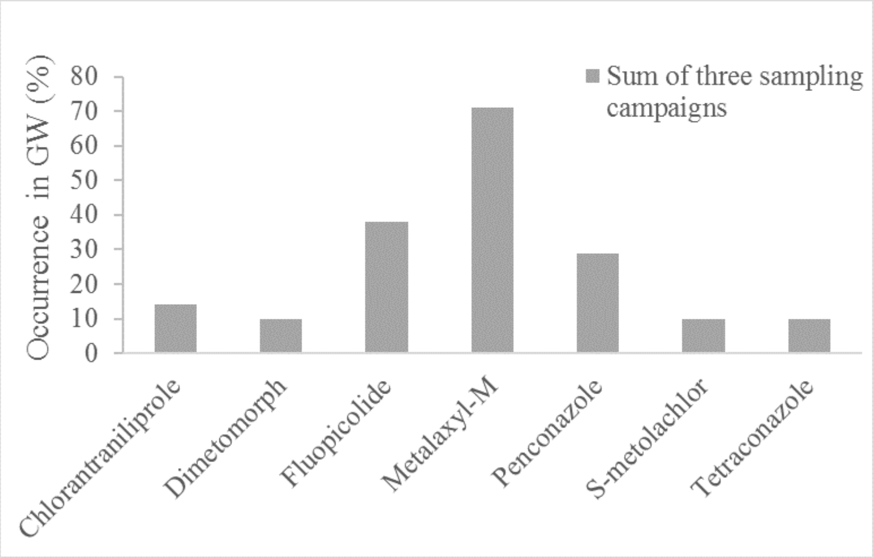
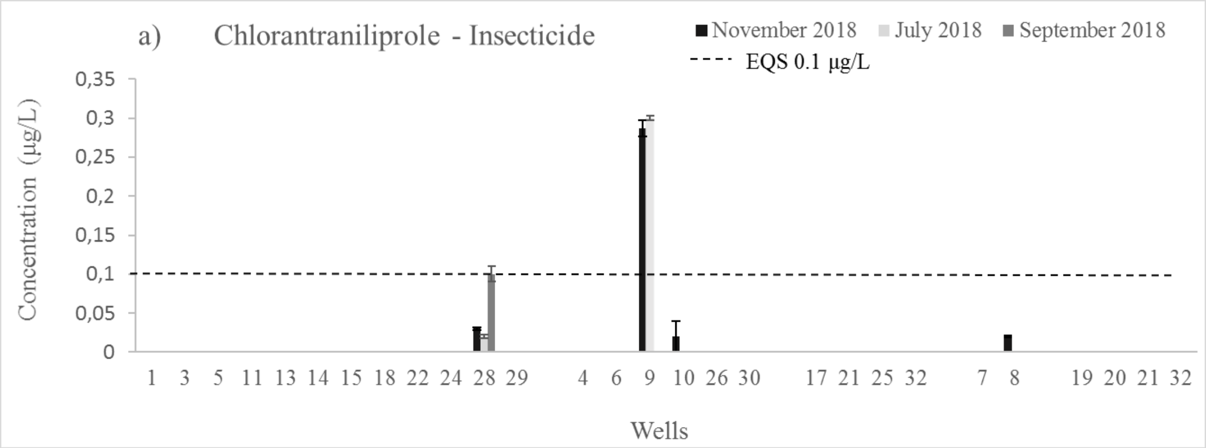
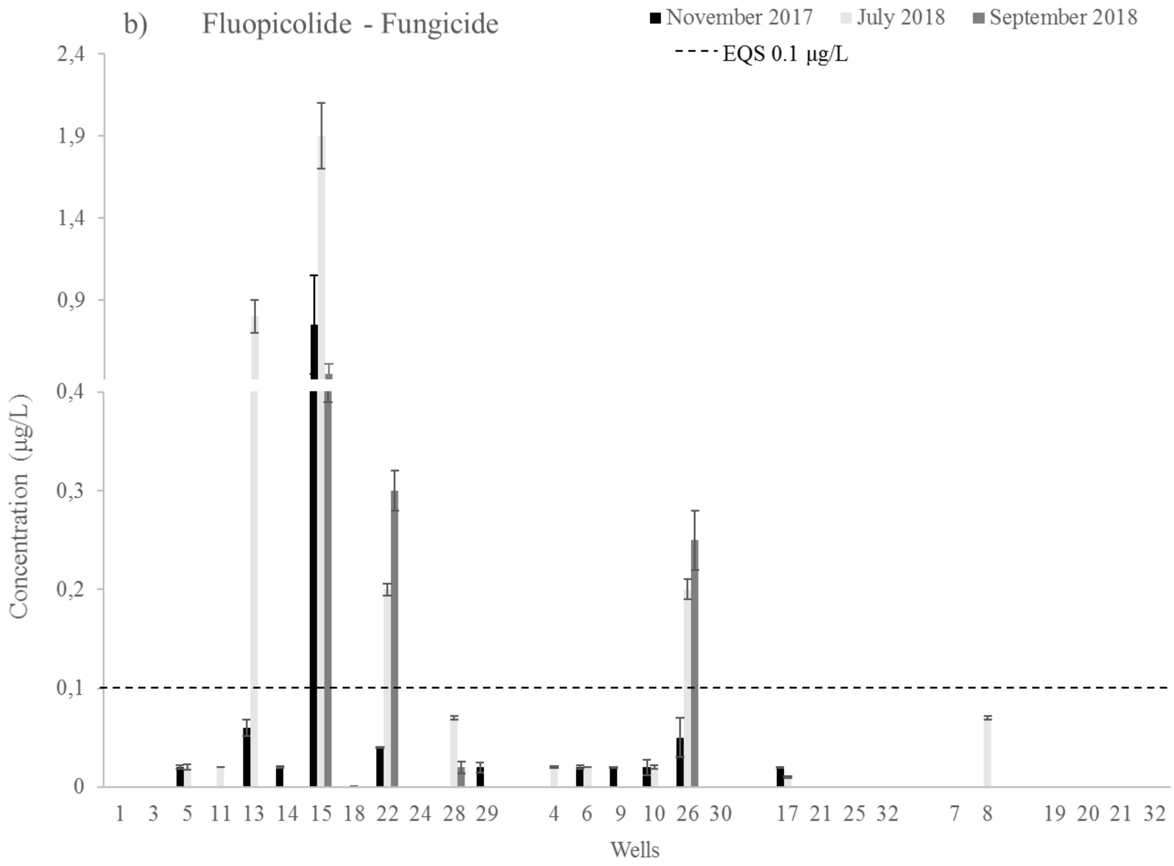
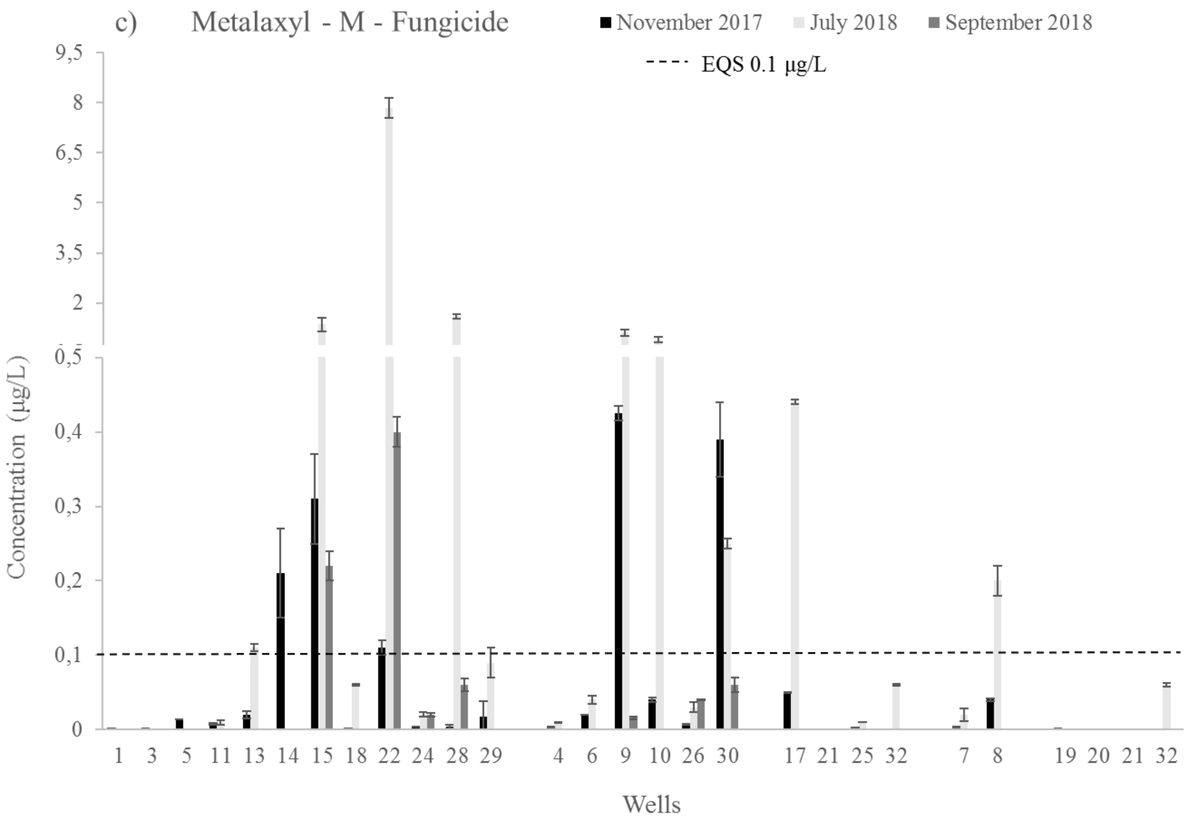


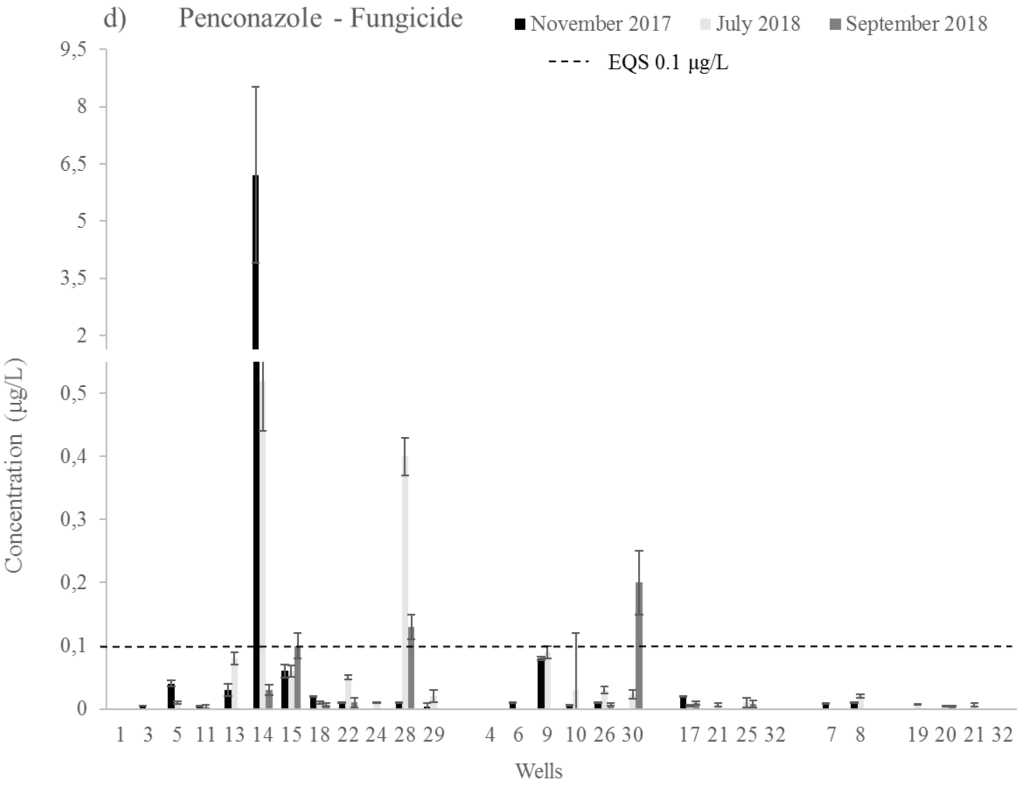
Fig 4. % of groundwater samples above EQS during the three sampling campaigns.

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


a)
Chlorantraniliprole - Insecticide
November 2018
July 2018
September 2018
EQS 0.1 µg/L
Concentration (µg/L)
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
1 3 5 11 13 14 15 18 22 24 28 29
4 6 9 10 26 30
17 21 25 32
7 8
19 20 21 32
Wells


b)
Fluopicolide - Fungicide
November 2017
July 2018
September 2018
EQS 0.1 µg/L
Concentration (µg/L)
2,4
1,9
1,4
0,9
0,4
0,3
0,2
0,1
0
1 3 5 11 13 14 15 18 22 24 28 29
4 6 9 10 26 30
17 21 25 32
7 8
19 20 21 32
Wells


c)
Metalaxyl - M - Fungicide
November 2017
July 2018
September 2018
EQS 0.1 µg/L
Concentration (µg/L)
9,5
8
6,5
5
3,5
2
0,5
0,4
0,3
0,2
0,1
0
1 3 5 11 13 14 15 18 22 24 28 29
4 6 9 10 26 30
17 21 25 32
7 8
19 20 21 32
Wells


d)
Penconazole - Fungicide
November 2017
July 2018
September 2018
EQS 0.1 µg/L
Concentration (µg/L)
9,5
8
6,5
5
3,5
2
0,5
0,4
0,3
0,2
0,1
0
1 3 5 11 13 14 15 18 22 24 28 29
4 6 9 10 26 30
17 21 25 32
7 8
19 20 21 32
Wells

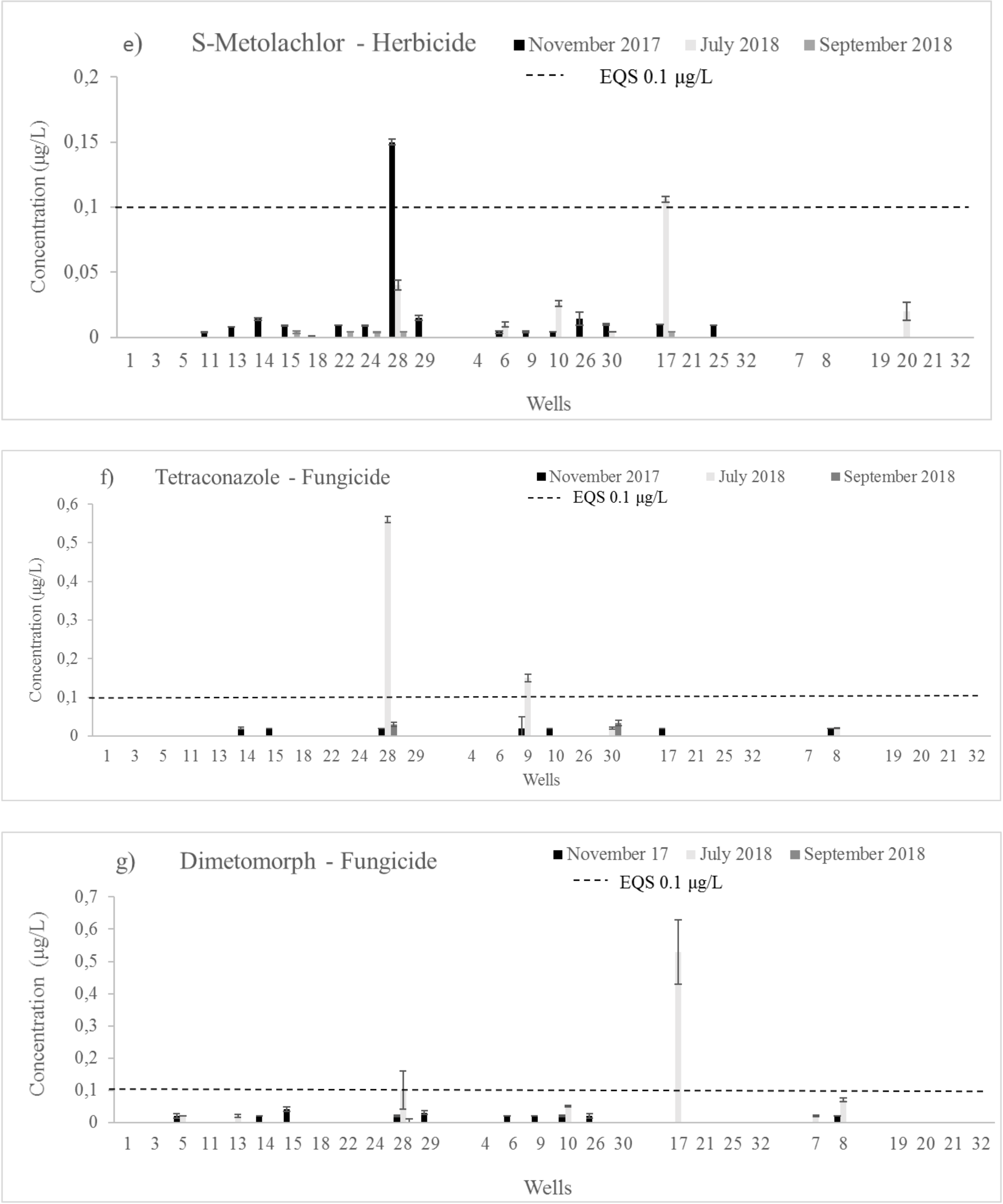


Fig 5. Concentration (µg/L) of the pesticides that exceed the EQS during the three sampling campaigns; a) Chlorantraniliprole, b) Fluopicolide, c) Metalaxyl-M, d) Penconazole, e) S-metolachlor, f) Tetraconazole and g) Dimethomorph.

Based on the physico-chemical properties and GUS Index, Metalaxyl-M, Penconazole, S-metolachlor and Tetraconazole are not persistent in the soil and have a low leaching potential (1.71; 1.36; 1.91; 1.81), making them unlikely to be found in groundwater. On the contrary, Chlorantraniliprole, Fluopicolide and

Dimethomorph are compounds with high persistence in soil and high leaching potential (4.22; 3.63; 2.56). However, further study on territorial hydrology, discussed by Suciu et al. (2020, under submission in this special issue), highlighted that for a sub-area of 7 km2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25), the occurrences and concentrations of PPPs are due to both point and diffuse contamination sources, but the position of the well in the territorial context may help to discriminate which of the two sources is the most influent.

Several studies were conducted on the impact of viticulture on groundwater, surface water or soils (Pose-Juan et al., 2015; Hildebrandt et al., 2008; Herrero-Hernández et al., 2013). The study of Pose-Juan et al. (2015), about the PPPs occurrence in vineyard soils in Spain, showed the presence in soil of herbicides, fungicides and insecticides typically used in viticulture, with the highest number detected in June. One of the highest concentrations was determined for the fungicide Metalaxyl, at a value of 11.5 μg/kg. Furthermore, the study revealed a more intensive use of herbicides in March, while the use of insecticides and fungicides may depend on the specific needs of crops and/or the onset of diseases. Their results were consistent with the residues found in groundwater in that region (Herrero-Hernández et al., 2013). Four of the forty-seven PPPs analyzed in the Spanish study are common with the present study: Chlorpyrifos, Cyprodinil, Dimethomorph and Penconazole, while for S-metolachlor and Metalaxyl – M, analyzed in the present study, the enantiomers Metalaxyl and Metolachlor were searched in Spanish groundwater. Metalaxyl, Penconazole, Dimethomorph and Metolachlor were found in 50%, 46%, <5% and <15%, respectively, of Spanish groundwater samples, with the highest concentration of Metalaxyl and Penconazole equal to 8.015 μg/L and 18.72 μg/L, respectively. Similarly, in the present study Metalaxyl-M and Penconazole show the highest presence (Fig. 4), with maximum concentrations equal to 7.85 μg/L (July 2018) and 6.21 μg/L (November 2017), respectively.

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

3.3 Statistical analysis

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

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

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

[1] the values reported are in $\log_e$

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

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

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

[1] the values reported are in $\log_e$

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

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

Furthermore, the most influencing variable was the sampling time (Tables 3 and 4). Indeed, the concentration of the fungicide Metalaxyl-M was significantly higher in July 2018, whereas those of Penconazole and S-Metolachlor were significantly higher in November 2017 ($P < 0.05$). Metalaxyl-M is a fungicide used against downy mildew, with the most treatments before July (expert statement). Hence, sampling the water in July may have influenced its occurrence and concentration in groundwater. This is in accordance with its physicochemical properties, as it is not persistent in the soil and it has a low leaching potential (GUS = 1.71). Furthermore, the wells location slightly affects the contamination of groundwater from Metalaxyl-M (P = 0.1), with higher concentration in the upstream wells. Therefore, this may indicate a possible point source contamination of wells by Metalaxyl-M. Indeed, Suciu et al. 2020 in the study on territorial hydrology of a sub-area of 7 km2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25), show that the contamination of upstream wells (ex: WP25, WP26) is mainly due to point contamination sources, as water movement in the period November 2017 – November 2018 was very low.

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

The concentration of the herbicide S-metolachlor decreases significantly over time, 0.01 µg/L in November 2017, 0.007 in July 2018 and 0.0008 in September 2018. S-metolachlor is an herbicide not authorized for the use in grapevine cultivation and its occurrence was in wells where the territory is used also for cereals cultivation. Furthermore, the concentration of S-metolachlor increased in the wells with a slope of type 1 (0-3 °) and located downstream, and decreased in the wells with a slope of type 2 (>3 °) and located upstream (P<

0.05 slope x stream). This is in accordance with the upstream-downstream approach, even if S-metolachlor is characterized by a low GUS index (1.91) and its leaching to groundwater is unlikely.

4. Conclusions

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

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

ANOVA statistical analysis revealed significant influence of the sampling time, the slope of the soil surrounding the wells, the wells depth and the location of the wells (upstream vs downstream) on the concentration of five of the fifteen PPPs monitored. Furthermore, study of territorial hydrology for a sub-area of 7 km2 and containing six of the twenty-six wells (WP 32, WP 13, WP 28, WP 11, WP 26 and WP 25) (Suciu et al.2020) helped to discriminate which of the two between point and diffuse contamination sources was more influent, in some cases, although additional information about farmers' practices are necessary to fully understand the actual contamination pathway(s). In conclusion, intensive viticulture may affect groundwater quality, thus suggesting the need for an urgent introduction of the best management practices and mitigation measures for a sustainable use of PPPs to enhance groundwater governance and ensure good groundwater quality (Calliera et al. 2020).

Supplementary material

S.1 Development of priority list of PPPs

S.1 Untargeted analysis

In order to investigate the presence of chemical substances in groundwater and obtain a general picture of land use, an untargeted analysis on groundwater samples was performed.

Aliquots of 60 mL of each sample were lyophilized, dissolved in 1.5 mL of methanol: water (1:1 V/V) and then transferred in amber glass vials for analysis. A High-resolution mass spectrometry (MS) analysis was performed using a hybrid quadrupole-time-of-flight instrument, coupled to an UHPLC chromatograph (UHPLC-ESI/QTOF-MS) to investigate chemicals occurrence in groundwater. In more detail, a 1290 liquid chromatograph system, equipped with a binary pump, degasser, thermostatted column compartment and a Dual Electrospray JetStream ionization system was coupled to a 6550 mass spectrometer detector (all from Agilent Technologies, Palo alto, CA), was used. Reverse phase chromatographic separation was achieved using an Agilent Zorbax eclipse plus C18 column (50 × 2.1 mm, 1.8 μm) and under a water-methanol binary gradient elution (from 5% to 90% organic in 34 min), as previously reported (Rocchetti et al., 2018). Injection volume was 20 μL, and electrospray source conditions were set up for untargeted screening purposes (Storck et al., 2016).

The mass spectrometer was operated in positive polarity, with a scan rate of 1 Hz, a mass range of 70-1000 m/z, and a nominal mass resolution of 30.000 FWHM. An absolute peak height threshold of 3000 counts was also adopted. The All-Ions acquisition algorithm, a tandem mass acquisition according to which no precursor's selection is adopted and all ions in the scan are fragmented, was used. Such data-independent approach used MS-only data and tandem MS fragmentation at three distinct collision energies (10, 20 and 40 V) to achieve a higher confidence of identification. The raw data were processed using the Mass Hunter B.05 software (Agilent technologies) and the find-by-formula algorithm, thus combining monoisotopic accurate mass and isotopic profiling for features deconvolution. The Pesticide Personal Compounds Database and Library B.04 (Agilent technologies), a commercially available library that includes MS and tandem MS data for pesticides and their metabolites, was used as reference. Candidates selected from MS data were then confirmed using MS/MS data, thus using fragments information from the library and matching elution profile of precursor and fragment ions through a chromatographic co-elution score. A minimum of three co-eluting fragments was used for confirmation.

S.2 Targeted multi-residue analysis

S.2.1 Extraction set up

The recovery tests have been performed in order to evaluate the accuracy and precision of the method. For the extraction of PPPs from groundwater samples, several types of cartridges and absorbents have been chosen based on the characteristics and properties of selected PPPs and literature research. SPE cartridges used for the recovery tests were Oasis HLB, Bond Elut ENV, Bond Elut PPL and C18. Oasis hydrophilic lipophilic balance® (HLB) is one of the more widely used sorbents in SPE and passive sampling applications. The HLB polymer, poly(N-vinylpyrrolidone-divinylbenzene), contains apolar (i.e., benzene and aliphatic chains) as well as polar (i.e., pyrrolidone) regions. This leads to a good water wettability and an increased ability to interact with both apolar and polar organic molecules (Jeong et al., 2017). The Oasis HLB is used for the extraction of a wide range of acidic, basic and neutral compounds. The Bond Elut ENV cartridge is packed with modified styrene-divinylbenzene polymers and can retain hydrophilic and polar organic compounds (Tang et al., 2016). The absorbent of Bond Elut PPL cartridge is a styrene-divinylbenzene polymer modified with a non-polar surface and it is able to retain the most polar classes of analytes, including phenols; the large particle size allows easy fluidity for samples of viscous or particulate rich water, while the high surface area and strong hydrophobicity ensure reproducible extractions with high recoveries at the time of the elution (Zherebker et al., 2015). The C18 cartridge based on octadecylsilyl absorbent represents the most hydrophobic silicone sorbent and it retains most of the organic analytes from aqueous matrices (Fu, 2008); it consists of a chain of eighteen carbons.

SPE extraction was performed by use of 5 mL of methanol and 5 mL of Milli-Q water for the conditioning of all cartridges. The recovery tests were carried out using both groundwater sampled in the Action lab area and tap water in order to evaluate possible matrix effects, at spiking level of 0.1µg/L. Since no significant differences have been observed, other two additional spiking levels, 0.5 and 1 µg/L, were used for recovery tests just with tap water. Then, 1000 and 500 mL of water were passed through the conditioned cartridges at a flow rate of approximately 8 mL min^{-1} under vacuum. The cartridges were then washed with a 2.5 mL of ultra-pure water and dried for 1 h under vacuum. The analytes were eluted from the solid phase by use of three different solvents based on the cartridges characteristics: methanol, methanol: acetonitrile (1:1 V/V) and hexane. A blank sample of tap water was always used during samples extraction as control. The results obtained for these trials were then used to optimize the final extraction method.

S.2.2 High Performance Liquid Chromatography-tandem mass spectrometry

A 1200 series liquid chromatograph system was used, equipped with quaternary pump, electrospray ionization system and coupled to a G6410A triple quadrupole mass spectrometer detector (all from Agilent technologies, Santa Clara, CA, USA) (Lucini et al., 2015).

The chromatographic separation was performed with an EC-C18 column (2.1 x 50 mm, 5 µm, Agilent technologies, Milan, Italy) connected to a 6410 triple quadrupole mass spectrometer, equipped with an Electron Spray Ionization (ESI) source operated in positive mode and multiple reaction monitoring (MRM). Injection volume was 20 µL, run time was 30 min and the flow rate was 0.2 mL/min. The mobile phases were ultra-pure water with 0.1% formic acid (phase A) and 0.1% formic acid in methanol (phase B). The gradient of solvent B was set up as follows: 0–5 min from 75 to 80%, 5-7 min from 80 to 85%, 7-23 min from 85 to 90% and finally 23-30 min at 75%. A post run of one minute was set up. The stop time selected was 30 min.

Individual standards of each pesticide solution at a concentration level of 5 mg L^{-1} were injected in HPLC-MS/MS in order to register the transitions in multiple reaction monitoring mode (MRM).

The transitions in MRM mode, the collision energies expressed in Volt and the retention time registered for each compound are showed in the Table 1S.

Table 1S. Multiple reaction monitoring (MRM) conditions in HPLC–MS/MS and the retention times (RTs)

Compound name	**Precursor Ion**	**Product Ions**	**Collision energy (V)**	**RT (min)**
Chlorpiriphos	352	200	15	23.9
		125		
Chlorpiriphos-methyl	323.9	291.8	10	19
		124.9		
Chlorantraniliprole	484	453	15	9
		286		
Cyflufenamid	413.1	295.2	15	17
		241.1		
		223.1		
Cyprodinil	226	118	35	15
		108		
		93		
Dimetomorph	388.2	301	25	11
		165		
Flufenacet	364.1	194.2	10	13
		152.1		
Fluopicolide	383	173	15	11
Isopropalin	310.2	226.1	20	27
		208.1		
Metalaxyl-M	280.2	220.1	10	8.8
		192.1		
Metsulfuron-methyl	382.1	167.1	10	6.8
S-metolachlor	284.2	252.2	10	15
Penconazole	284.1	173	20	16
		158.9		
Tetraconazole	372.1	159	25	13
Tribenuron-methyl	396.1	155.1	10	8.1

S.2.3 Method validation

The proposed method was validated by evaluating parameters as linearity, matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability). The linearity was evaluated through the coefficient of determination (R^2) of the analytical curves at concentration levels between 1 and 2500 µg L^{-1}. The solutions for the analytical curves were prepared in methanol. Matrix effect was calculated comparing the slope of curves prepared in solvent and in the blank extract. Precision was evaluated regarding repeatability and intermediate precision by estimating the relative standard deviation (RSD) of the recovery percentage for each spiked level. The LOD and LOQ were calculated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1.

S.2.4 Optimization of SPE and HPLC-MS/MS method

Different sample volumes and sorbents were evaluated based on the characteristics of the selected PPPs. Four SPE columns with different adsorbent including n-vinilpirrolidone-divinilbenzene (HLB), polystyrene-divinylbenzene (ENV), styrene-divinylbenzene polymer modified with a non-polar surface (PPL) and octadecylsilyl (C18) were tested.

The SPE PPL cartridge (styrene-divinylbenzene) and the use of methanol for the elution of the analytes, showed the highest recovery rates ranging from 41% to 103%. Therefore the following optimized SPE method was used for the selected pesticides in groundwater samples: Bond Elut PPL cartridges were conditioned with 5 mL of methanol, followed by 5 mL of ultra-pure water Milli-Q at a flow rate of 2,5 ml min^{-1}, without allowing the cartridge to dry out. Then, 500 mL of groundwater samples were passed through the conditioned cartridges at a flow rate of approximately 8 mL min^{-1} under vacuum. The cartridges were firstly washed with a 2.5 mL of ultra-pure water and dried for 1 h under vacuum. Afterwards the analytes were eluted from the solid phase with 5 mL of methanol. The extracts were then evaporated to dryness under a stream of nitrogen and the residues were dissolved in 0.2 mL of methanol for HPLC-MS/MS analysis.

For validation and quantitation purposes, additional recovery studies were carried out by adding a mix of analytes standard solutions in 1000 and 500 mL of tap water and groundwater, obtaining the following final concentration levels: 0.1, 0.5, 0.75, 1, 2.5 mg L^{-1}. Each sample was extracted in triplicate.

The limit of quantification (LOQ), ranging from 0.0008 to 0.02 µg L^{-1}, was found for the 15 compounds, under the optimized experimental conditions, and were below the environmental quality standard (EQS) imposed by the legislation for groundwater (Table 2S).

According to the results, a volume of 500 mL was considered sufficient for PPPs detection under level required by the legislation (0.1 µg/L). Additionally, it was observed that extraction efficiency increases when adding few drops of formic acid in each sample flask. Methanol proved to be the best solvent for the final suspension of the extracts compared to a mixture of methanol:acetonitrile solution (1:1) and to hexane. Concerning the HPLC-MS/MS method, technical parameters, flow and gradients percentage were optimized for a better resolution of the chromatographic peaks.

For each pesticide two transitions were obtained, exept for Cyflufenamid and Cyprodinil for which three transitions were acquired. The collision energy was between 10 and 25.. The method was optimized testing several gradient percentages of mobile phases and different run times. The final run time selected was 30 min. A post run of one minute was set up.

Table 2S. Limit of Quantification and R^2 obtained for each pesticide

Pesticide	**LOQ (µg L^{-1})**	**Linearity (R^2)**
Chlorpiriphos	0.02	0.95
Chlorpiriphos-methyl	0.02	0.96
Chlorantraniliprole	0.02	0.97
Cyflufenamid	0.004	0.97
Cyprodinyl	0.02	0.98
Dimetomorph	0.02	0.98
Flufenacet	0.02	0.97
Fluopicolide	0.02	0.99
Isopropalin	0.02	0.99
Metalaxyl-m	0.0008	0.99
Metsulfuron-methyl	0.0008	0.99
S-metolachlor	0.004	0.99
Penconazole	0.004	0.96
Tetraconazole	0.02	0.98
Tribenuron-methyl	0.02	0.99

S.2.5 Results of recovery tests

Table 3S shows the results of the recovery test averages and the respective standard deviation obtained for each cartridge and pesticide, expressed as percentage.

Table 3S. Recovery percentage average of PPPs for each SPE cartridge

Pesticide	**HLB**	**ENV**	**PPL**	**C18**
Chlorpyrifos	63 ± 4.4^{a}	24 ± 24^{ab}	65 ± 3.4^{a}	45 ± 0.7^{b}
Chlorpyrifos-methyl	44 ± 10.3^{ac}	13 ± 12.5^{bc}	43 ± 4.6^{ab}	23 ± 0.4^{c}
Chlorantraniliprole	64 ± 1.6^{a}	58 ± 1.6^{a}	68 ± 2.1^{a}	5 ± 0.7^{b}
Cyflufenamid	45 ± 10.6^{b}	113 ± 41.5^{a}	56 ± 2.7^{a}	0 ± 0^{c}
Cyprodinil	35 ± 1^{a}	26 ± 26.4^{ab}	70 ± 2.7^{a}	14 ± 1.5^{b}
Dimetomorph	46 ± 13.3^{a}	19 ± 19.3^{ab}	42 ± 0.05^{a}	0 ± 0^{b}
Flufenacet	117 ± 12.7^{a}	68 ± 27.6^{abc}	45 ± 2^{b}	0.1 ± 0.1^{c}
Fluopicolide	40 ± 2.1^{a}	34 ± 5.4^{a}	48 ± 4.6^{a}	0 ± 0^{b}
Isopropalin	0 ± 0^{b}	0 ± 0^{b}	41 ± 4^{a}	0 ± 0^{b}
Metalaxyl-m	56 ± 1^{a}	55 ± 1.5^{a}	63 ± 3.6^{a}	0 ± 0^{b}
Metsulfuron-methyl	51 ± 3.9^{a}	82 ± 18.5^{ab}	68 ± 1.7^{ab}	42 ± 2.1^{b}
S-metolachlor	61 ± 4.9^{a}	39 ± 17.5^{ab}	51 ± 6.2^{a}	0 ± 0^{b}
Penconazole	89 ± 4.5^{a}	63 ± 13.4^{ab}	76 ± 2.7^{b}	19 ± 0.7^{c}
Tetraconazole	82 ± 2.3^{a}	56 ± 12.5^{ab}	52 ± 3.2^{b}	0 ± 0^{c}
Tribenuron-methyl	76 ± 3.4^{a}	88 ± 0.7^{a}	72 ± 12.9^{a}	28 ± 2.6^{b}

Note: the letter “a”, indicated at the apex of each value, suggests the highest average value and if there is no significantly difference among the cartridges the letters indicated are equal, on the contrary, if the letters are different, this means there is a significantly difference.

The one way ANOVA, performed taking into consideration a P value of ≤ 0.05, shows that at least one of the calculated percentage averages was significantly different from the other. The *student t* was then performed for each pesticide in order to determinate which cartridge had the highest recovery percentage. Table 3S shows an average of the total recovery tests carried out. The cartridge C18 revealed to be the worst filter because seven compounds were not recovered. The cause can be attributed to the lack of affinity for pesticides under study and therefore to absorbent phase.

Based on the statistical analysis the *Bond Elut PPL* was the cartridge with an accettable performance for most of thepesticides selected and the only one able to recover Isopropalin, Additional recovery tests were further carried out in triplicate by use of PPL cartridge and adding a concentration equal to the EQS limit of 0.1 µg L^{-1} in 500 mL of tap water.

S.2.6 Priority list of PPPs

Table 4S. List of chemicals and their properties found by the untargeted analysis carried out on the groundwater samples

Compound name	**Type**	**GUS index**[1]	**K_{oc}**[1]	**DT50**[1]	**Water solubility**[1]
2,3,5-Trimethacarb (Landrin)	Insecticide	2.49	400	50	58
Ascaridole	Anthelmintic in veterinary medicine	-	-	-	-
Atrazine-2-ethylamino	Atrazine metabolite	-	-	-	-
BTS 27919 (N-(2,4-dimethylphenyl)formamide)	Amitraz metabolite	-	-	-	-
Butyl paraben	Generic preservative	-	-	-	-
Chlorantraniliprole	Insecticide	4.22	362	204	0.88
DEET (Diethyltoluamide)	Insecticide	-	277	-	912
Defenuron	Herbicide	-	-	-	-
Dimetan	Insecticide (revoked)	-	-	-	-
Dimethirimol	Fungicide	4.25	90	120[2]	1200
Dimetomorph	Fungicide	2.56	348	44	28.95
Fluopicolide	Fungicide	3.63	321.1	271	2.8
Formetanate	Insecticide				
Glufosinate	Herbicide	-	-	-	-
Isopamphos	Fungicide				
Isopropalin	Herbicide	0.00	10000	100	0.11
Metalaxyl-m	Fungicide	1.71	78.9	14.1	26000
Metaldehyde	Molluscicide	1.5	240	5.1[2]	188
Nitrophenol, 4-	Intermediate of generic synthesis	-	-	-	-
Pindone (Pival)	Rodenticide	-	-	-	18
Pirimicarb	Insecticide	2.63	388	9	3100
Pirimicarb, desmethyl	Pirimicarb metabolite	-	-	-	-
Pirimicarb-desmethyl-formamide	Pirimicarb metabolite	-	-	-	-
p-Nonylphenol (4-Nonylphenol)	Surfactant	-	-	-	-
Salbutamol (Albuterol)	Bronchodilator drug	-	-	-	-
Terbutaline	Bronchodilator drug	-	-	-	-
Trimethacarb	Insecticide	2.49	400	50	58

[1] Lewis K.A., Tzilivakis, J., Warner, D. and Green (2016) An international database for pesticide risk assessments and management. International Journal of Human and Ecological Risk Assessment; [2]Typical value

Table 4S shows that fourteen PPPs were detected in the groundwater samples: five insecticides (Chlorantraniliprole, DEET, Dimetan, Pirimicarb, Trimethacarb), three herbicides (Defenuron, Glufosinate, Isopropalin) and five fungicides (Dimethirimol, Dimetomorph, Fluopicolide, Isopamphos, Metalaxyl-m). Among the insecticides and the herbicides found, three result revoked: DEET (Diethyltoluamide), Dimetan and Isopropanil, but the latter was taken into consideration for the pesticides list because it was declared to be used by farmers (see Table 5S).

Table 5S. List of PPPs and their properties with high interest for stakeholders

Compound name	**Type**	**GUS index**[1]	**K_{oc}**[1]	**DT50**[1]	**Water solubility**[1]
Acetolachlor	Herbicide	1.58	156	12.1	282
Benomyl	Fungicide	-0.07	1900	67[2]	2
Chlorantraniliprole	Insecticide	4.22	362	204	0.88
Flufenacet	Herbicide	2.02	401	19.7	51
Fluopicolide	Fungicide	3.63	321.1	138.8	2.8
Isopropalin	Herbicide	0.00	10000	100	0.11
Metsulfuron-methyl	Herbicide	3.99	12	13.3	2790
Parathion-methyl	Insecticide	1.46	240	10	55
S-metolachlor	Herbicide	1.91	226.1	21	480
Terbuthylazine	Herbicide	3.04	231	21.8	6.6
Tribenuron-methyl	Herbicide	2.4	35	3.6	2480

[1] Lewis K.A., Tzilivakis, J., Warner, D. and Green (2016) An international database for pesticide risk assessments and management. International Journal of Human and Ecological Risk Assessment; [2]Typical value

Table 6S. List of PPPs and their properties with intensive uses in the investigated area

Compound name	Type	GUS index[1]	K_{oc}[1]	DT50[1]	Water solubility[1]
Chlorpyrifos	Insecticide	1.04	5509	27.6	1.05
Chlorpyrifos-methyl	Insecticide	0.92	4645	12	2.74
Cyflufenamid	Fungicide	1.85	1592	25.3	0.52
Cyprodinil	Fungicide	1.11	2277	45	13
Mancozeb	Fungicide	-1.45	998	0.05[2]	6.2
Metiram	Fungicide	-0.22	500000	7	2
Penconazole	Fungicide	1.36	2205	90	73
Tetraconazole	Fungicide	1.81	1152	430	156.6
Thiamethoxam	Insecticide	4.69	56.2	39	4100

[1] Lewis K.A., Tzilivakis, J., Warner, D. and Green (2016) An international database for pesticide risk assessments and management. International Journal of Human and Ecological Risk Assessment; [2]Typical value

The outcomes of stakeholders and expert judgement consultation produced the above lists of PPPs (Table 5S and Table 6S) for which our stakeholders show a high interest and have an intensive uses in the investigated area.

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Chapter 2.2

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

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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, sub-surface 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 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 organized with the farmers of the entire Valley in order to show its functionality and promote its diffuse use.

Keywords

Pesticides, Vineyards, Tidone Valley, Groundwater monitoring, Stakeholder involvement, Best management practices

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

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 meter 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^{-1} were detected for 37 of the 47 compounds studied, and in several cases recorded values of over 18 µg L^{-1}. 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^{-1}. 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 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 characterized 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/).

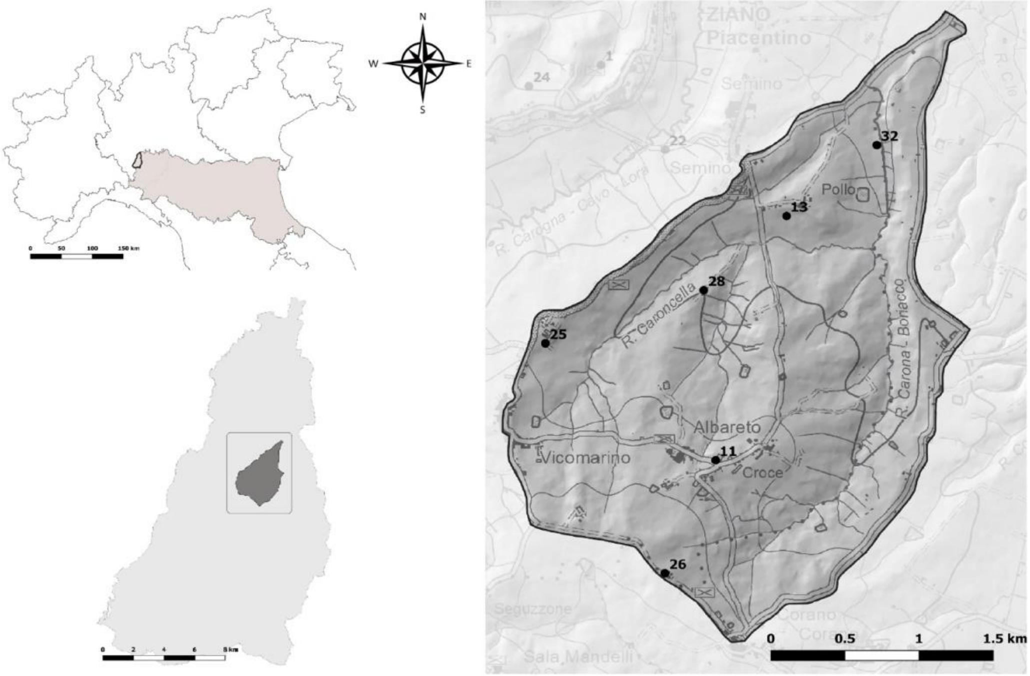
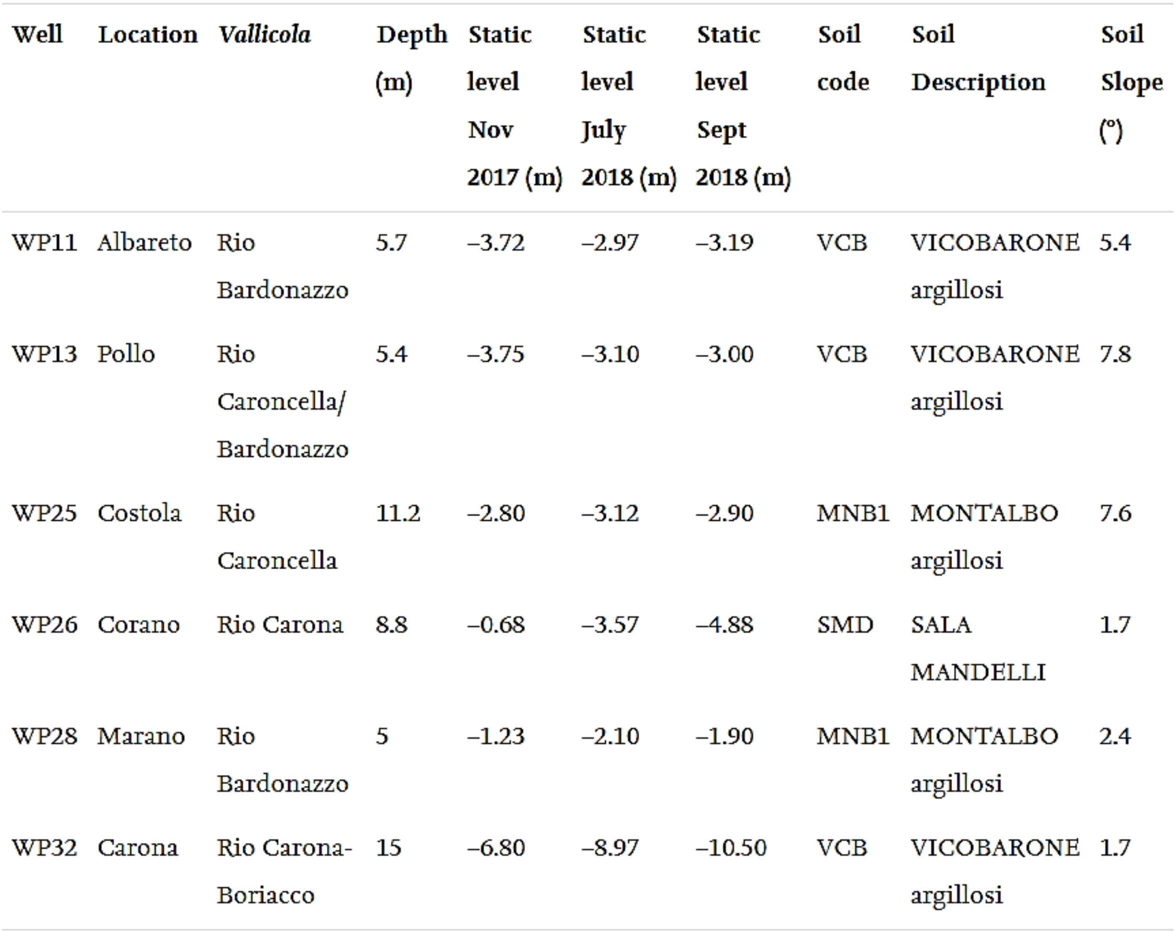


Fig 1. Study area, as sub-area of the WaterProtect Action Lab (described by Zambito Marsala et al., 2020), located in Emilia - Romagna Region, north-west of Italy.

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

2.2 Stakeholders involvement

As stated by Zambito 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 farmers' 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).

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) 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, 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).

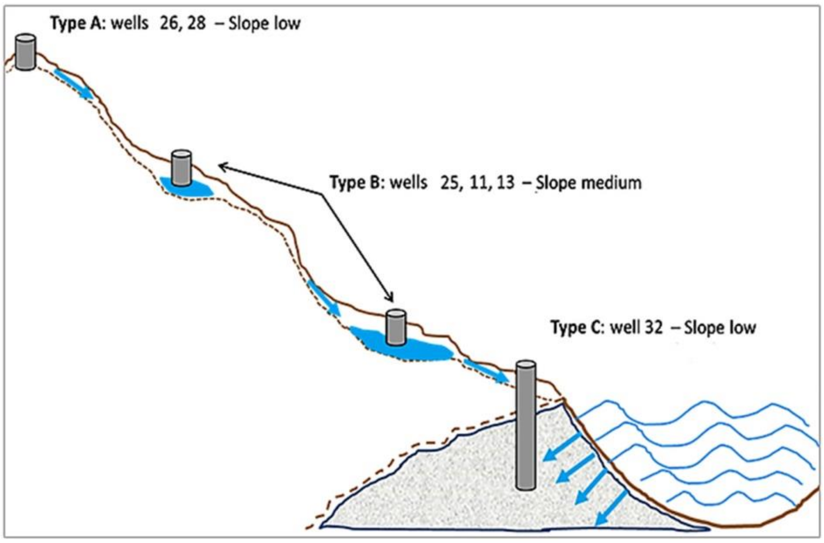


Fig 2. Conceptual model of shallow aquifer (CMA)

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 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.

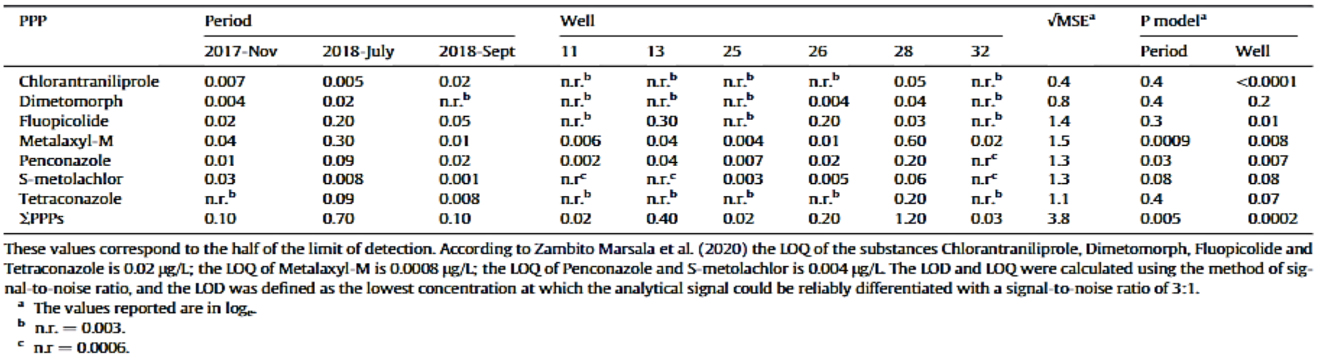
CRITERIA-3D has already been coupled in previous works with phenology and plant growth models specific for grapevine (Bois et al., 2014). The phenology models (Bindi et al., 1997; Caffarra and Eccel, 2011) simulate the main development stages for grapevine and are computed at a daily time step. Plant 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 sub-surface 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 characterized 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).

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. 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) 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).

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.

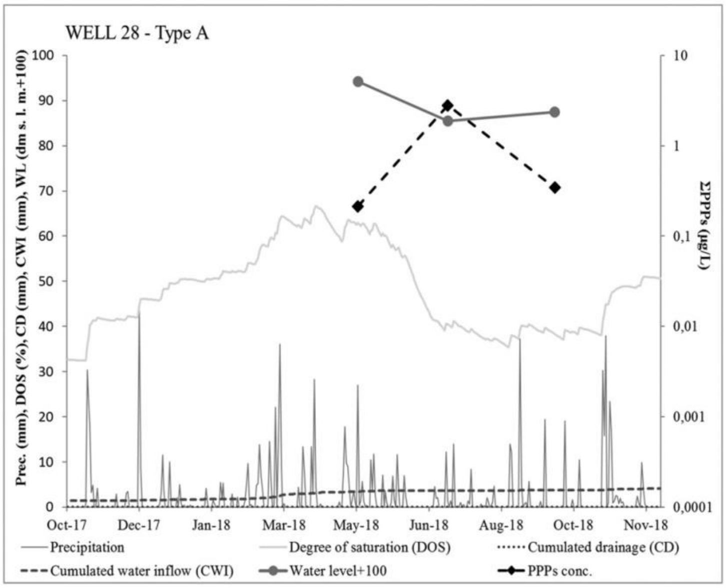
3.2 Groundwater monitoring

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 characterized 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 Ogdan (2010), Croghan et al. (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 below 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 favor 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 Fig. 3, Fig. 4, Fig. 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).

a



b

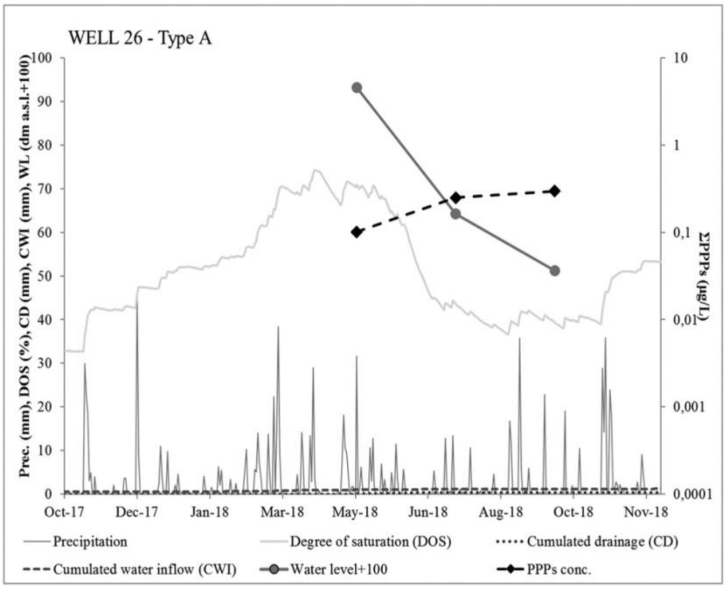


Fig 3. Integration of modelling outputs with precipitation data and PPPs concentration in wells of type “A”; a) well WP 26 and b) well WP 28.

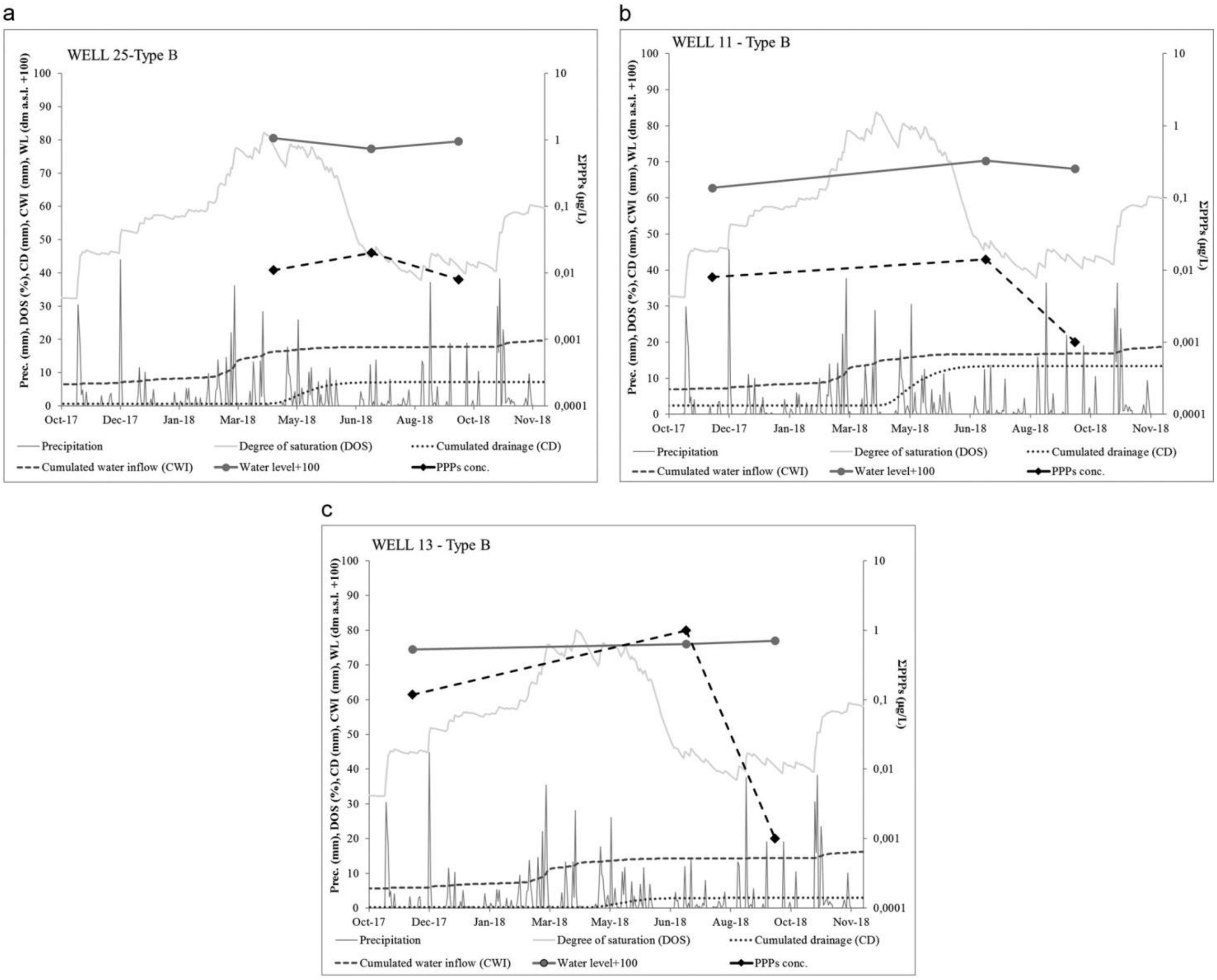


Fig 4. Integration of modelling outputs with precipitation data and PPPs concentration in wells of type “B”;

a) well WP 25, b) well WP 11 and c) well WP 13

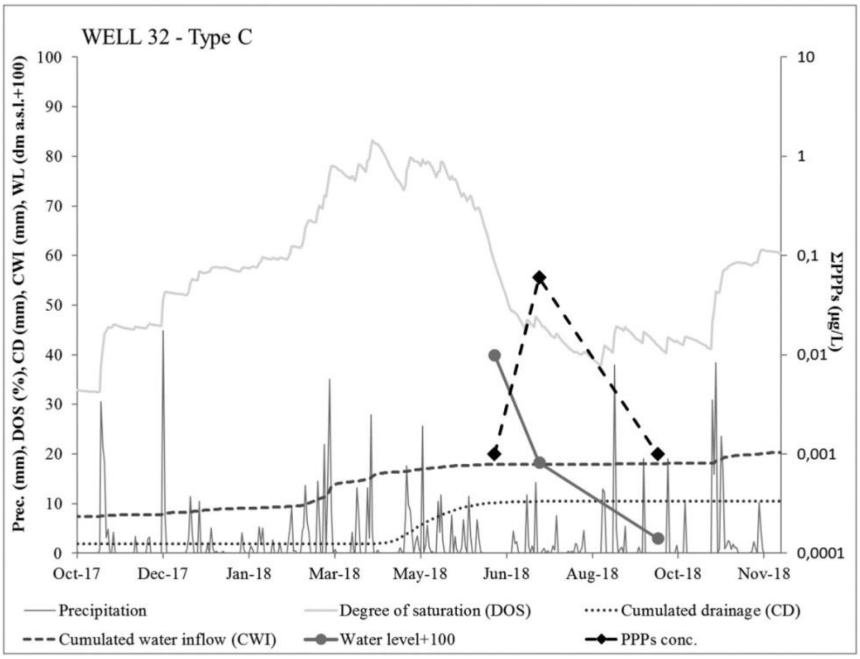


Fig 5. Integration of modelling outputs with precipitation data and PPPs concentration in well 32, type "C"

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 - 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, 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 utilized 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 organized 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.

Supplementary material

Table S1. Soil characteristics used for CRITERIA 3 D simulations.

Soil code	**Horizon nr**	**Upper depth [cm]**	**Lower depth [cm]**	**Gravel[1] [%]**	**Organic matter [%]**	**Sand[2] [%]**	**Silt[2] [%]**	**Clay[2] [%]**
MNB1	1	0	20	0	1.1	15	29	56
MNB1	2	20	80	45	0.5	24	28	48
MNB1	3	80	110	45	0.6	23	30	47
MNB1	4	110	160	45	0.5	14	36	50
VCB	1	0	30	0	2.8	8	51	41
VCB	2	30	60	0	1	12	29	59
VCB	3	60	80	0	0.7	9	37	54
VCB	4	80	140	0	0.3	21	42	37
SMD	1	0	25	0	1.5	20	35	45
SMD	2	25	70	3	0.6	24	40	36
SMD	3	70	110	20	0.4	14	52	34
SMD	4	110	160	20	0.4	31	35	34

1. Particles > 2 mm.
2. Percentages refer to soil texture only (particles < 2 mm).

Table S2**.** Soil texture parameters used for CRITERIA 3 D simulations.

Soil texture	**Alpha [kPa^{-1}]**	**n [-]**	**Air entry [kPa]**	**Theta r [m^3 m^{-3}]**	**Theta sat [m^3 m^{-3}]**	**K sat [cm day^{-1}]**
clay	0.17	1.20	0.33	0.04	0.48	1.2
silty clay loam	0.14	1.20	0.31	0.03	0.46	2.4
clay loam	0.19	1.20	0.27	0.03	0.45	4.8
sandy clay	0.22	1.20	0.25	0.03	0.43	4.8
silty clay	0.18	1.20	0.33	0.04	0.47	2.4
sand	0.50	1.70	0.07	0.01	0.38	192
loamy sand	0.40	1.50	0.10	0.01	0.39	96
sandy loam	0.30	1.40	0.15	0.02	0.40	48
silt loam	0.14	1.20	0.26	0.03	0.44	9.6
loam	0.18	1.21	0.23	0.03	0.42	12
silt	0.10	1.24	0.27	0.03	0.44	2.4
sandy clay loam	0.23	1.22	0.20	0.03	0.41	12

Note: Water retention & water conductivity model was developed based on Van Genuchten-Mualem model (modified by Ippisch et al. 2006)

Table S3. Grapevine parameters used for CRITERIA 3 D simulations.

Parameters		**Units**
cultivar	default (Chardonnay)	
radiation_use_efficiency	1	g MJ^{-1}
bindi_d	0,000539	m^2
bindi_f	2,06	-
fruit_biomass_offset	0,04	-
fruit_biomass_slope	0,00328	day^{-1}
hydrall_psileaf	1800	kPa
hydrall_stress_threshold	0,4	-
hydrall_vpd	1300	Pa
hydrall_alpha_leuning	10	-
hydrall_carbox_rate	115	umol m^{-2} s^{-1}
phenovitis_force_physiol_maturity	95.7	-
phenovitis_ecodormancy	176.2	-
phenovitis_critical_chilling	78.7	-
phenovitis_force_flowering	24.7	-
phenovitis_force_veraison	75.9	-
phenovitis_force_fruitset	34.7	-
degree_days_veraison	2547	°D

Note: The development model is based on Bindi et al, (1997) the growth & transpiration model is based on HYDRALL model (Magnani et al.2009) and phenology model is based on PHENOVITIS model (Caffarra & Eccel, 2011).

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Chapter 3

Influence of nitrogen-based fertilization on nitrates occurrence in groundwater of hilly vineyards

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Abstract

Nitrogen losses from intensive agricultural production may end up as high nitrate (NO_3^-) concentrations in groundwater, with a long-term impact on groundwater quality. The main objective of this study was to evaluate the impact of fertilization practices used for grape cultivation on groundwater quality of Tidone Valley, northwest of Italy, following an integrated socio-hydrogeological approach that consists on (i) the involvement of 175 farmers in the description of agricultural and fertilization practices, using a survey of *ad hoc* questionnaires, (ii) the evaluation of NO_3^- occurrence in groundwater and (iii) the identification of NO_3^- sources through isotopic and hydrochemical analysis. In this area, as for certain particular Apennines shallow aquifers, groundwater is of reduced interest due to its limited storage capacity and there are insufficient wells currently monitored by the local Environmental Agency (ARPAE) to evaluate the impact of agricultural fertilization on existing local aquifers. Farmers' questionnaires results highlighted an extensive use of inorganic nitrogen fertilization and a tendency of farmers to follow their own experience for fertilization. Chemical analyses revealed high variability of major and trace elements concentrations isotope data. NO_3^- concentrations were significantly higher in deeper wells with respects to shallow wells. Isotopic results indicated that groundwater NO_3^- origin is inorganic, in agreement with the land use and the declared viticultural practices. Comparing groundwater NO_3^- occurrence from the studied area with values of entire Emilia-Romagna Region, only 7.7 % of groundwater samples showed values above the EQS (50 mg NO_3^-/L) between Nov 2017 and Sept 2018, while in the entire region 11.5 % of groundwater samples showed values above the EQS in the same period. Considering that the vineyards surface in the studied area represents almost 75 % of the entire regional vineyard surface, the obtained results suggest a low to moderate impact of viticulture on NO_3^-concentration of regional groundwater.

Keywords

Nitrogen and oxygen isotope data, Tidone Valley, Agriculture, Socio-hydrogeology

Abbreviations

ANHI Agricultural Nitrate Hazard Index

ARPAE	Regional Agency for Prevention, Environment and Energy
BMP	Best Management Practices
CAP	Common Agriculture Policy
EQS	Environmental Quality Standard
GLM	Generalized Linear Model
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IRMS	Isotope Ratio Mass Spectrometer
MM	Mitigation measures
NVZ	Nitrate Vulnerable Zone
OES	Optical Emission Spectrometry
PPP	Plant Protection Product
WFD	Water Framework Directive

1. *Introduction*

Today more than half of the world's population depend on agricultural outputs that have been produced applying artificial fertilizers (Hansen et al., 2017). Throughout the world, nitrogen (N) losses from intensive agricultural production may end up as undesirably high nitrate concentrations in groundwater, with a long-term impact on groundwater quality (Bryan et al., 2012; Puig et al. 2017; Hansen et al., 2017; Ahmed et al., 2017). Nitrate occurrence in groundwater represent a big issue because they can persist for decades and accumulate to high levels as more nitrogen is applied to the land surface every year (Nolan et al., 2002). Waters containing high nitrate concentration can lead to health problems both in humans and animals. Nitrate, however, is not directly toxic for humans, but their possible reduction to nitrite (NO_2^-) and a following reaction with secondary or tertiary amines can result in the formation of carcinogenic N-nitrosamines in adults and can produce methahemoglobinemia in infants (Pham et al., 2018). For this reason, since 1998 the Council of European Union, through the Directive 98/83/EC, established a nitrate concentration threshold in drinking water of 50 mg/L. In Italy the implementation of Directive 98/83/EC relating to the quality of water intended for human consumption is made by the Legislative Decree 31/2001. Indeed, in Europe nitrate pollution is still a major threat for groundwater quality as the maximum nitrate concentration allowed for human consumption is exceeded in 18 % of groundwater bodies (EEA, 2018). Besides, about 50 % of drinking water supply at European level, including many large cities, rely on groundwater to fulfil their needs (EEA, 2018).

At European level, the measures taken in the last few decades under the Nitrates Directive (EU, 1991), aimed to protect water quality, have resulted in a reduction in the use of mineral fertilizer, and nutrient surpluses of agricultural origin have progressively decreased in the EU (EEA, 2018). Between 2000 and 2013, agricultural nitrogen surplus decreased by 7 %, while phosphorus surplus decreased by 50 % (EC, 2017). Nevertheless, the overall level of fertilization remains high in parts of Europe. Large variations exist between Member States in nitrogen and phosphorus surplus (Eurostat, 2016) and, on average, fertilizer use has started increasing again in the last few years. Nutrient balances at river basin level are now used in several countries to define nutrient load reduction targets to support the achievement of European Water Framework (Directive (WFD) (EU, 2000) objectives. The WFD aimed to achieve a good chemical status for the groundwater bodies in Europe by the year 2015. Since 2015, every six years new national objectives have to be established and included in the *River Basin Management Plan*. During the last years, Member States have taken measures at national level or at the River Basin level (e.g. general binding rules, taxes, manure surplus management), while other measures are more local (e.g. protection of areas with wells used for drinking water supply). Most of the EU countries developed maps for the "Nitrate Vulnerable Zones" (NVZ), territories that drain into waters and thereby can cause a risk of water pollution by nitrate. Emilia Romagna Region recently issued the new delimitation of the NVZ, adopted with DGR No. 619 (2020), following the infringement procedure on nitrates that involved Italy. Recently, the European Commission presented its legislative proposals on the future of food and farming, i.e. the Common Agriculture Policy (CAP) for the period 2021-27. With its new legislative proposals, the EU Commission is proposing that EU countries introduce a Farm Sustainability Tool for Nutrients for farmers (https://ec.europa.eu/info/food-farming-fisheries/key-policies/common-agricultural-policy/future-cap_en). Such a Nutrient Management Tool should not be based on the quantity of nutrients applied, but rather on the nutrient use efficiency. Therefore, the CAP post-2020 must promote knowledge-intensive farming and tap into the potential of the increasing amount of data available, in order to enable all types of farmers in Europe to become more competitive and have a better environmental performance at the same time. Furthermore, involving the local farmers in the water governance process is increasingly seen as a way of strengthening the likelihood of implementing more effective management practices for water protection.

Indeed, sustainable agriculture is the result of complex "systemic interactions" between different subjects involved in various ways, such as researchers, farmers, entrepreneurs, regional and national organizations etc. All of them have different forms of knowledge (practical, scientific, policy based, etc.) and there is the need to create conditions for interaction between them combining their knowledge, perspectives, resources, and experiences, to identify and discuss solutions and new ideas (Calliera et al., 2020). It is obviously challenging to identify the most effective approach, but one of the key elements is to ensure that groundwater management strategies are based on a full understanding of local peculiarities and needs. Indeed, adopting a more holistic approach by combining geosciences and social sciences clearly facilitates the assessment of the relations between groundwater and society (Re, 2015).

A full understanding of the natural concentration, identification of pollution sources and biogeochemical transformation of nitrate are important for a successful groundwater management strategy (Kim et al., 2015; Elisante et al., 2017). The occurrence of nitrate in groundwater may be affected by considerable temporal variations, depending on precipitation, hydrogeological conditions and land-use (Capri et al. 2009, Menciò et al., 2011, Groenendijk et al. 2014). Several studies report the development and successful use of parametric approaches, as the Agricultural Nitrate Hazard Index (ANHI), to assess potential risk of nitrate contamination in groundwater (Padovani and Trevisan, 2000; Capri et al. 2009).

The inflow of N into groundwater in agricultural areas can be attributed to multiple sources such as organic and inorganic fertilizers, manure, soil organic N, sewage (e.g. septic wastewater), and atmospheric precipitations (Kaushal et al., 2011; Biddau et al., 2019). N originating from each source is characterized with distinct ranges of ^{15}N-NO$_3$ isotopic values, which can be used to determine its origin, and to estimate to some extent the relative contribution of the different NO_3^- sources (Nikolenko et al., 2018; Valiente et al., 2018; Chae et al., 2009). The organic and inorganic fertilizers, indeed, are characterized by different isotopic signatures, which is explained by their production processes. According to Nikolenko et al. (2018), the lowest values of δ^{15}N-NO_3^- are typical for inorganic fertilizers, followed by NO_3^- derived from soil organic matter, while the highest values are usually related to the impact of manure and/or wastewater.

In a study conducted by Martinelli et al., (2018) on nitrate impact in the Po Plain area, northwest of Italy, manure represents one of the main nitrate sources in groundwater from agriculture, the other being synthetic fertilizers. This is in agreement with data reported by Viaroli et al. (2018) in a work on space and time variations of watershed N and P budgets in the Po River basin. In the northwest of Emilia Romagna Region (province of Piacenza), part of Po River basin, monitoring studies of groundwater of three small catchments, in an area known as Tidone Valley and characterized by intensive viticulture, show nitrate concentrations that exceed the threshold of 50 mg/L (ARPAE, 2017). Furthermore, ISTAT data reports an increase of 45 % in the period 2012-2017 with respect to 2007-2011s (https://webbook.arpae.it/indicatore/Uso-di-fertilizzanti-00001/?espandi=grafici) of synthetic nitrogenous fertilizers and organic manure use in Emilia Romagna Region. However, the existing monitoring network, of the local Environmental Agency, did not allow to adequately evaluate the local stressors due to a limited and unsuitable number of groundwater wells.

In this context, the main objective of this study, part of the EU H2020 WaterProtect Project, is to evaluate the impact of fertilization practices used for grape cultivation on groundwater quality of Tidone Valley, in the northwestern part of Italy, following an integrated socio-hydrogeological approach that consists in (i) the involvement of all stakeholders in the farmers engagement for the description of agricultural and fertilization practices, (ii) evaluation of NO_3^- occurrences in groundwater and the (iii) identification of NO_3^- sources through isotopic and hydrochemical analysis. The present study is the first of its kind in the study area, on one side there is a lack of previous studies since shallow groundwater in the Apennines is not an important resource due to the limited storage capacity, and on the other side, the stakeholder involvement in the investigation, known as socio-hydrogeological approach (Re, 2015), was not been carried out before to the authors knowledge.

2. *Materials and methods*

2.1 Study area

The study area is in Tidone Valley, northwestern of Italy, Emilia Romagna Region, Province of Piacenza (Fig. 1), described in detail by Zambito Marsala et al. (2020), Suciu et al. (2020) and Calliera et al. (2021). To be concise, the area covers 206.72 km^2 and includes part of *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, 2941 hectares of vineyard in 2016 (ISTAT, 2016). As shown in Figure 1, the Nitrate

Vulnerable Zone (NVZ) map, established in Emilia-Romagna through Decree 570/1997, covers a small part of the study area.

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 meters and the substrate morphology, are the main parameters that govern 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, it is due to rainfall infiltration in the subsurface. Only in the alluvial porous deposits in the valley bottom, the groundwater flows are mainly dependent on the *Tidone Torrent*, *Lora-Carogna* and Carona-Boriacco water levels (Fig S1) (Suciu et al., 2020).

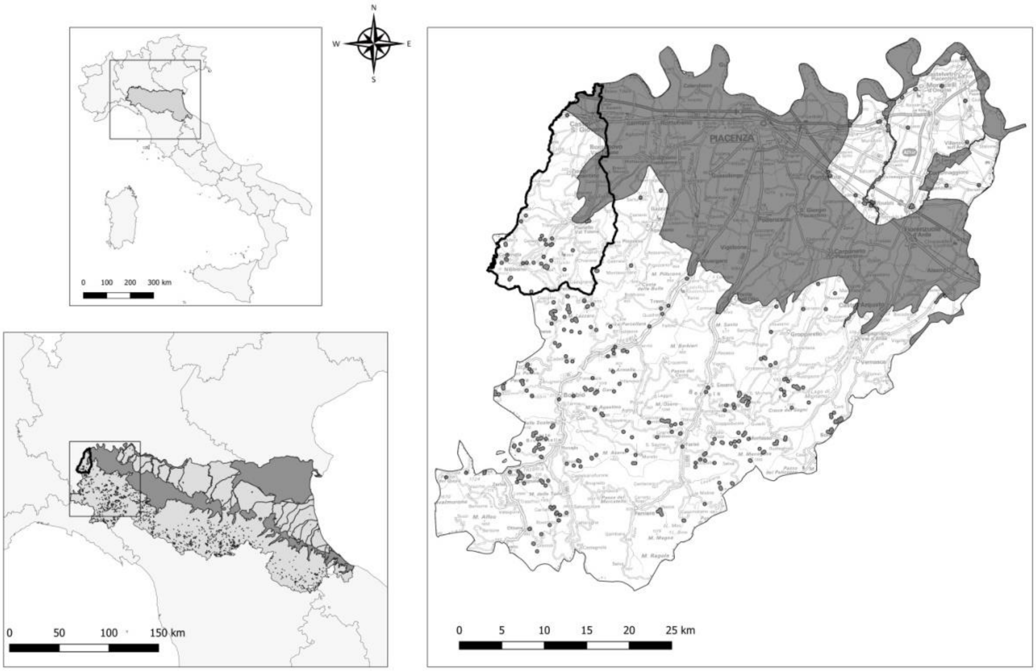

Fig 1. Study area (black line) in the north-west of Italy, Emilia Romagna Region, and Province of Piacenza. In dark grey is represented the Nitrate Vulnerable Zone of Emilia Romagna Region (NVZs, DCR 570/1997).

2.2 Development of the sampling network

As described in detail by Zambito et al. (2020), a sampling network with 26 wells was developed, selected from groundwater wells already existent in the study area. The wells were selected taking into consideration the upstream and downstream of the small water bodies crossed by tributaries (*Vallicola*) of *Tidone Torrent* and of two Streams *Lora-Carogna* and *Carona-Boriacco*, where the vineyards are treated with pesticides and fertilizers. 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 soil surface and transport of surface water body and drainage to groundwater. The wells selected are coded from WP01 to WP32 and include 3 wells used for drinking water and part of the network of the Regional Environmental Agency (ARPAE) and the water supply company (IRETI) (Table 1). The other selected wells are in the middle of vineyards or in the farms and have depths between 2 m and 34 m (Fig. 2, Table S1).

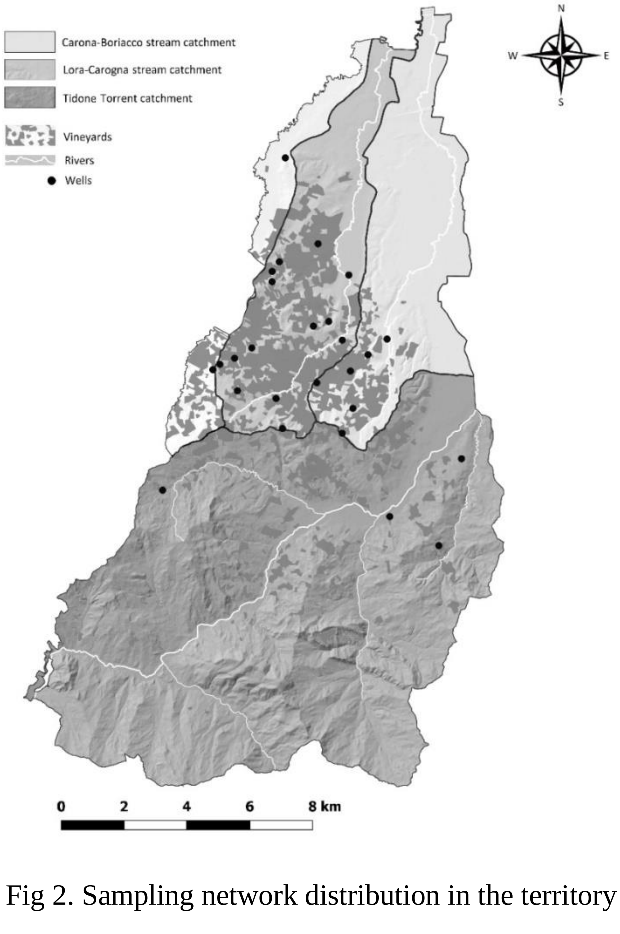

Fig 2. Sampling network distribution in the territory

2.3 Stakeholders involvement

For the development of the sampling network and the characterization of the territorial agricultural and fertilization practices, two survey campaigns were conducted between August 2017 and June 2018, by the use of *ad hoc* questionnaires and involving 175 farmers form the study area. The farmers involved were from: 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 %. (Calliera et al., 2020, submitted for this special issue). For farmers' involvement, the support of farmers' organization *Cantina Sociale Vicobarone*, of farmers' unions *Coldiretti*, *Confagricoltura* and CIA (farmer's association) and also of farmers' consultancy organization *Consorzio Fitosanitario Provinciale*, was fundamental. In the present study, the stakeholder involvement was conceptualized as an "active engagement", through bilateral and multi-actor conversations and selecting strategic places and time periods, as for example during grape delivery to the Social Winery by the farmers. A complete description of stakeholder engagement is provided by Calliera et al. (2020).

In particular, in the first survey, taken by 175 farmers, questions related to the use and type of fertilizers, existence of groundwater wells in the farm, implementation in the farms of best management practices (BMPs) and mitigation measures (MM) to avoid point source water contamination, existence of nitrates monitoring data, were made. For the second survey, based on the outputs of the first survey, fifty farmers were involved and specific questions were made concerning the timing of fertilization, the specific use of manure, the availability of analysis for organic matter and major elements (N, P, K) contents in soil, the use of specific decision support for fertilization and the need and willingness of implementation of new BMPs and MMs.

Finally, in November 2018, at the end of the surveys and after three sampling campaigns, all collected data and information were presented to the farmers and all the other actors involved in water use and governance in order to have their feedback and to find together the most sustainable solutions.

2.4 Groundwater sampling

During three years' time (2017–2019), a total of 130 groundwater samples were collected from the 26 network wells. Five sampling campaigns were carried out: November 2017, July and September 2018 and July and September 2019. The sampling periods were chosen based on grapevine treatments, in particular after pesticides and fertilizers spraying. Before sampling, wells were purged for several minutes to avoid the effects of stagnant water. The temperature and the static groundwater level of the wells were measured in the field using a digital thermometer and a portable acoustic water level meter, respectively.

The samples were collected and filled into 10 mL plastic tubes for nitrates analysis (in triplicate), into 1 liter plastic bottles for pH and electrical conductivity and into 50 mL for water and N and O isotopic composition of dissolved nitrate leaving no air space in order to avoid bubbles formation and to prevent any further fractionation. All groundwater samples were kept in the fridge at 4 °C and analyzed within 72 h. Before the analysis the samples were thawed at room temperature. For analysis of chemical composition, the groundwater samples were collected in 50 ml plastic tubes and, filtered through a 0.45-µm glass membrane and acidified by adding 1% of nitric acid within 12 h. Until analysis the samples were stored at 4 °C.

2.5 Hydrochemical and isotopic analysis

Electrical conductivity and pH were analyzed after sample filtration through a 0.45 mm cellulose membrane filters. For pH determination a pH-meter with a resolution of 0.01 pH units was used, while electrical conductivity (µS/cm) was measured with a Mettler Toledo probe with an automatic temperature compensation. The electrical conductivity is referred to 20 ° C.

Nitrate concentration was measured following an ultraviolet spectrophotometric screening method, which involves the use of “Cuvette test LCK 339 Nitrate" kit for samples with expected concentrations between 0.23 and 13.5 mg/L NO_3-N, corresponding to 1.0 to 60.0 mg/L of NO_3^-, and the "Cuvette Test LCK 340 Nitrate" kit for samples with expected concentrations between 5.0 and 35.0 mg/L NO_3-N, corresponding to 22.0 to 155.0 mg/L of NO_3^-. The instrument used was Spectrophotometer DR6000 (Hach-Lange, Milan, Italy). The technical data for cuvette test LCK339 and LCK340 were determined in conformity with ISO 8466-1 and DIN 38402 A51 “Calibration of analysis methods” and are available in the website of the producer (https://it.hach.com/asset-get.download.jsa?id=2559362544). The analyses were carried out in triplicate for each sample and a stock solution of 1 mg/L of NO_3^- , obtained using KNO_3, was used to control the kit’s performance. The robustness and validity of the kit test was also demonstrated by Dimitrova et al., (2013), highlighting its particular advantages, such as lower sample volumes, lower chemical reagents need and less waste production.

Elemental analyses were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7800 Agilent) for Li, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Rb, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb with the exception of chlorine (ICP-QQQ, 8900 Agilent) and Optical Emission Spectrometry (ICP-OES, 5800 Agilent) for main major elements (Al, Ca, Fe, K, Mg, Na, P, S, Zn, Cl). These analyses were performed on samples of the two last monitoring campaigns (July and September 2019; n = 52).

For δ^{15}N and δ^{18}O of NO_3^- a total of 25 groundwater samples were analyzed, twelve collected in May 2019 and thirteen collected in September 2019. The samples were selected based on their nitrate concentrations and according to the upstream-downstream criterion described above. The δ^{15}N-NO_3^- and the δ^{18}O-NO_3^- analyses were performed following the Cd reduction method (McIlvin and Altabet, 2005) with an automatic pre-concentrator (Pre-Con, Thermo Scientific) coupled to an isotope ratio mass spectrometer (IRMS) (Finnigan MAT-253, Thermo Scientific). The δ^{2}H H_2O and δ^{18}O H_2O were measured using ^{2}H and CO_2 equilibrium techniques, respectively, following standard methods (Epstein and Mayeda, 1953). δ^{2}H H_2O and δ^{18}O H_2O were measured by use of a Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Fisher) coupled with an automatic Gasbench II Thermo Fisher. The system requires a preliminary conditioning: the vials containing the water samples are flushed with a mixture of He/H_2 and He/CO_2, to measure the isotopic ratios D/H and ^{18}O/^{16}O respectively, followed by a balance between the aqueous phase of the sample and the gas mixture introduced. Subsequently, the balanced gaseous fraction is injected into a gas chromatographic column and sent for mass analysis.

According to Coplen (2011), several international and laboratory standards were interspersed among samples for normalization of analyses. Three international standards (USGS 32, 34 and 35) and one internal laboratory standard (CCIT-IWS (δ^{15}N = +16.9 ‰ and δ^{18}O = +28.5 ‰)) were employed to correct δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values. Results are expressed in δ (‰) values relative to international standards, atmospheric N_2 (AIR) for δ^{15}N, and Vienna Standard Mean Ocean Water (V-SMOW) for δ^{18}O and δ^{2}H.

Samples for isotopic analyses of δ^{15}N-NO_3^-, δ^{18}O-NO_3^- and δ^{15}N-NH_4^+ were prepared at the laboratory of the MAiMA-UB research group and analyzed at the Centres Científics i Tecnològics of the Universitat de

Barcelona (CCiT-UB), whereas $\delta^{2}H\ H_2O$ and $\delta^{18}O\ H_2O$ were analyzed at Environmental Isotope Laboratory, ARPAE, Piacenza.

2.6 Statistical analysis of nitrates concentration

A statistical analysis was performed in order to investigate if i) the location of the wells, ii) the slope of the soil in which the wells are located and iii) the wells depth, may affect groundwater NO_3^-contamination. The normal distribution of the data was verified by using UNIVARIATE procedure (SAS Inst. Inc., Cary, NC; release 8.0) by NORMAL option. Data were not normally distributed, and a *log* normal transformation was applied to satisfy normality and homogeneity of variance assumptions underlying linear models. Through the text, in tables and graphs, the average data were presented in their original scale, whereas pooled error terms (i.e., root means square error or √MSE) were associated to *log* normal transformed data (Petrie and Watson, 2006). The experimental design corresponded to a completely randomized design with a 2 x 2 x 4 factorial arrangement of treatments. A generalized linear model (GLM procedure) was applied to *log* transformed data and main tested effects in the model were the location of the wells (Stream, n=2; upstream vs downstream), the degree of the slope of the soil in which the wells are located (Slope, n=2) and the wells depth (Deep, n=4). Two slope levels were defined, slope level I, with a slope between 0 and 3 ° and slope level II, with a slope > 3°. Based on the wells depth, four levels were defined, level I, with a depth < 6m, level II, with a depth between 6 and 10 m, level III, with a depth between 10 and 15 m and level IV, with a depth > than 30 m. First and second order interactions of main tested effects were also included in the model

3. Results and discussion

3.1 Farmers interviews

The results of the first survey, in which 175 farmers were interviewed, revealed that in 107 farms there is a groundwater well, used for drinking (8 %), irrigation (18 %), for mixture for pesticide treatments (80 %) and not used (4 %). However, just 14 % of the 175 farmers interviewed are aware about the existence of nitrate monitoring data on the ARPAE portal. Concerning fertilization practices, 118 farmers (67 %) use nitrogen-based fertilizers in their vineyards. In particular, 22 % of them only use manure, 10 % fertilize every two years, while 2.6 % fertilize every 3/4 years. The remaining 65.4% didn't give details about the type and use of fertilizer.

The results of the second survey, in which 50 of the 175 farmers previously interviewed were involved, have shown that 20 % of farmers decide the fertilization scheme based on consultant technical support, 26 % based on soil chemical analysis, 40 % based on personal experience and leaf vigor of grapevine, 12 % don't use fertilizers in the vineyards and 2% didn't give an answer. Manure is used in 28 % of the vineyards after grape harvest while 30 % of famers declared to use it just for the planting of a new vineyard. 50 % of famers carry out analysis for organic matter and major elements (N, P, K) contents in soil and 84 % considers these analyses an important data to avoid groundwater contamination by nitrates. However, 8 % considers that the grapevine is able to adsorb all the fertilizers given. Based on these survey results, the introduction of a Farm Sustainability Tool for Nutrients, as proposed by European Commission, would increase the knowledge concerning fertilization efficiency and induce a harmonization of fertilization practices. The prevalent use of inorganic nitrogen fertilization, declared by the farmers, is in line with previous studies (Martinelli et al., 2018), which highlight the habit of farmers in Piacenza area to use inorganic fertilizers, which are more practical, more comfortable to manage and have a higher performance than the organic fertilizers. Furthermore, in a study conducted by Musacchio et al., (2020) in Lombardy region on the support given by local groundwater governance for the correct implementation of Nitrate Directive, the stakeholder network analysis has shown that the governance framework does not support knowledge dissemination and changes in farmers' attitudes, hindering water quality improvements. Moreover, all interviewees reported that control-based strategies represent the only real tool to guarantee the adoption of sustainable practices by farmers but, at the same time, it is extremely difficult to perform systematic and widespread controls due to the number of farms and the associated costs. Farmers observed that recurrent controls may be a life-long learning opportunity if associated to structured capacity building and to a mutual trust relationship between farmers and authorities. Therefore, the authors highlight the need for Member States to provide to EU commission not only environmental monitoring data but also an assessment of governance dynamics supporting the Directive implementation.

3.2 Hydrochemical data

The analysis of chemical elements in groundwater and additional physicochemical parameters such as pH, electrical conductivity, temperature, static level, δ^2H and δ^{18}O and the study of their change over time (seasonality) allow to characterize the investigated aquifer. Tables S1 and S2 in supplementary materials show the mean, the minimum and the maximum values for temperature, static level (Table S1) and electrical conductivity (EC), pH, δ^2H and δ^{18}O (Table S2) of 130 groundwater samples monitored during the five sampling campaigns. In general, the average temperature values ranged from 13 to 18 ° C. A constant temperature value in a well over time represents an indicator of quality (Memberg et al., 2014) suggesting that the aquifer is protected from outside, and therefore just slightly affected by air temperature changes. As the depth of the well increases, the temperature remains constant, with values around 14 - 15 ° C. The wells with constant temperature were WP04, WP07, WP08 and WP32 with a depth of 8 m, 34 m, 30 m and 12 m respectively. This high heterogeneity of wells depth is due to the presence of more than one shallow aquifer in the area, as reported by Suciu et al. 2020. The pH values vary from 7.0 to 8.0 indicating a neutral to slightly alkaline water, typical of the Tidone valley (ARPAE, 2017). The groundwater electrical conductivity shows a high variation between wells, with values between 52 and 2341 µS/cm.

A summary of average concentrations of major and trace elements for groundwater sampled in 2019, is provided in Table 2, while detailed values are provided in Tables S3 and S4 of supplementary material. As a general trend, a high variation between wells and between sampling periods was observed for both major and trace element concentrations in groundwater, as confirmed by the high standard deviations. Furthermore, for most of the elements analyzed, higher values were observed in September 2019.

Very high concentrations were observed for Na, with values ranging from 1 to 260 mg/L, suggesting a strong water–aquifer interaction related to direct cation exchange between groundwater and the clay fraction of the aquifer material and/or pollution from wastewater (Wayland et al., 2003). Indeed, the area is characterized by clay and clay-silty type of soils (Suciu et al, 2020). The highest Na:K ratio was obtained for well WP 18 while a Na:K below one was observed for well WP 26, for both sampling campaigns. This relatively abundance of K may indicate the presence of sedimentary rather than igneous rocks. However, the main source of K in the area could be weathering of potash silicate minerals and/or agro-chemicals (K fertilizers are used for grapevine cultivation). The source of Na ion may be due to its displacement from absorbed complex of rocks and soils by Ca and Mg. Ca and Mg show high concentrations in groundwater, with values between 8 and 135 mg/L and 2 and 53.7 mg/L, respectively.

Soluble anions, as chloride, sulfur, phosphate, show values in groundwater in the range of 0.2–622 mg/L, 1-109 mg/L and 0.001 – 0.685 mg/L, respectively, indicating a high variability between wells and salty water in some cases.

Concerning the trace elements, the results indicated high values for Mn, and Fe, between 0.1 and 484.3 µg/L, and 0.6 and 200 µg/L, respectively, (Table S4), and a significant increase from July to September (R^2Mn correlation = 0.88 and R^2Fe correlation = 0.76), suggesting a significant susceptibility of land surface to agricultural practices (Devic et al., 2014). This is in agreement with a study on PTEs distribution and origin in soil of Lombardy Region, Northern Italy, conducted by Sacchi et al., 2020, who reports lower concentrations of Mn in soil during cropping seasons and an increase of both Fe and Mn concentrations in groundwater. Furthermore, Mn show values above the Emilia Romagna Region quality standards for GW (50 µg/L) in 20 % of the samples, while for Fe the Emilia Romagna Region quality standard (200 µg/L) was exceed in one sample. Monitoring data of Emilia Romagna Region between 1988 and 2008 reported values for Mn and Fe in groundwater of *Conoide Tidone-Luretta - confinato inferiore* above the quality standards in 5 % and 5.1 %, respectively, of groundwater samples monitored. Beside these two elements, Ni was reported, by the above-mentioned monitoring data, with values above the Emilia Romagna Region quality standard (20 µg/L) in 2.8 % of groundwater samples monitored. In our study, no groundwater sample shows Ni values above the quality standard of Emilia Romagna Region.

Table 2. Summary of major and trace elements in groundwater of Tidone Valley

Elements	**Measure unit**	**July 2019**		**Sept 2019**	
		mean	SD	mean	SD
Al	mg L-1	0.01	0.01	0.02	0.01
Ca	mg L-1	59.96	32.48	97.83	44.87
K	mg L-1	5.27	11.95	10.43	17.12
Mg	mg L-1	24.08	15.99	20.66	13.66
Na	mg L-1	42.42	38.96	52.22	58.34
P	mg L-1	0.06	0.14	0.08	0.21
S	mg L-1	33.00	24.90	28.96	28.26
Zn	mg L-1	0.09	0.11	0.12	0.06
Cl	mg L-1	114.58	149.99	75.00	115.41
Li	µg L-1	13.23	12.63	23.87	23.16
Ti	µg L-1	0.19	0.18	0.49	0.75
V	µg L-1	2.65	5.02	2.89	4.73
Cr	µg L-1	1.64	4.05	1.07	1.49
Mn	µg L-1	24.17	50.00	58.89	111.77
Fe	µg L-1	4.11	3.63	34.06	56.16
Co	µg L-1	0.12	0.15	0.19	0.26
Ni	µg L-1	1.61	1.28	2.36	2.65
Cu	µg L-1	8.02	19.38	11.40	25.89
As	µg L-1	0.48	0.48	0.57	0.62
Se	µg L-1	1.25	1.78	1.04	1.67
Rb	µg L-1	2.48	2.64	3.95	4.46
Sr	µg L-1	647.58	445.53	1116.43	717.11
Mo	µg L-1	0.67	0.67	0.49	0.39
Ag	µg L-1	0.04	0.03	0.06	0.03
Cd	µg L-1	0.03	0.02	0.01	0.01
Sb	µg L-1	0.18	0.08	0.12	0.11
Ba	µg L-1	259.46	263.39	1072.96	551.49
Pb	µg L-1	0.12	0.11	0.21	0.16

3.3 δ^2H and $\delta^{18}O$ results of groundwater

Stable oxygen and hydrogen isotope compositions of groundwater samples are detailed in Table 2S (n=130) and presented in Fig 3. The δ2H and δ18O of all groundwater samples analyzed follow the equation δ2H = 7.24 δ18O + 4.28 with R2 = 0.86, plotting between the Global Meteoric World Line (GMWL; with δ2H,= (8.17±0.06) 18O + (10.35±0.65) r2 = 0.99 n = 206 (Rozanski et al. 1993) and a Local Meteoric Water Line of North Italy (NIML) (Longinelli and Selmo 2003), which follows the equation δ2H = 7.709 δ18O + 9.403, and having average δ18O values of 8±0.7 ‰ and average δ2H values of 53.8±5.4 ‰. Since rainfall is the main recharge of groundwater, the latter has an isotopic footprint similar to that of precipitation.

During the investigated period eleven wells, WP4, WP5, WP7, WP8, WP11, WP19, WP20, WP21, WP29, WP30 and WP32, did not show significant differences for δ18O (SD δ18O between 0.05 and 0.16, Table S2) and of these, four wells, WP4, WP7, WP8 and WP32 had also rather constant temperature values, indicating conservative conditions. This group of wells includes the deepest ones, such as WP7 (depth = 34 m), WP8 (depth = 30 m) and those used for drinking water production, WP21 and WP32. Well WP11 and spring WP19 (at 420 m above the sea) have shown the most negative δ18O values, indicating infiltrations or mixing with old waters and possible influence of altitude. On the contrary, wells WP9, WP10, WP15, WP17 and WP28, have shown a certain variability of δ18O (SD δ18O between 1.0 and 1.5 Table S2), indicating a higher influence of the surrounding conditions. However, wells WP17 and WP28 are characterized by a different geographical position and altitude with respect to all the others (WP17 = 344 m above the sea; WP28 = 205 m above the sea).

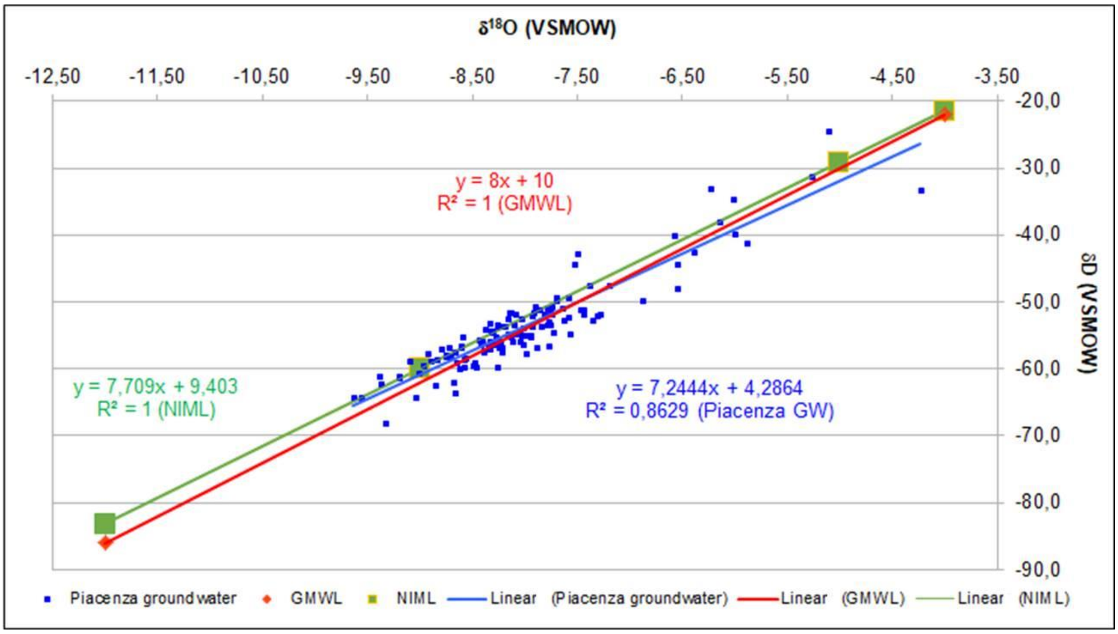

Fig. 3. δD and δ^{18}O of groundwater samples related to the GMWL.

3.4 Nitrate occurrence in groundwater

NO_3^- was detected in groundwater samples (n=130) at values ranging from 5 to 101 mg/ L, with four wells having NO_3^- concentration higher than the EQS of 50 mg/L (Fig. 4). In the most superficial (shallow) wells (up to 6 m depth) the variability of the NO_3^- concentration during the five monitoring campaigns was very high and three wells , WP03, WP18 and WP22, had NO_3^- concentrations higher than EQS, representing 75% of total wells with NO_3^- concentration above EQS.

This particular trend may indicate that the contamination is dependent on the proximity to the surface and that the vertical and /or lateral supply waters, especially during intensive rain events, quite frequent in the last years, are able to quickly renew the aquifer and dilute concentrations. At the same time, their surface proximity makes them highly vulnerable to surface fertilization practices.

However, the other shallow wells (WP01, WP11, WP13, WP15, WP24 and WP28) showed very low NO_3^- concentrations (Fig. 4), indicating a possible recent contamination maybe due to the fact that the ammonium ion (NH_4) is not yet nitrified. Increasing the depth of the wells, the concentration of NO_3^- tends to be higher, but remains constant over the three sampling years, suggesting that the aquifer is less vulnerable to atmospheric conditions and recent fertilization practices than the shallower wells (WP04, WP06, WP09 and WP26). These regular concentration values are marked in wells with a depth between 10 and 15 m (WP17, WP21, WP25 and

WP32) and confirmed by well WP08, characterized by a 30 m depth. Well WP07, characterized by a 34 m depth and without a declared use, showed the highest NO_3^- concentration during the five monitoring campaigns, probably due to the non-renewal of the water. Well WP19 is a spring used for drinking purposes and, considered as the "blank" well of the study, due to its location upstream of the whole viticultural territory. Groundwater's flow has a South West-North East direction, as all the tributaries of the right bank of Po River (Fig S2 in supplementary material). Indeed, WP19 showed very low NO_3^- concentration (<4.5 mg/L) during all monitoring campaigns. On the contrary, well WP20, which represents the downstream well of the study, due to its location at the end of the area covered by vineyards, showed a NO_3^- concentration values around 40 mg/L during all monitoring campaigns. It may collect the residues of all fertilization treatments of the upstream area. Furthermore, the well is located in a livestock farm and this may influence NO_3^- concentration.

Comparing NO_3^- concentration in groundwater of the present well network with that of Emilia Romagna Region network, a lower NO_3^- concentration in groundwater of Tidone valley was observed. Indeed, in Tidone Valley only 7.7 % of groundwater samples showed values above the EQS between Nov 2017 and Sept 2018, while in the entire Emilia Romagna Region 11.5% of groundwater samples showed values above the EQS in the same period, suggesting a low to moderate impact of the viticulture on NO_3^- concentration of regional groundwater. It must be kept in mind that the vineyards surface in the study area represents almost 75% of the entire vineyard surface of Emilia Romagna Region (ISTAT, 2016).

A statistical analysis was performed in order to evaluate the influence of soil slope surrounding the wells, of wells depth and of wells location (upstream vs downstream) on NO_3^- groundwater contamination. Table 3 reports the three variables in relation to the root mean squared error (√MSE) and the P values, while the values represent the average NO_3^- concentrations (mg/L) in all 26 wells during the five monitoring campaigns (n = 130).

The slope of the soil and the interaction between the wells location with the soil slope and the depth did not show a significant effect on NO_3^- concentration ($P > 0.05$), while well depth seems to affect significantly NO_3^- concentration ($P < 0.05$). Indeed, NO_3^- concentration increases when increasing the depth (14.6; 13.8; 19.1; 45.3), suggesting a higher contamination of deeper aquifers. This contradicts the general assumption that shallow aquifers are more vulnerable to pollution, due to their proximity to the surface (Sacchi et al., 2013), but reflects the local reality. Indeed, Suciu et al. (2020) reports the presence of more than one aquifer in the study area and a low recharge rate of deeper aquifers due to the very low water flow. Therefore, this higher contamination of deeper aquifers is probably the result of historical fertilization of vines, being vines a perennial crop.

The wells location (upstream vs downstream) and the interaction between the soil slope and the depth showed to affect slightly the NO_3^- concentration ($P = 0.1$). In fact, the concentration decreases in the downstream wells and increases in the upstream wells, in discordance with the upstream-downstream approach that suggests that wells located downstream should collect the residues of the treatments due to run-off at soil surface, transport of surface water body and drainage to groundwater, as stated by Zambito Marsala et al., (2020). However, also the soil type may affect groundwater NO_3^- concentration. Indeed, soils with clay contents greater than 20 %, seem to retain NO_3^-, possibly by inhibiting leaching and recharge (Sacchi et al., 2013).

Therefore, the distribution on the territory of the wells with the higher NO_3^- concentrations does not seem to be related to any specific groundwater flow direction. This could be explained by the presence of more than one aquifer in the study area and their distinct recharge areas, and also by the mixing of waters from distinct origins and qualities in the well. Indeed, Suciu et al. (2020) showed a low drainage and lateral water movement in the clayey soils of the area for the period 2017-2018 and pointed out that point source contamination has an important contribution to groundwater contamination by pesticides.

The presentation of surveys and analytical results during the Workshop organized in November 2018, that had seen the participation of all actors involved in water use and governance of Tidone Valley, pointed out that farmers and their organizations do not feel responsible for NO_3^- groundwater contamination, as that other sources, as for example wastewater discharges, could have an influence and should be analyzed. Indeed, the samples collected during 2019 were used for isotopic analysis to determine the sources of NO_3^- in groundwater.

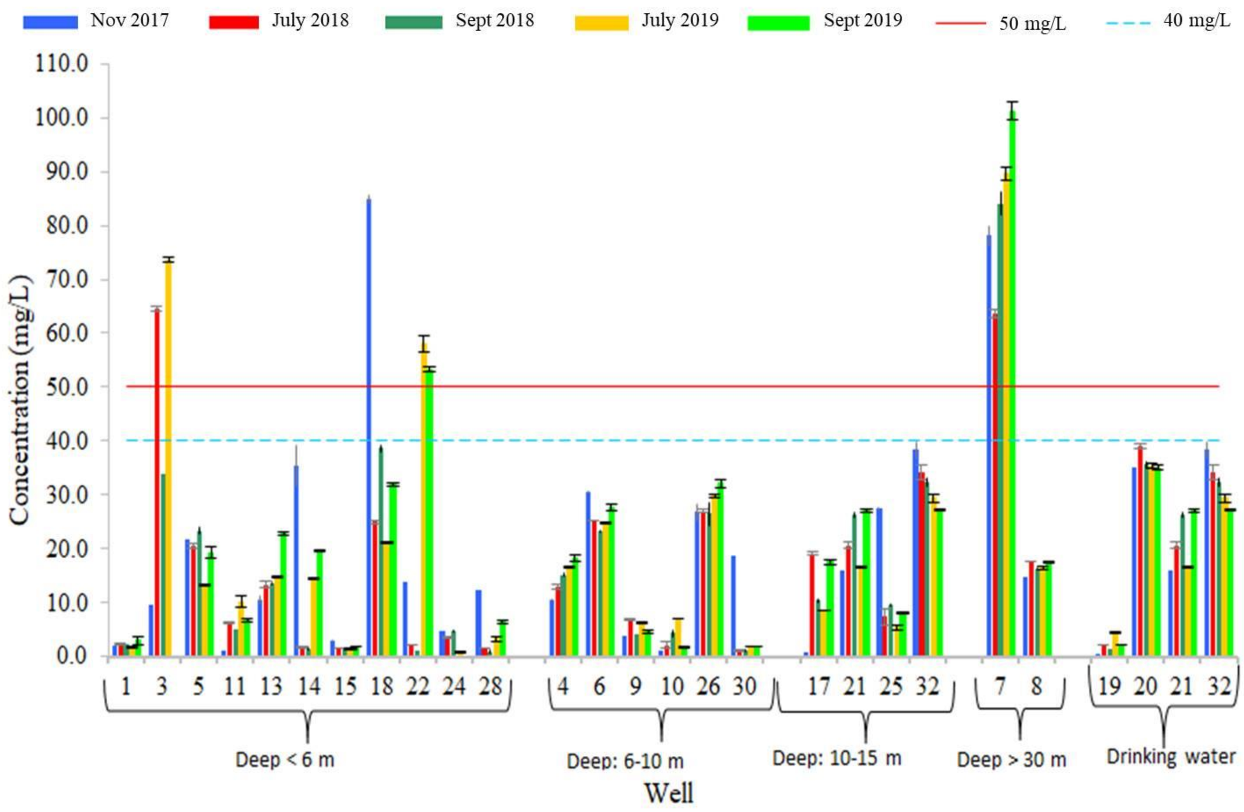

Fig 4. Results of nitrates occurrence in groundwater (expressed only with the number that characterized the code). The wells are ordered according to their depth in ascending order.

Table 3. Effect of the wells location (upstream vs downstream), the slope degree of the soil (type 1= 0°-3°; type 2 = >3°) and wells depth (type 1= less than 6 meters; type 2 = 6-10 meters; type 3= 10-15 meters; type 4= over 30 meters) on NO_3^- concentration.

Stream		**Slope**		**Deep**				**√MSE**	**P of the model**					
1	2	1	2	1	2	3	4		Stream	Slope	Deep	Stream*Slope	Stream*Deep	Slope*Deep
21.2	16.1	25.1	15.3	14.6	13.8	19.1	45.3	1.1	0.1	0.2	0.0006	0.2	0.3	0.1

3.5 Source of nitrates through dual isotopic analysis

Nitrogen and oxygen isotopes in groundwater were analyzed in order to determine the sources of NO_3^- in the study area and to find correlation between the use of nitrogen-based fertilizers and NO_3^-. In 2019 the NO_3^- concentration in GW ranged from 5.1 to 87.9 mg/L, in May, and from 6.5 to 101.2 in September.

Fig. 5 shows the δ^{15}N and δ^{18}O analyzed in the groundwater samples in two monitoring campaigns (May and September 2019). In the groundwater samples collected in May 2019 (n=12), isotopic values ranged between +4.2 ‰ and +20.5 ‰ for δ^{15}N, and between +1.5 ‰ and +18.7 ‰ for δ^{18}O. In particular, groundwater samples of two wells (WP11 and WP20) presented δ^{15}N and δ^{18}O values compatible with organic fertilizers and sewage, suggesting the use of manure for the fertilization of vineyard or discharge of household wastewater. Indeed, according to Xue et al. (2009), δ^{15}N values of NO_3^- originating from manure usually range between + 5 ‰ to + 25 ‰, and that originating from household sewage vary between + 4‰ and + 19 ‰. The owner of well WP 11 doesn't use manure as fertilizer, therefore accidental household wastewater discharge could be the source of NO_3^- occurrence.

Most of the groundwater samples (WP6; WP17; WP25; WP26; WP28; WP32) presented δ^{15}N ranging between +4.2 ‰ and +8.8 ‰, and δ^{18}O ranging between +6.2 ‰ and 18.7 ‰ suggesting that NO_3^- may originate from NH_4^+ and NO_3^- fertilizers or soil organic nitrogen. Furthermore, the samples with δ^{18}O-NO_3 not fully equilibrated with the δ^{18}O of groundwater, suggesting a low residence time in the soil and a fast contamination transfer to groundwater. The origin of NO_3^- in these samples may be potentially related to the application of ammonium fertilizers nitrified to NO_3^- in the unsaturated zone. Furthermore, values of δ^{15}N between +5 ‰ and +8 ‰, can also be derived from nitrification of soil nitrogen or from mixing between synthetic fertilizers and anthropogenic organic matter, being most probably the origin in samples with NO_3^- concentration below 10 mg/L (Chae et al., 2009), except for WP26 and WP32. However, groundwater samples of the wells WP07, WP05 and WP13 show δ^{15}N values between +11‰ and +20.5 ‰, and δ^{18}O values between +6.3 ‰ and +12.5 ‰, indicating the uncertain origin of NO_3^- and an influence of denitrification process. Denitrification is the transformation of nitrate into gaseous N_2. It is considered the main natural process attenuating nitrate concentration in groundwater. This requires the presence of denitrifying bacteria and electron donors (organic carbon, reduced sulphur and/or reduced iron), abundant presence of NO_3^- and an anaerobic environment (Koba et al., 1997, Rivett et al., 2008). Furthermore, although the isotopic fractionation (ε) for the study area was not characterized, the denitrification percentage was estimated based on bibliographic values. Table 4 represents a simplified model for denitrification based on literature isotopic fractionation values (Grau-Martinez et al., 2017). The model assumes a closed system and calculates the isotopic composition of the remaining nitrate if denitrification is taking place.

In September 2019, the groundwater of well WP22 was also analyzed for isotope data as NO_3^- concentration in the last two monitoring campaigns were higher than the EQS of 50 mg/L (58 mg/L and 53.3 mg/L respectively; Fig.4). The isotopic results of the total 13 GW samples showed NO_3^- isotope composition ranging between -5.8 ‰ and +19.3 ‰ for $\delta^{15}N$, and between +4.3 ‰ and +41.3 ‰ for $\delta^{18}O$.

Comparing the isotopic results of the two sampling campaigns, a similar isotopic composition was observed for wells WP05, WP06, WP07, WP13, WP17, WP18, WP20, WP25 and WP26, and an NO_3^- inorganic origin, as a mix between NH_4^+ and NO_3^- fertilizers (Fig 6), for three of them (WP06, WP17 and WP25). According to Mengis et al. (2001) in soils with high microbial activity the $\delta^{18}O$ of dissolved NO_3^- fertilizers is modified through the recycling of NO_3^- in soil in a process abbreviated as MIT (mineralization-immobilization-turnover). When this process takes place, it shifts the $\delta^{18}O$ of dissolved NO_3^- from +23.5‰ to values similar to those produced by nitrification of NH_4^+ fertilizers. Therefore, the observed values in wells WP06, WP17 and WP25 can also be attributed to the partial recycling of NO_3^- fertilizers in the soil.

Wells WP05, WP07, WP13 and WP18 showed an uncertain origin influenced by denitrification processes (Fig. 5). Since denitrification processes shifts the isotopic composition of both N and O with a slope $\varepsilon^{18}O/\varepsilon^{15}N$ varying from 0.5 to 1 (Böttcher et al., 1990; Wunderlich et al., 2013), when this process takes place, it can hinder the interpretation of the nitrate source. In any case, a significant denitrification, highlighted by a progressive enrichment in $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-, was identified in wells WP07, WP05, WP13, and, to a lesser extent in WP18, suggesting that a natural attenuation of nitrate pollution is taking place in these wells. Finally, isotopic data of the wells WP20 and WP26, with similar $\delta^{15}N$ and $\delta^{18}O$ values in the two campaigns, fall in the field of soil nitrogen.

On the other hand, wells WP 11 and WP 32 show completely different values in the two monitoring campaigns. As plotted in Fig. 5, well WP11 shows an NO_3^- origin linked to sewage/manure in May and an NO_3^- uncertain origin in September, influenced by denitrification, while well WP32 shows an NO_3^- origin linked to NO_3^- fertilizers in the May and linked to soil NO_3^- in September.

With regards to the correlation between nitrates and isotopic data, the high NO_3^- concentration detected in samples WP07, WP18, WP22 (higher than 50 mg/L) (Fig. 5) suggests a contribution from inorganic fertilizers rather than a soil nitrate contribution, but in the present cases denitrification processes hinder the interpretation of isotopic data. As stated by Hosono et al. (2013), groundwater samples with moderate to high NO_3^-

concentrations tended to have narrow isotope compositions (δ^{15}N = +2 – +8‰ and δ^{18}O = −3 – +5‰). In contrast, the samples with the lowest NO_3^- concentrations tended to have higher isotopic compositions (δ^{15}N= +8 – +46 ‰ and δ^{18}O= +5 – +48‰), suggesting the occurrence of denitrification. This principle, however, is not in agreement for samples of well WP07, in which the highest NO_3^- concentration was detected, coupled with high δ^{15}N (+17.6 ‰ and +19.3 ‰) and δ^{18}O (+10.1 ‰ and +11.3 ‰). This suggests that if denitrification processes stop, NO_3^- concentration in well WP07 would be higher, and thus the contamination is very significant. Thus, despite the significant denitrification and the lack of renewable water, the high NO_3^- concentration within the well WP07, is likely due to local pollution or to historical fertilization of vines, as stated in the paragraph 3.4.

According to Lasagna and De Luca (2017) a positive correlation, especially in the shallow aquifer, between the NO_3^- concentrations and δ^{15}N-NO_3^- would support the presence of a nitrification process in aquifer. However, in this case study, a positive correlation between δ^{15}N-NO_3^- and NO_3^- was not observed.

Furthermore, despite Martinelli et al. (2018) reported that in the Po Plain, of which our study area is part of, the main source of NO_3^- in groundwater was manure, with δ^{15}N median values significantly correlated with the pig density, followed by synthetic fertilization, in the present work the main source of NO_3^- in groundwater was inorganic fertilizers. This is in agreement with the land use and viticulture practices declared by most of the farmers during the surveys. Indeed, in the study area, no significant livestock farming was reported, with the exception of the cattle livestock where well WP 20 is located.

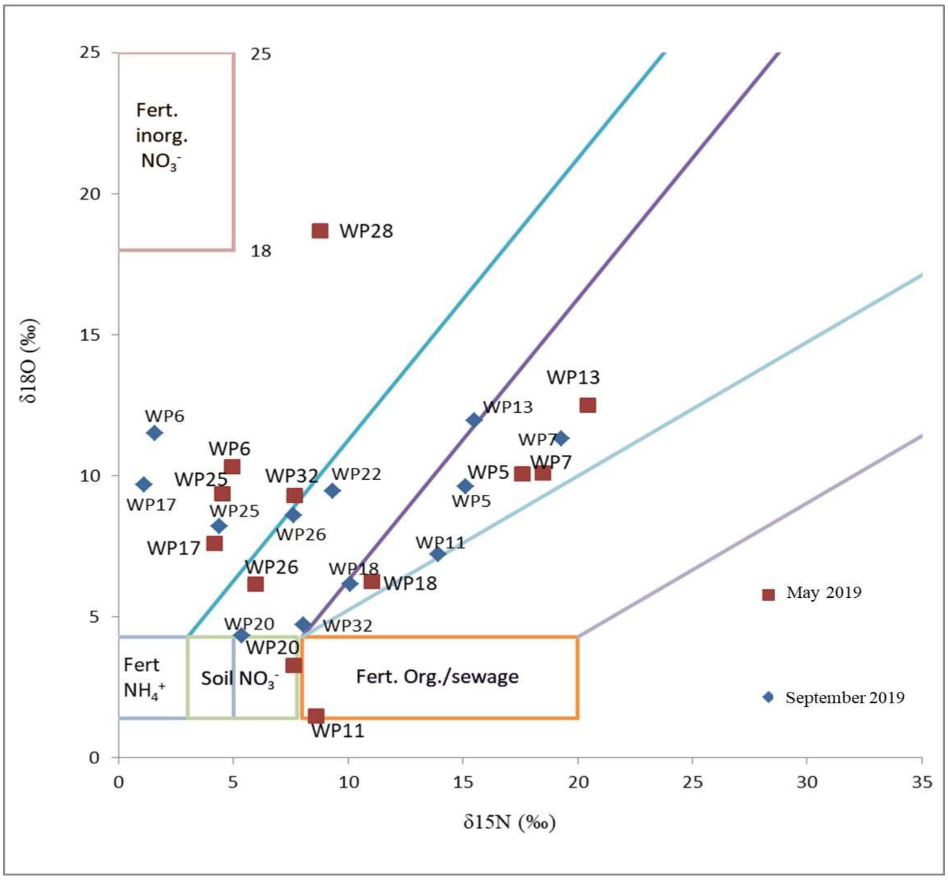

Fig 5. δ^{15}N and δ^{18}O of NO_3^- in groundwater of Tidone Valley.

4. *Conclusions*

In this work, the influence of nitrogen-based fertilization on nitrates occurrence in groundwater of Tidone Valley, a hilly area with intensive viticulture activity, was evaluated for the first time. First, for the characterization of the territorial agricultural and fertilization practices, two survey campaigns, involving 175 farmers and other stakeholders, were conducted by use of *ad hoc* questionnaires. The survey results revealed an extensive use of inorganic nitrogen fertilizers, whereas the organic fertilization with manure is manly used for planting of new vineyards.

Secondly, for aquifer characterization and its interaction with land surface, water isotope data, hydrochemical and NO_3^- analyses were carried out. The results have shown a high variability of water isotope values and of major and trace elements concentrations in most of the wells, suggesting the presence of more than one aquifer in the area under study. Furthermore, Mn and Fe have shown high concentrations in groundwater and a significant increase from July to September, suggesting a certain susceptibility of land surface to agricultural practices. This is in accordance with NO_3^- analyses results, which revealed high variability during the five monitoring campaigns in shallow wells, in which NO_3^- used as fertilizer for grapevine cultivation could readily drain. In the deeper wells NO_3^- concentration was higher but constant in time, suggesting that the aquifer is more protected and less vulnerable to external conditions. Indeed, statistical analysis showed a significant influence of well's depth on NO_3^- concentration, with higher values in the deeper ones. However, just 4 out of 26 groundwater wells have shown values above EQS, three of them being shallow wells, while the deeper ones show constant values around 40 mg/L, confirming the vulnerability of the zone to NO_3^- contamination.

Lastly, nitrogen and oxygen isotopes in groundwater were analyzed in order to determine the sources of NO_3^- in groundwater. The results have shown that most of the NO_3^- found in the groundwater samples is derived from the use of inorganic nitrogen fertilizers, in agreement with the land use and viticulture practices declared by most of the farmers during the surveys.

Comparing NO_3^- concentration in groundwater of the present well network with that of Emilia Romagna Region network, a lower NO_3^- concentration in groundwater of Tidone valley was observed. Indeed, in Tidone Valley just 7.7% of groundwater samples have shown values above the EQS between Nov 2017 and Sept 2018, while in the entire Emilia Romagna Region 11.5% of groundwater samples have shown values above the EQS in the same period. Considering that the vineyards surface in the study area represents almost 75% of the entire vineyard surface of Emilia Romagna Region, the obtained results suggest a low to moderate impact of viticulture on NO_3^- concentration of Emilia Romagna Region groundwater.

Finally, as survey results indicated a tendency of farmers to follow their own experience for fertilization, the introduction of a Farm Sustainability Tool for Nutrients, as proposed by European Commission, as well as the assessment of governance dynamics supporting the Directive implementation by Member States, as suggested by previous literature studies, would increase the knowledge concerning fertilization efficiency and facilitate the achievement of a fully resilient socio-environmental system.

Supplementary material

Table S1. Depth, Temperature (T) and Static Level (SL) of groundwater monitored during the five sampling campaigns, Nov 2017, Jul 2018, Sep 2018, Jul 2019 and Sep 2019

Sample	Depth (m)	T (° C)			SL (m)		
		Mean	Min	Max	Mean	Min	Max
WP01	2.0	17.5	12.4	19.3	-1.21	-1.23	-1.14
WP03	6.0	15.3	11.6	17.0			
WP04	8.1	14.2	13.7	14.7	-6.00	-6.22	-5.42
WP05	3.0	16.0	11.9	18.6	-1.78	-2.18	-1.48
WP06	7.0	17.2	15.0	19.6	-3.69	-5.82	-2.47
WP07	34.0	14.0	13.4	14.3	-31.19	-31.38	-31.1
WP08	30.1	14.2	13.4	14.6	-21.29	-21.61	-21.03
WP09	6.2	15.5	12.0	17.0	-3.21	-4.98	-2.20
WP10	9.0	18.0	14.0	19.8	-1.49	-1.57	-1.43
WP11	5.7	14.9	14.0	15.8	-3.22	-3.72	-2.97
WP13	5.4	16.5	14.5	17.9	-3.25	-3.72	-3.00
WP14	4.5	16.0	11.4	17.4	-2.88	-3.75	-2.24
WP15	4.6	15.7	12.3	17.0	-2.99	-3.43	-2.60
WP17	11.4	15.3	10.4	17.5	-2.08	-2.18	-1.98
WP18	3.5	15.3	10.1	17.0	-2.22	-2.95	-1.60
WP19	*	16.4	13.0	21.0			
WP20	117.0	16.1	15.1	17.7			
WP21	11.0	13.2	11.8	14.0	-3.74	-4.20	-3.10
WP22	5.3	16.6	15.2	17.7	-2.17	-2.90	-1.27
WP24	3.7	14.9	12.4	17.0	-2.97	-3.71	-1.67
WP25	11.2	16.2	12.4	18.7	-3.07	-3.52	-2.80
WP26	8.8	15.9	12.7	19.6	-2.20	-4.88	-0.68
WP28	4.9	17.4	15.3	19.0	-1.70	-2.10	-1.23
WP29	2.9	16.2	14.9	17.0	-1.78	-2.08	-1.22
WP30	7.8	14.8	14.0	16.0	-3.61	-5.12	-2.55
WP32	12.0	13.1	13.0	13.3	-8.83	-11.07	-6.80

* Water source has no depth

Table S2. Electrical conductivity (EC), pH and Deuterium (D) and Oxygen isotopes (^{18}O) of groundwater monitored during the five sampling campaigns, Nov 2017, Jul 2018, Sep 2018, Jul 2019 and Sep 2019

Sample	**EC (µS/cm)**			**pH**			**δ^2H**			**^{18}O (‰VSMOW)**		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
WP01	1811	1425	2341	7.4	7.2	7.7	-53.4	-58.3	-50.8	-8.12	-8.56	-7.79
WP03	1211	737	1389	7.3	7.2	7.6	-56.7	-56.9	-56.8	-8.48	-8.73	-8.25
WP04	990	941	1054	7.1	7.0	7.2	-51.5	-53.5	-49.4	-7.75	-7.94	-7.63
WP05	1173	1107	1294	7.0	6.9	7.3	-53.0	-54.7	-51.6	-8.15	-8.22	-8.06
WP06	306.4	248	348	8.0	7.6	8.1	-57.5	-68.2	-49.4	-8.51	-9.33	-7.58
WP07	1268	1189	1444	7.6	7.5	7.9	-53.6	-55.8	-51.6	-8.02	-8.17	-7.92
WP08	715	677	803	7.7	7.6	7.9	-51.5	-53.5	-50.6	-7.75	-7.86	-7.64
WP09	547	518	603	7.8	7.7	7.9	-55.0	-63.6	-39.8	-7.81	-8.68	-6.00
WP10	228	163	298	7.4	7.2	7.6	-48.9	-64.3	-41.2	-7.53	-9.64	-5.89
WP11	1756	1666	1823	7.6	7.3	8.1	-60.6	-61.2	-58.9	-9.18	-9.39	-9.01
WP13	942	886	980	7.2	7.0	7.7	-55.9	-57.2	-55.0	-8.37	-8.59	-8.01
WP14	784	694	843	7.5	7.3	8.1	-54.9	-59.8	-44.5	-8.01	-8.61	-6.55
WP15	460	361	647	7.4	7.1	7.6	-55.2	-64.4	-47.6	-8.06	-9.57	-6.89
WP17	143	52	313	7.2	6.9	7.7	-34.9	-44.3	-24.4	-5.80	-7.54	-4.23
WP18	798	774	809	7.3	7.1	7.6	-54.4	-57.5	-51.8	-8.15	-8.34	-7.82
WP19	1165	1093	1234	7.3	7.2	7.5	-59.5	-62.5	-57.9	-8.87	-8.98	-8.76
WP20	917	873	990	7.2	7.1	7.4	-54.5	-54.9	-53.6	-8.10	-8.20	-7.98
WP21	829	750	884	7.4	7.1	7.5	-56.6	-59.8	-54.1	-8.34	-8.58	-8.15
WP22	782.4	624	891	7.7	7.5	8.2	-54.0	-56.7	-51.2	-7.68	-7.89	-7.44
WP24	882.5	622	1165	7.4	7.3	7.7	-57.2	-59.9	-54.9	-8.39	-8.65	-8.13
WP25	1216	903	1641	7.4	7.0	7.7	-59.7	-64.3	-58.1	-8.76	-9.04	-8.59
WP26	872	490	1242	7.7	7.4	8.0	-55.0	-59.7	-48.0	-7.92	-8.47	-6.55
WP28	448	253	880	7.2	7.2	7.4	-41.3	-54.6	-31.2	-6.71	-8.07	-5.27
WP29	1085	1036	1119	7.3	7.2	7.4	-55.9	-56.9	-54.6	-8.28	-8.32	-8.22
WP30	1177	768	1598	7.2	7.1	7.3	-55.0	-56.3	-53.5	-8.14	-8.30	-7.93
WP32	827	781	863	7.2	7.1	7.3	-52.5	-54.8	-51.1	-7.46	-7.58	-7.31

Table S3. Average major elements concentration in groundwater of Tidone Valley in Jul and Sep 2019

Well	**Al**		**Ca**		**K**		**Mg**		**Na**		**P**		**S**		**Zn**		**Cl**	
	mg L-1		**mg L-1**		**mg L-1**		**mg L-1**		**mg L-1**		**mg L-1**		**mg L-1**		**mg L-1**		**mg L-1**	
	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019	Jul2019	Sep 2019
WP 01	0.051	0.073	63	135	0.34	25.0	8.7	23.0	14	**260**	0.004	0.968	12	9.73	0.286	0.130	25	**540**
WP 03	0.022		58		49.66		48.6	28.0	68		0.002		55		0.376		123	
WP 04	0.010	0.030	27	130	0.72	1.5	36.1		39	36.	0.001	0.002	17	17.92	0.156	0.330	**407**	100
WP 05	0.019	0.023	69	114	0.98	1.7	53.7	33.7	40	27	0.001	0.008	57	44.49	0.166	0.182	**317**	65
WP 06	0.022	0.023	16	35	6.97	15.1	3.1	3.1	19	23	0.088	0.032	7	9.15	0.117	0.045	56	38
WP 07	0.016	0.027	36	83	1.30	3.0	39.3	40.7	112	110	0.006	0.006	43	43.01	0.169	0.084	**307**	164
WP 08	0.014	0.026	27	60	1.23	3.3	10.2	9.5	65	67	0.082	0.031	26	28.77	0.119	0.086	205	109
WP 09	0.012	0.027	38	70	1.63	3.8	13.5	10.4	21	32	0.014	0.019	24	32.88	0.195	0.079	30	18
WP 10	0.019	0.033	18	26	2.57	11.7	2.0	4.9	7	12	0.685	0.434	3	0.88	0.262	0.098	15	10
WP 11	0.031	0.020	65	135	39.84	73.4	53.6	48.1	156	134	0.012	0.007	97	108.92	0.267	0.110	**622**	235
WP 13	0.005	0.010	134	105	0.18	2.8	26.1	26.0	15	125	0.008	0.001	34	26.52	0.015	0.108	50	24
WP 14	0.004	0.022	111	159	0.80	2.3	12.3	10.3	12	12	0.001	0.006	22	22.81	0.026	0.158	21	18
WP 15	0.006	0.028	40	61	1.88	5.0	6.6	7.5	8	15	0.104	0.097	5	3.92	0.012	0.097	8	10
WP 17	0.008	0.023	8	14	0.57	1.9	0.6	0.9	1	4	0.197	0.066	1	1.58	0.040	0.087	0.2	5
WP 18	0.004	0.012	48	107	0.09	0.9	24.2	21.1	32	34	0.002	0.002	15	13.38	0.005	0.090	17	18
WP 19	0.005	0.022	81	159	0.86	0.8	27.4	21.5	121	18	0.001	0.009	68	60.68	0.007	0.140	54	39
WP 20	0.001	0.007	68	113	0.61	1.6	31.7	22.0	44	36	0.001	0.004	18	13.51	0.010	0.083	106	63
Wp 21	0.003	0.011	56	101	1.71	4.5	26.1	26.3	41	46	0.001	0.004	47	2.45	0.017	0.137	20	39
WP 22	0.009	0.019	114	135	1.87	3.7	20.3	17.8	17	20	0.006	0.006	42	36.82	0.022	0.087	68	49
WP 24	0.001	-	100	-	0.35	-	32.8	-	83	-	0.018	-	56	-	0.010	-	137	-
WP 25	0.004	0.017	64	111	6.88	35.4	28.6	46.8	29	65	0.030	0.040	58	89.38	0.010	0.126	11	30
WP 26	0.004	0.013	33	96	9.36	34.3	7.5	14.9	6	14	0.151	0.063	7	13.94	0.032	0.115	9	16
WP 28	0.002	0.030	41	20	5.18	3.5	14.5	3.8	19	9	0.037	0.021	8	1.79	0.010	0.079	21	8
WP 29	0.002	-	99	-	0.25	-	49.0	-	64	-	0.007	-	70	-	0.005	-	204	-
WP 30	0.004	0.026	75	165	0.64	2.7	28.2	34.5	44	70	0.005	0.005	37	56.45	0.026	0.158	86	82
WP 32	0.005	0.013	70	116	0.57	2.0	21.5	20.3	26	32	0.003	0.001	29	26.99	0.022	0.101	60	45

Note: Bolded numbers represents values above EQS for GW

Table S4. Average trace elements concentrations in the groundwater of Tidone Valley in Jul and Sep 2019

Well	Li		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		As		Se		Rb		Sr		Mo		Ag		Cd		Sb		Ba		Pb	
	µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1		µg L-1	
	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019	Jul2019	Sep2019
WP01	8	26	0.1	3.6	0.2	1.2	0.7	1.2	13.3	**169.2**	8.5	84.0	0.09	1.30	1.1	5.6	5.6	1.2	0.11	1.03	0.43	0.19	0.4	15.94	275	1315	0.23	0.30	0.03	0.03	0.03	0.007	0.24	0.10	849	423	0.18	0.39
WP03	36		0.1		1.3		0.4		0.3		1.8		0.05		1.2		1.7		0.31		6.76		3.9		1244		0.60		0.03		0.03		0.30		401		0.12	
WP04	14	16	0.1	0.2	0.2	0.1	0.4	0.3	0.1	1.2	1.4	7.0	0.04	0.06	1.3	1.2	0.7	1.2	0.07	0.09	1.86	1.37	0.3	0.40	309	1278	0.30	0.24	0.04	0.04	0.03	0.011	0.06	0.03	500	3344	0.07	0.16
WP05	18	21	0.1	0.3	0.8	0.4	0.8	0.8	2.4	24.9	4.3	10.0	0.12	0.39	4.0	4.2	1.7	4.2	0.23	0.26	0.98	0.37	0.7	0.67	375	1332	0.60	0.85	0.04	0.07	0.03	0.041	0.12	0.09	491	1231	0.19	0.24
WP06	9	14	0.2	0.1	8.3	9.7	1.7	2.3	0.8	0.5	6.3	5.0	0.07	0.13	1.8	1.0	14.3	7.8	1.96	2.20	0.37	0.28	6.2	8.34	151	345	1.16	1.13	0.04	0.05	0.05	0.027	0.25	0.34	580	1084	0.25	0.11
WP07	6	11	0.1	0.2	2.4	1.9	1.6	1.2	0.3	1.1	2.7	6.0	0.05	0.07	0.9	0.7	1.0	1.2	0.46	0.39	1.27	0.83	1.3	1.29	265	612	0.67	0.38	0.04	0.08	0.04	-0.004	0.15	0.08	498	1238	0.14	0.12
WP08	9	11	0.5	0.3	25.2	21.3	2.0	4.5	2.9	1.7	5.5	29.0	0.26	0.27	0.8	0.7	8.9	8.8	1.60	1.86	2.07	2.35	5.4	6.56	327	492	1.04	1.01	0.04	0.05	0.04	0.019	0.15	0.25	595	650	0.15	0.61
WP09	17	26	0.2	0.1	3.1	3.4	0.8	0.8	0.6	5.4	4.9	71.0	0.08	0.08	3.0	1.3	25.4	25.6	0.79	0.91	0.65	0.69	2.8	4.21	781	1144	1.09	0.99	0.02	0.03	0.03	0.012	0.21	0.15	800	851	0.15	0.11
WP10	2	10	0.5	1.6	0.7	1.0	0.7	0.3	26.1	**202.5**	14.7	**200.0**	0.06	0.09	1.3	1.2	4.8	1.4	0.70	0.27	0.11	0.03	4.1	6.30	83	279	1.64	0.20	0.04	0.03	0.04	-0.002	0.32	0.06	394	659	0.15	0.15
WP11	60	93	0.4	0.2	5.4	5.6	3.2	2.5	0.6	26.6	2.4	7.4	0.05	0.09	1.0	1.1	1.2	2.1	0.34	0.47	6.50	5.97	10.6	12.96	994	2049	0.89	0.88	0.03	0.02	0.03	-0.003	0.12	0.08	527	911	0.10	0.09
WP13	1	2	0.1	0.3	0.7	0.6	0.1	0.3	**165.9**	**154.5**	2.1	10.8	0.14	0.20	0.9	1.5	1.1	2.3	0.14	0.20	0.13	0.11	0.2	0.34	856	962	0.19	0.22	0.02	0.11	0.03	0.032	0.08	0.06	99	1254	0.06	0.27
WP14	11	14	0.1	0.4	0.3	0.8	0.1	0.3	46.9	**127.3**	2.6	19.0	0.23	0.26	1.7	2.9	7.3	13.7	0.13	0.22	0.55	0.76	1.7	2.40	708	904	0.20	0.30	0.04	0.12	0.03	0.027	0.15	0.16	98	798	0.04	0.29
WP15	4	7	0.8	0.8	1.4	0.8	0.3	0.3	**90.3**	**484.3**	12.1	197.0	0.28	0.26	3.1	3.7	7.2	3.7	0.94	0.77	0.22	0.05	2.4	2.82	304	488	3.44	0.20	0.16	0.02	0.12	0.003	0.37	0.05	53	657	0.14	0.17
WP17	1	2	0.3	0.7	4.3	3.6	0.3	0.5	5.5	21.9	7.6	31.2	0.06	0.11	0.6	0.8	99.2	127.3	0.29	0.37	0.11	0.04	0.9	0.93	41	86	0.66	0.24	0.08	0.08	0.04	0.014	0.26	0.18	20	830	0.50	0.70
WP18	6	12	0.1	0.3	0.2	0.2	0.2	0.5	0.5	1.8	1.1	7.5	0.02	0.05	0.3	0.4	0.3	1.0	0.07	0.09	0.30	0.32	0.2	0.27	470	1126	0.27	0.08	0.05	0.07	0.03	0.003	0.12	0.02	39	1193	0.05	0.08
WP19	28	57	0.1	0.1	0.1	0.0	0.0	0.2	0.1	0.2	1.1	4.1	0.01	0.03	0.3	0.8	0.6	6.9	0.04	0.03	0.63	0.50	1.4	1.51	1098	1618	0.25	0.14	0.01	0.06	0.02	0.001	0.13	0.01	29	1066	0.03	0.19
WP	7	12	0.1	0.1	0.5	0.5	7.5	6.1	0.2	0.6	0.9	4.3	0.	0.07	0.8	1.2	0.3	2.4	0.	0.11	1.	1.25	0.3	0.38	279	566	0.	0.14	0.	0.08	0.	-0.0	0.	0.02	104	13	0.	0.13

20													05						08		38						24		02		03	05	12			33	03	
Wp21	20	41	0.1	0.1	0.0	0.0	0.0	0.2	0.1	0.4	5.4	4.2	0.02	0.09	0.6	8.3	0.4	5.1	0.05	0.06	0.77	1.01	0.8	0.86	967	1780	0.59	0.44	0.04	0.04	0.02	0.018	0.13	0.03	35	1150	0.03	0.22
WP22	15	28	0.2	0.3	0.5	0.5	20.0	0.2	0.6	1.3	2.8	8.9	0.05	0.15	1.2	1.9	8.2	9.2	0.27	0.42	0.22	0.13	1.2	1.20	1199	1797	0.37	0.42	0.06	0.07	0.03	0.003	0.17	0.13	81	1095	0.16	0.16
WP24	6		0.1		1.3		0.3		**89.8**		1.6		0.74		2.9		1.6		0.71		0.23		1.6		645		0.43		0.04		0.03		0.16		50		0.28	
WP25	22	77	0.1	0.3	3.9	6.4	0.4	0.8	0.2	3.0	2.4	7.6	0.04	0.08	2.1	1.0	3.6	4.3	0.61	1.54	2.61	6.08	3.2	8.52	1556	2926	0.76	1.34	0.04	0.02	0.03	0.003	0.15	0.16	33	805	0.03	0.08
WP26	7	26	0.1	0.3	4.2	5.0	0.3	0.4	0.6	1.6	1.7	6.7	0.05	0.12	0.6	1.2	4.0	7.5	0.84	1.30	0.32	0.56	6.6	10.02	265	992	0.72	1.13	0.05	0.06	0.03	0.015	0.32	0.49	140	955	0.06	0.12
WP28	5	3	0.1	0.3	2.2	2.6	0.2	0.5	**175.6**	42.2	8.7	46.0	0.35	0.11	1.5	0.6	3.5	4.0	0.41	0.33	0.15	0.11	6.4	2.65	520	267	0.40	0.27	0.05	0.10	0.03	0.011	0.17	0.15	53	856	0.03	0.21
WP29	12		0.1		1.0		0.1		0.6		0.9		0.04		0.7		1.9		0.21		3.16		0.5		1582		0.26		0.05		0.02		0.20		39		0.02	
WP30	10	21	0.1	0.5	0.5	0.7	0.4	0.1	4.1	**81.9**	2.0	14.0	0.04	0.19	5.8	10.9	3.0	7.2	0.90	0.19	0.21	0.16	1.1	1.74	1022	2294	0.15	0.20	0.04	0.07	0.03	0.006	0.14	0.10	95	1321	0.05	0.14
WP32	10	19	0.1	0.1	0.2	0.2	0.2	0.3	0.1	0.4	1.4	2.7	0.16	0.16	2.4	2.1	0.9	14.1	0.09	0.11	0.56	0.76	0.4	0.48	521	1026	0.25	0.21	0.02	0.07	0.03	0.005	0.15	0.02	143	974	0.05	0.17

Note: Bolded numbers represents values above EQS for GW

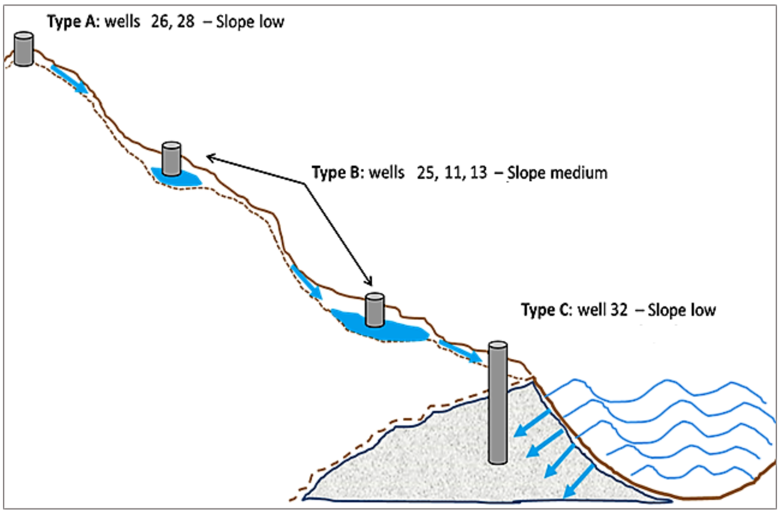

Figure S1: Conceptual model of shallow aquifer (CMA) (for more details see Suciu et al. 2020)

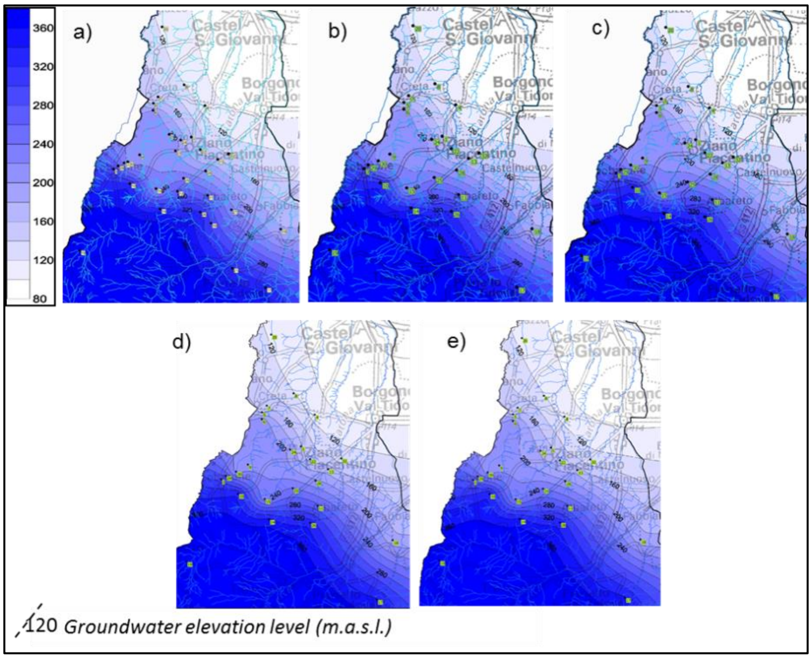

Figure S2 Piezometric maps of groundwater in Nov 2017 (a), Jul 2018 (b), Sep 2018 (c), Jul 2019 (d), Sep (e).

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Chapter 4

Multi-actor approach and engagement strategy to promote the adoption of Best Management Practices and a Sustainable Use of Pesticides for groundwater quality improvement in hilly vineyards

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Abstract

The adoption of pesticide mitigation measures and innovation at farm level, are seen as a drivers to reach the sustainable water policy objectives. With the aim to prevent the pesticide pressure of hilly vineyards on groundwater contamination, a stepwise approach in Tidone Valley was applied using different consultation mechanisms and involvement strategies throughout the overall process. Face to face meetings, direct surveys, participatory monitoring and planning of several activities aiming to inform, educate, improve skills, change of individual behavior or raise awareness, or even initiatives to build institutional trust or support for new investment in innovation are some examples. These activities allowed us to involve key actors of water use and governance (such as farmers, advisors, representatives of drinking water management, farmer's associations, Winemaking cooperatives, local Health Authority), and to have a deeper knowledge of the context agricultural practices, of farmer's knowledge and skills concerning factors influencing water contamination and also to promote the most suitable Best Management Practices aimed at limiting the pesticide occurrence in groundwater. Indeed, the survey’s results highlighted that the majority of the farms are small (64% of vineyards <10 ha), that most of the farmers (62%) are not aware of the current legislation on water, even if 64% of them declare to participate regularly to training courses for the prevention of water contamination and that there is a low to moderate level of adoption of Best Practices able to prevent contamination by pesticides. At the end of the overall process, it can be stated that the multi-actor approach and engagement strategy adopted were successful in improving attitudes to more sustainable practices. This is supported also by the monitoring data that show in 2019 a decrease by 44% of pesticides occurrences and a fall by 68% of values above EQSgw if compared with the period 2017–2018.

Keywords

Sustainable pesticide use, Engagement, Point source contamination, Groundwater

Abbreviations

SUD Directive on Sustainable pesticide Use

WFD Water Framework Directive

BMPs Best Management Practices

MM Mitigation Measure

PPPs Plant Protection Products

EQSgw Environmental Quality Standards groundwater

1. *Introduction*

Sustainable agriculture is a key objective of the European Union and a focus of its sustainable development policies. In this framework, adequate solutions are considered necessary to contrast negative impacts to human health and the environment, connected with the use of chemicals as pesticides. (COM 2003). At present, approaches are mainly based on regulatory interventions including the approval for placing on the market, after a very comprehensive risk assessment,, each active substance as well as the products containing that substance, with Regulation 1107/2009/EC, (EU 2009a) and for the use phase of pesticides in agriculture with the Directive on Sustainable pesticide Use (SUD), (EU 2009b), and the required National Action Plans, adopted by Member States that should contain quantitative objectives, targets, measurements and timetables to reduce the risks and impacts of pesticide use. This legal framework gives the possibility of implementing risk-mitigation measures to supplement the product approval conditions, with the aim to set specific practices of application of the products that will further limit human and environmental exposure. Awareness and understanding of the implication of labelling instructions is a critical factor, to ensure that products are applied according to the conditions designed in the risk evaluation process, so that to ensure that safety rules and protection goals are met (Alix et al. 2018). In parallel, the Water Framework Directive (WFD) is the principal legislative instrument for protecting water resources and to endorse sustainable water resource management at European level. Main challenges addressed by WFD are also found in other of the policy-oriented sustainability assessment approaches such as those promoted to achieve the sustainable use of pesticides (EU, 2000). The implementation of such legislation influences the production in the agricultural sector, but the effectiveness of these laws can be reduced or slowed by several factors. As stated in the latest report of Commission (COM 587/2017) the National Action Plans set in conformity the SUD "suffer from delays, are developed mechanically to strictly comply with a pre-set list of measures, resulting in minimal changes in practices and with not sufficient impact to preserve or restore water quality". Member States are currently working on reviewing their first plans although there has been substantial progress, the report identifies that there are significant gaps in many areas of the plans, for example in relation to [..] "information to the public, the gathering of information regarding poisoning cases, measures to protect the aquatic environment" (COM 587/2017). In Italy, despite the various measures taken to prevent or to minimize the impact of agricultural activity on water contamination, the results of pesticides water monitoring reveal, in several cases, an inadequate quality of the aquifers and surface water, limiting the achievement of national WFD objectives. Some compulsory measures like training, storage, equipment inspections or respect of non-spray zones are in place at national level, but their effectiveness cannot really be assessed since it is not possible to understand if they have been implemented properly by all farmers. UC Davis Agricultural Sustainability Institute states that "making the transition to sustainable agriculture is a process. For farmers, the transition to sustainable agriculture normally requires a series of small, realistic steps. Family economics and personal goals influence how fast or how far participants can go in the transition"(Feenstra, 2016). Recent review on factors influencing farmer's adoption of Best Management Practices suggest to focus on study scale, including micro (farms) scale, on measuring and modelling of adoption as a continuous process, and on incorporation of social norms and uncertainty into decision-making (Tingting Liu, 2018). The adoption of mitigation measures and innovation at farm level, is seen as a strategy or driver to reach the sustainable policy objectives. But different problems in addressing the challenges are present, especially at farm level. It is supported by a recent growing body of literature, that sustainable agriculture is not the result of a simple linear, one-way process that goes from the scientific production of technics or knowledge to its application, but the result of complex "systemic interactions" between different subjects involved in various ways (GCSA, 2014). The community involved in pesticide risk analysis and pesticide use is highly diverse, including all interested and affected parties such as regulatory risk assessors, risk managers and risk communicators as well as applicants for product authorization, the wider scientific community, consultants and farmers. Several EU research projects (eg. BROWSE, HEROIC), given the enormous variability and uncertainty associated with the behavioral component that characterizes the pesticide use activity, agreed that there is a need for improvement in measuring different stakeholders risk perception to increase trust in the pesticide risk evaluation process, and then the pesticide use according to the conditions designed in the risk evaluation process and in the labels. Research in HEROIC project highlight that socio-behavioral aspects are not generally addressed except for very few cases, and commonly, it is argued that engagement in unsafe pesticide use and disposal practices is the result of a lack of knowledge and misperceptions of the risks associated with pesticides amongst operators and workers (Calliera, 2016). Research in EU Browse project regarding Operators, revealed several short-comings in terms of appropriate behaviour (mainly concerning wearing appropriate PPE, use of the recommended spray volume, compliance with wind speed limits and applying of measures to avoid and address unintended events during application, variable linked to climate condition) (Sacchettini, 2015). Recent works analyse farmer's risk perceptions regarding pesticide use (Remoundou, K,2014) to stimulate their sustainable behaviour and compliance to Good Agriculture Practice (GAP) as written in the pesticide labels. In all these projects and research, a participative and inclusive approach is considered as necessary in all phases of the relationship with stakeholders, in a bottom up perspective starting from a deep understanding of the farmers realities and behaviour of the various actors, to more interactive communication and demonstration strategies, up to training activities that overcome the traditional top-down (from expert to farmers) approach and consider local knowledge as an important key for the transition towards sustainability (Calliera, 2018). This paper complements this stream of works by evaluating the farmers intentions to adopt sustainable agricultural practices to limit or prevent water contamination and by analysing the bottlenecks in their implementation. The study is part of a broader project on water governance, funded under the EC program H2020, WATERPROTECT, which aims to contribute to a better knowledge and understanding of how water governance is organized at catchment level and how the agricultural activities can be improved in order to limit their impact on drinking water. The Italian case study considers three catchments in Tidone Valley, northern Italy, characterised by an intensive viticulture production. In particular, the present study aims to develop a communication and engagement strategy effective in providing good agriculture practices and a comprehensive and acceptable list of pesticide mitigation measures able to prevent or limit the pressure of hilly vineyard cultivation on groundwater contamination in Tidone Valley. In the following paragraph will be described the engagement methodologies, the strategies, the analysis of point source and diffuse source of water contamination at context level and also the strategies adopted to reduce the water contamination.

2. *Materials and methods*

2.1 Area of study: Tidone Valley

The study area is Tidone Valley, located in the north-west of Italy in Emilia Romagna region, in the province of Piacenza (Fig 1). The landscape variety of the province influences its agricultural productions, particularly extensive in the plain; viticulture has been properly focused and established in the hilly area. Indeed, Tidone Valley represents a hilly zone characterized by an elevation level between 100 and 350 m above sea level and it is known for the deeply rooted tradition and vocation to viticulture. As described by Zambito et al. (2020) the area is characterized by a mix of urban, peri-urban and rural areas and covers five municipalities for a total of 28.548 inhabitants (10% of total province inhabitants). The main culture is vines, with 2.941 hectars in 2016 (75% of total ha of the province) and the inhabitants of the rural villages are mainly involved in grape and wine production, organized as private farms or as wine cooperatives. The peculiar orographic features of the territory have determined the development and adoption of agricultural/hydraulic plumbing systems that represent a sort of mitigation measure applied in order to limit the erosion and control the water speed, slowing down the water flow that shapes hills, turning them into an orderly sequence of longitudinal lines.

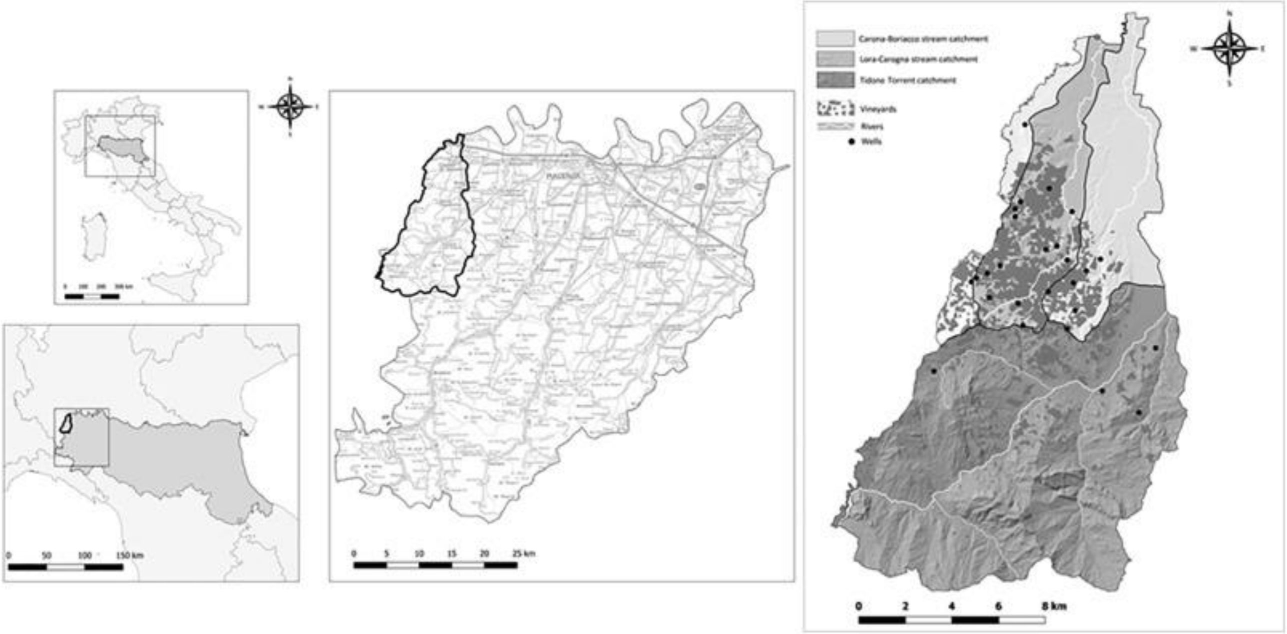


Fig 1. Area of study: Tidone Valley

In total 455 farms were present in 2017 in the study area (CCIAA, 2017 https://www.pc.camcom.it/, data available on request). Two types of farms structures are present:

1. Vineyard with a cellar. In this case, grape transformation into wine and wine retail is independent. This is the case for 25% of the total vineyards present on the investigated area;
2. Vineyard without a cellar. In this case, grape growers deliver their grapes to wine cooperatives. This is the case for 75% of the total vineyard surface present on the investigated area. The situation is characterized by many farms with small/medium vineyard area and few farms with a very large vineyard area.

The groundwater in the area is rather susceptible to this production, as demonstrated by Zambito et al. (2020) that shows the occurrence of pesticides used for grape cultivation in 80% of a total of twenty-six groundwater wells monitored in the period November 2017 – September 2018. In addition, 30% of the twenty-six groundwater wells have values for seven pesticides above the Environmental Quality Standard (EQS) for groundwater. Suciu et al. (2020) highlighted that these occurrences and concentrations are related to both diffuse and point source contamination, with the point source having an important contribution for the wells located in low slope soil, where the water drainage and its lateral movement are low.

2.2 Community engagement and stakeholders participation at the scale of study area

A complex socio-ecological issue such as water quality related to agriculture cannot be solved by just one actor but rather from a multi-actor approach perspective (Els Belmans, 2018). As stated in the introduction, sustainable agriculture is the results of complex "systemic interactions" between different subjects involved in various ways , such as researchers, farmers, entrepreneurs, regional and national organizations etc. All of them have different forms of knowledge (practical, scientific, policy based, etc.) and there is the need to create conditions for interaction between them and combine their knowledge, perspectives, resources, and experiences, to identify and discuss solutions and new ideas. Therefore, in the present study, all actors considered to have an influence on, or that are influenced by, the water and the farming systems were engaged in the study activities. Since it is recognized that at context level an "ideal approach do not exist ", in our study the engagement design was conceptualized as an "active engagement". All stakeholders that adequately represent the views of the broader community were engaged, interviewed, involved in the process of collecting data and spreading the information. The bilateral conversation and multi-actor conversation were fundamental in establishing effective and productive relationships to enable a shared understanding of goals or a shared commitment to change and to ensure that public and farmers concerns and aspirations are understood and considered. To be as efficient as possible, and with the purposes to (i) increase the knowledge concerning the level of pollution, (ii) increase the awareness concerning the pollution prevention (iii) facilitate the access BMPs and training and increase the interactions with the experts, it was decided to adopt a stepwise approach that included both water quality analysis and stakeholders analysis, with different levels of participation that range from the consultation to the active involvement, as described in Figure 2.

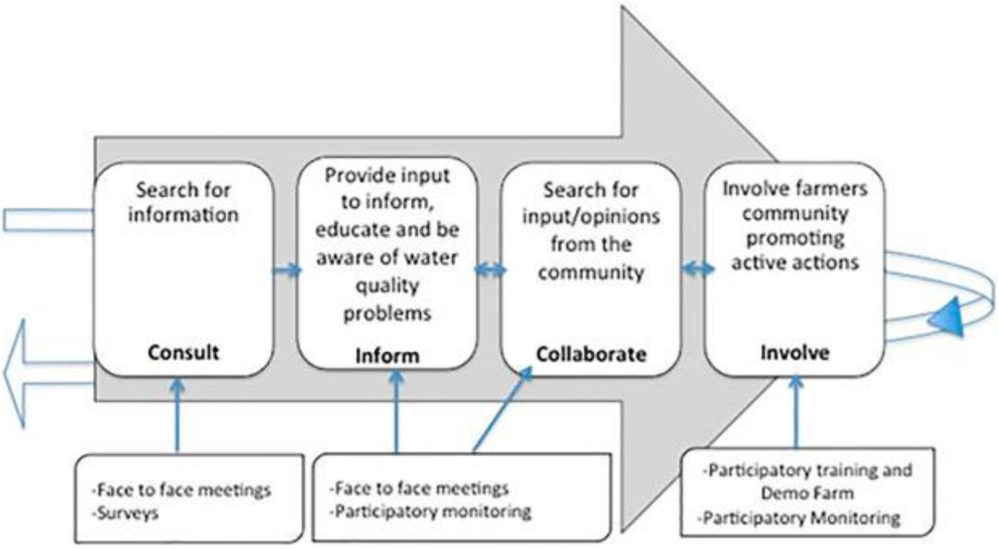


Fig 2. Stepwise approach and levels (in bold) of participation

This approach led to a range of different strategies throughout the overall process, such as face to face meetings, direct survey, participatory monitoring and the planning of several activities aiming to inform, educate, improve skills, change of individual behavior or raise awareness, or initiatives to build institutional trust or support for new investment in innovation and synthetized below.

- The face-to-face meetings (such as seminars, workshops, community events, or site tours) are a qualitative "dialogue-based method". The advantage is that it allows greater spontaneity and interaction between the researcher and participant, who has the opportunity to respond more elaborately and in greater detail. In turn, researchers have the opportunity to respond immediately to what participants say by tailoring subsequent questions to information the participant has provided (Calliera, 2016). This method was adopted throughout the project to obtain information, provide information and knowledge, give adequate and accessible information on the project and on the course of the process, and also to exchange opinions.

- Surveys are questionnaire-based quantitative tools, where stakeholders are requested to individually answer questions by choosing from a limited number of provided answers. Because there are only multiple-choice questions, it represents an efficient way to obtain sufficient data in a short time. However, as a passive consultation method, it doesn’t allow a deeper discussion (Calliera, 2016). The surveys in the study were conducted by trained survey operators, to ensure the ‘consistency’ of the responses. This methodology was adopted in the first phase of the project in order to obtain information on the existence in the study area of groundwater wells, on best management practices and pesticide mitigation measures already implemented to avoid diffuse and point sources water contamination and on the willingness to implement new proposals, but also on the interest of farmers to participate in the project.
- Participatory monitoring. In Italy monitoring is usually conducted by environmental agencies (in our case ARPAE) and designed for the status evaluation and trend assessment of water bodies in respect to WFD and are not planned to assess the effectiveness of the measures introduced to prevent or limit the inputs of pollutants. The engagement of farmers in the design and the setup of water monitoring, as well as in the results of the monitoring through the appropriate ICT tools and monitoring apps available in the project website (https://water-protect.eu/en), are fundamental to increase the credibility of the monitoring data and help to reduce the information gap between farmers and monitoring agencies (Els Belmans, 2018).
- Participatory training approach and demonstration farm. In Italy a system of compulsory certified trainings for professional users, distributors and advisors is established by the National Action Plan as requested by the Directive on Sustainable pesticide Use 2009/128/EC (EC, 2009). The competent Regional or Provincial authorities shall assess the knowledge acquired by course participants by means of an examination. However, as reported in the Standing Committee on Agricultural Research (SCAR; 2015) report, this method of teaching does not necessarily imply a change of behaviour or adoption of

innovation, especially in agriculture. Indeed, traditionally, for farmers the changing of farming management practices is full of risks (eg. economic) that have to be managed. To be effective, a context specific training should understand how farmers make up their decisions and link knowledge to actions to identify the so-called training need that is “the gap between what is and what should be in terms of incumbents’ knowledge, skills, attitudes, and behaviour for a particular situation at one point in time" (FarmPath project; 2014). These activities have also been associated with recreational events such as dinners, concerts, scientific coffees; this is to encourage the aggregation and sharing of different experience (students, professionals, citizens, etc.) and to increase the awareness of the community about the efforts and commitment necessary to achieve a more equitable and sustainable future, where at the centre there is the figure of a responsible farmer.

2.3 Stakeholders involved

The stakeholders involved as key actors were met individually during the first phase. This occurred thanks to the presence in the working group of individuals operating in the area who have a good reputation and credibility from previous work carried out in the territory, like the regional environmental Agency - ARPAE-ER, the consumer Association PiaceCiboSano – APCS and the Catholic University - UCSC.

The key actors engaged were: the regional drinking water management company – IRETI, the provincial plant health farmers consultancy - Consorzio Fitosanitario Provinciale, the three farmers’ associations present on the territory - Confagricoltura, Coldiretti and CIA, the local manager of irrigation water in Val Tidone catchment - Consorzio di Bonifica, one of the two Wine cooperatives present in the territory - Vicobarone, the farmers’ organization Consorzio Vini Doc Colli Piacentini and the local Health Authority - AUSL. All were contacted by phone or by email, interviewed and involved in the process of collecting data, of contacting and engaging grape growers, spreading both the information and the work progress as well as the outputs. Finally, with their contribution were involved 175 grapegrowers, coming from: 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 areas and municipalities, 12.5%. However the selection of strategic places and time periods was fundamental for farmers engagement. Indeed, in the first phase 97 farmers were met during the grape delivery at the Wine cooperative Vicobarone, in the structures of the social cellar, while 40 farmers were met in the offices of farmers unions Coldiretti, Confagricoltura and CIA, during the declaration of the quantity of grapes produced. Finally, the remaining 38 were met directly in the estates or by phone. Also newsletters and media campaigns, with articles in local newspapers were used as instruments for information purposes on the initiatives.

In a second step, the regional and catchment leaders of water governance, Emilia-Romagna Region and catchment Authority of Po River, ADPO, were involved. For their involvement, the use of preliminary data from groundwater monitoring and surveys about farmer's practices was fundamental.

2.4 Strategies adopted for farmer engagement and the analysis related to sustainable use of pesticide

2.4.1 Surveys - conceptual framework

Sustainable water management shall ensure the achievement and maintenance of the good water status, meeting legal and/or agreed quality standards in all affected river basins, as requested by WFD (EC, 2000). Water pollution is a global challenge and agriculture represents in many cases a pressure on water quality, mainly due to the use of pesticides. Water contamination by pesticides used in agriculture could be caused by both diffuse and point sources contamination, the latter should to be considered mostly accidental. Good Agriculture Practices and Mitigation Measures are key components in defining the conditions of use of pesticides in crop protection strategies. They are specific to the type of risk they intend to mitigate, for example, they may consist in a recommendation for special protection for users while handling the product, or to adjust the conditions of use to minimize transfers to groundwater.

Based on the conceptual framework, in the project several hypotheses are put forward to be tested. The list of the hypotheses is as follows:

- viticulture could be a source of water quality pressure the study area;
- farmers are not aware of the current and local legislation on water;
- farmers are not aware of local monitoring data for pesticides and nitrates in surface and groundwater;

- farmers are not aware of good practices and mitigation measures efficacy in limiting or preventing water contamination;
- compulsory training courses on sustainable pesticide use needs to be improved.

In detail, water contamination by pesticides could be caused by both diffuse and point sources contamination, the latter should to be considered mostly accidental. In order to understand the contribution that the farming system of our study area can have on water quality, two survey campaigns were carried out. The first was undertaken between August - November 2017, and the second - in the period of March - May 2018. The dates on which the surveys were carried out are directly connected to the starting time of WaterProtect project and to the availability of the farmers, who were more available in that period as the work in the vineyards is less pressing. Questions related to the type of grape cultivation (following the integrated pest management), number of PPP applications and type of PPPs (insecticides, fungicides and herbicides) and the management of point sources contamination were included in the questionnaire submitted in the first survey while the second survey focused mainly on mitigation measures and good agricultural practices for limiting or preventing drift and runoff for hilly vineyards (with a slope> 2%) .

2.4.2 Survey 1

Data collection took place through face-to-face interviews conducted by trained survey operators and involving 175 farmers, 38.5% of the total farms acting in the study area. The respondents were informed about the survey goals before the interview and farmers were interviewed on the basis of their willingness to participate in the project. To reach a higher number of respondents, a mixed tools and approach were adopted (such as direct interviews in farms, in the Cellars, indirect interviews by phone call, one line questionnaire...). Indeed, 97 farmers were interviewed during the grape delivery to the Wine cooperative Vicobarone, in the structures of the social cellar, while 40 farmers were interviewed in the offices of farmers unions Coldiretti, Confagricoltura and CIA, during the declaration of the quantity of grapes produced. Finally, the remaining 38 were interviewed directly in the estates, by phone and for farmers whose familiarity with IT tools was known, an on-line questionnaire was submitted. The questionnaire was composed by 24 multiple-choice questions and was divided in the following four different parts:

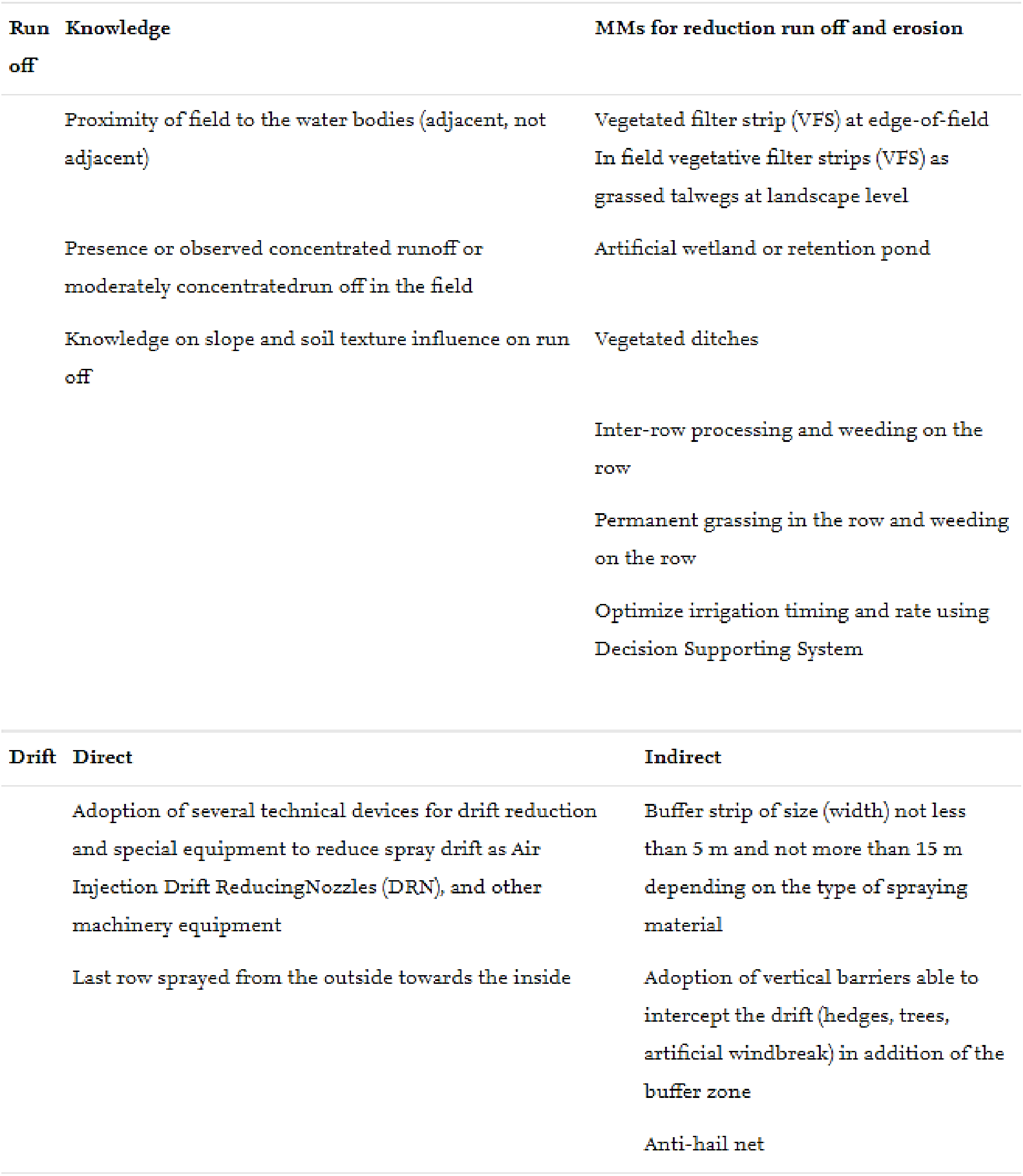
- Presence of wells, depth, use of well water;
- Fertilization and phytosanitary treatments: use and frequency;
- Sustainable pesticide use and prevention - respect of good practices and mitigation measures;
- Knowledge and awareness of the problem (possible pressure of viticulture on ground water quality).

The frequencies of the observations for homogeneous groups was analysed using Microsoft Excel. Observation of BMPs, correct behaviors in the pesticide management at farm level and adoption of innovative technologies as bioremediation systems were selected as measures with high level of efficacy to limit or prevent point source contamination. Some measures, such as sprayer technical inspection, were not taken into account in the survey, as mandatory under Directive 128/2009/EU and subject to official inspections and sanctions. Indeed, regular technical inspection of pesticide application equipment is compulsory by Article 12 of Legislative Decree 150/2012, and shall be performed by dedicated Test Centres. In addition to that, professional users shall conduct adjustments and calibrations of equipment used, in order to ensure pesticide mixtures spraying in correct amounts and equipment's proper working conditions, thus guaranteeing high level of safety and protection for both human health and environment. For this reasons questions on these topics were not included in the questionnaire.

2.4.3 Survey 2

Out of the 175 farmers involved in the first survey, fifty farmers were selected and involved in the second survey, based on the interest showed for the present research and the size of their vineyards, possibly adjacent to the monitoring wells. In particular, 30 farmers have vineyards with less than 10 ha surface area (62% of total farmers), 18 in between 11 and 40 ha (36% of total farmers) and only 1 farmer has a vineyard with a surface area higher than 40 ha. The total acreage of land whose owners responded to the questionnaire was 599 ha. The frequencies of the observations for homogeneous groups was analysed using Microsoft Excel. MMs selection was carried out using as reference the MagPie toolbox (MAGPIE SETAC; 2017) and the latest available version of the Italian Ministry of Health Guidance Document on the topic (Azimonti, 2017) and following four main criteria: (i) applicability at our landscape conditions, (ii) availability for implementation, (iii) sufficient knowledge/level of confidence and strength of scientific evidence, and (iv) possibility to demonstrate or measure the efficacy of the GAPs and MMs to support their implementation. The MMs and BMPs selected and suggested in the survey to limit or prevent diffuse contamination in vineyard with slope >2% are listed in the Table 1. The runoff MMs selected and monitored in the survey have a high level of efficacy as they are located near the runoff source or where runoff/erosion starts (as for Vegetated Filter Strip), and/or may provide additional benefits for soil conservation and erosion prevention and for reduction of nitrate leaching. For drift two type of drift reduction strategies were identified: no spray zones and use of spray drift reduction technology. As stated in literature, the selected and monitored mitigation measure allow high percentage of drift reduction (MAGPIE SETAC; 2017).

Table 1. MMs and GAPs selected and suggested to farmers reduce water contamination due to run off and drift at catchment level.



Run off	Knowledge	MMs for reduction run off and erosion
	Proximity of field to the water bodies (adjacent, not adjacent)	Vegetated filter strip (VFS) at edge-of-field In field vegetative filter strips (VFS) as grassed talwegs at landscape level
	Presence or observed concentrated runoff or moderately concentratedrun off in the field	Artificial wetland or retention pond
	Knowledge on slope and soil texture influence on run off	Vegetated ditches
		Inter-row processing and weeding on the row
		Permanent grassing in the row and weeding on the row
		Optimize irrigation timing and rate using Decision Supporting System

Drift	Direct	Indirect
	Adoption of several technical devices for drift reduction and special equipment to reduce spray drift as Air Injection Drift ReducingNozzles (DRN), and other machinery equipment	Buffer strip of size (width) not less than 5 m and not more than 15 m depending on the type of spraying material
	Last row sprayed from the outside towards the inside	Adoption of vertical barriers able to intercept the drift (hedges, trees, artificial windbreak) in addition of the buffer zone
		Anti-hail net

Therefore, the survey's aim was to select the measures most fitting to our vineyard conditions and to obtain information for:

- Farmers knowledge about factors influencing run off and drift and skills or ability to identify specific risk situations. The knowledge of the factors involved in the contamination processes allow to adopt behaviours or structural changes aimed at limiting and controlling the occurrence.

- Existence in loco of selected MMs and farmers knowledge and skills for MMs implementation and management, acquired through experience or education, and MMs efficacy in limiting the contamination;
- Farmers motivation and availability to implement the MMs suggested and, if not, their motivations and barriers.

2.5 Monitoring activities within the study area in the framework of participative engagement

The focus of the monitoring campaigns was the occurrence of pesticides in groundwater, resulted relatively exposed to pesticides used for grape production, as demonstrated by Zambito et al. (2020). Therefore, in our strategy, in order to achieve a change, farmers must first of all, be aware of the problem of water quality, independently of the social pressure. Indeed "risk is what matters to people" (Renn, O. 1998). Typically individual is willing to accept a higher risk if it is associated with a personal benefit (e.g. pharmaceuticals). Vice versa people are much more risk averse when they do not expect a direct personal benefit (e.g. concerns about pesticide application) (Wilks, 2015). Being themselves users of groundwater for drinking purposes or personal care, farmers perceive drinking water quality as an important issue. Therefore, if data presented to them is related to drinking water in a communication context aimed at raising awareness and risk-benefit considerations, farmers could be more motivated in adopting technical practices or behavioural change improving their environmental performance. This is why, in order to increase farmers interest on the monitoring campaign and data, they were engaged in the development of wells monitoring network and selection of pesticides to be monitored In addition, to collect data on PPPs with the highest use and sale in the study area an expert judgement consultation was conducted. All the obtained information, was then compared with the indications given by the Integrated Pest Management guidelines of Emilia-Romagna Region (http://agricoltura.regione.emiliaromagna.it/produzioni-agroalimentari/temi/bio-agro climambiente/agricoltura-integrata/disciplinariproduzione-integrata-vegetale/Collezione-dpi/2019/norme-generali-2019) for the active ingredients authorized for grapevine cultivation and the most recent data concerning the active ingredients quantity sold in Emilia Romagna Region. Collection of data about the main diseases affecting the grapevine, through interviews with the technicians of the Provincial Plant Protection Consortium and other local stakeholders, allowed the identification of the pesticides mostly used in the study area. For more details on pesticides selection and monitoring outputs refer to Zambito et al (2020). However, the list of pesticides monitored, the application frequency and amounts, the occurrences and amounts in groundwater, as above or below the Environmental Quality Standard for groundwater (EQSgw), and the information on their hazardousness for both human health and environment are summarised in Tables 2 and 3. The ISTAT data, elaborated by AAAF (Gruppo di lavoro Fitofarmaci) group, concerning the active ingredients quantity sold in Emilia Romagna Region in 2012 (no other recent data was available) confirm the high use of our monitored PPPs in Emilia-Romagna Region, with values ranging between 16 kg (Cyflufenamid) and 117069 Kg (Chlorpyrifos)

Table 2. List of pesticides monitored, their frequency and quantity of use and occurrences in groundwater.

Category: pesticide	**Frequency (max)**	**Amount**	**Detected in water monitored**[d] **(yes/no)**	**Over the legal limits (yes/no)**
Chlorpiriphos	1 per year[a]	360 g/ha[a]	Yes	Yes
Chlorpiriphos-methyl	1 per year[b]	230 g/ha[b]	Yes	No
Chlorantraniliprole	1 per year[a]	54 g/ha[a]	Yes	Yes
Cyflufenamid	2 per year[a]	25 g/ha[a]	Yes	No
Cyprodinil	2 per year[b]	300 g/ha[b]	No	No
Dimetomorph	3 per year[b]	250 g/ha[b]	Yes	Yes
Flufenacet	4 per year[a]	1.350 g/ha[a]	Yes	No
Fluopicolide	3 per year[a]	133 g/ha[a]	Yes	Yes
Isopropalin[c]			No	No
Metalaxyl-M	3 per year[a]	97 g/ha[a]	Yes	Yes
Metsulfuron-methyl	3 per year[a]	6 g/ha[a]	Yes	No
Penconazole	3 per year[a]	40 g/ha[a]	Yes	Yes
S-metolachlor	1 per year[a]	1920 g/ha[a]	Yes	Yes
Tetraconazole	3 per year[a]	30 g/ha[a]	Yes	Yes
Tribenuron-methyl	3 per year[a]	30 g/ha[a]	No	No

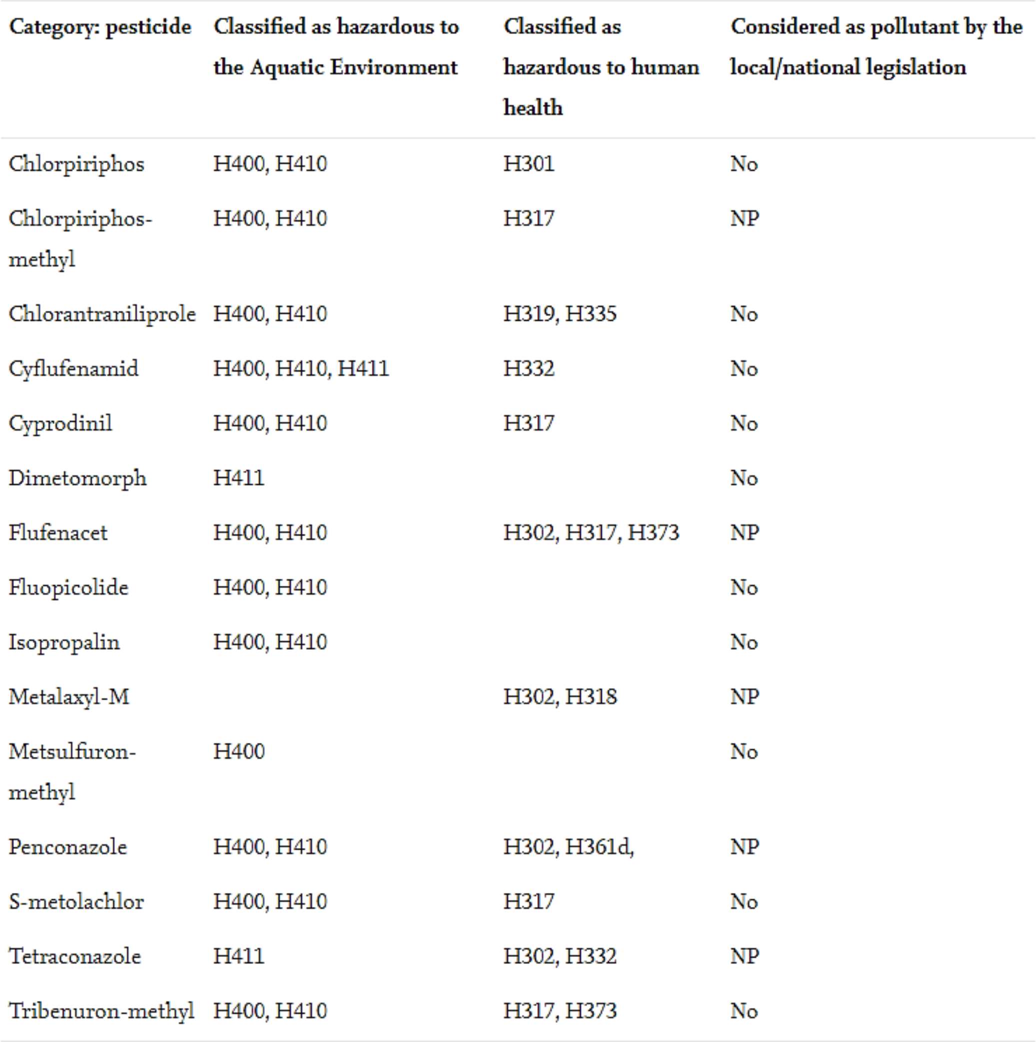
[a] The frequency and amount values derive from EFSA peer reviews.

[b] The frequency and amount values derive from label.

[c] Revoked.

[d] Sampling campaigns were made from November 2017 to September 2019.

Table 3. Pesticide monitored in the catchment and additional information for communicative program.



Category: pesticide	Classified as hazardous to the Aquatic Environment	Classified as hazardous to human health	Considered as pollutant by the local/national legislation
Chlorpiriphos	H400, H410	H301	No
Chlorpiriphos-methyl	H400, H410	H317	NP
Chlorantraniliprole	H400, H410	H319, H335	No
Cyflufenamid	H400, H410, H411	H332	No
Cyprodinil	H400, H410	H317	No
Dimetomorph	H411		No
Flufenacet	H400, H410	H302, H317, H373	NP
Fluopicolide	H400, H410		No
Isopropalin	H400, H410		No
Metalaxyl-M		H302, H318	NP
Metsulfuron-methyl	H400		No
Penconazole	H400, H410	H302, H361d,	NP
S-metolachlor	H400, H410	H317	No
Tetraconazole	H411	H302, H332	NP
Tribenuron-methyl	H400, H410	H317, H373	No

NP = Considered as pollutant by the local/national legislation, Hazard statement is designated as code, starting with the letter H and followed by three digits. Eg. H4xx refer to aquatic Environment and H400 and H410 means respectively Very toxic to aquatic life and Very toxic to aquatic life with long-lasting effects. H3xx refer to human health and H302 means Harmful if swallowed, H317, H318, H319 respectively May cause an allergic skin reaction, eyes damage, eye irritation, H332 Harmful if inhaled, H373 May cause damage to organs through prolonged or repeated exposure. (http://www.appa.provincia.tn.it/fitofarmaci/programmazione_dei_controlli_ambientali/Criteri_vendita_prodotti_fitosanitari/pagina123.html). The EQS groundwater for the active ingredients correspond to the limit for drinking water and is 0.1 μg/L. The contextualisation of the monitoring results, by giving the information collected and presented in the Tables 2 and 3, should improve the results communication in the process of participatory water governance, towards farmers and citizens.

3. Results

The involvement of all the actors of the study area, having a role in water governance and water use, allowed us to characterize the territory, to have a deeper knowledge about agricultural practices, farmers knowledge and skills concerning pesticides handling and water protection but it also allowed us to promote the most suitable MMs and BMPs. The main outputs of the two surveys and of the participatory activities are presented in the following sections.

3.1 Survey 1

The total acreage of farms, of which owners responded to the questionnaire, was 1088.2 ha. In particular, 64% of vineyards are less than 10 ha surface area, 25 % of vineyards are between 11 and 39 ha surface area, 7,5% of vineyards are more than 40 ha surface area and 3,5 % didn't give an answer. 44 % of the farmers follow the integrated pest management guidelines for grape cultivation and in 107 farms there is a groundwater well, used for drinking (8 %), irrigation (18 %) and for treatments mixtures (80 %) and only small percentage is not used (4%). For 88% of the respondents the PPPs treatments carried out within a year are less than 10, mainly fungicides and insecticides, while 95% of them haven't been involved before in projects or actions that concern the prevention of water contamination. Furthermore, 62% and 90% of farmers are not aware of the current legislation on water and of monitoring data for pesticides and nitrates in surface and groundwater in Val Tidone, respectively, even if 64% of them declare to participate regularly/have participated in training courses concerning the prevention of water contamination.

Lack of information exchange between farmers in Val Tidone on water contamination as well as the existence of geographical information systems (GIS) that allow to visualize the vulnerability of water to pesticides, was highlighted by 80% of famers. However, 50% of them are not interested in using such tools and 66% do not perform farm analysis to identify built-up areas, areas frequented by the population and protected natural areas. A regional resolution has recently been approved (Resolution of the Regional Council n.2051 of 03 December 2018, which replaces the previous Resolution n.541 of 18 April 2016) which, as required by the PAN, incorporates specific obligations regarding these issues at local level. This information has become part of the compulsory course program. Finally, 54% of farmers expressed interest for participation to information and training courses and 40% allow the use of their well for monitoring PPPs and nitrates occurrences in groundwater.

Regarding the answers to questions related to point source contamination, the results pointed out that:

- Sprayers washing in dedicated areas equipped with waste water recovery or disposal systems are present in 39% of farms;
- Dedicated areas for mixing and filling sprayers are present in 44% of the farms. Of these, 19% are used for both sprayer washing and waste management at the end of the treatment while 28% are used just for external sprayer washing;
- Storage of pesticides in appropriate places and proper disposal of containers are applied by 90% of respondents. Correct handling and appropriate storage of plant protection products and for treatment of their packaging and remnants is compulsory. By 1 January 2015 all professional users have to comply with provisions of Annex VI of the Italian National Action Plan; these obligations are easily controllable and linked to sanctions for non-compliance;
- 40% of farmers are interested in the adoption of bio purification system to treat the wastewater collected after sprayer washing. It is significant that almost half of farmers are willing to do more to protect the environment going beyond existing rules.

3.2 Survey 2

he results of the second survey, in which questions about 14 MM and BMPs able to reduce diffuse sources contamination of groundwater were made, highlighted that:

- 88% of respondents are familiar with factors that affect runoff, eg. slope and soil type and 58% recognize the need for a water body/well to be safeguarded from a runoff. In Italy professional farmers undertake compulsory trainings in these issues by certified training companies; before 2016, the legislation reserved the purchase of pesticide classified and labelled as very toxic, toxic and harmful exclusively to people holding the authorisation to purchase and use them. From that date on, through the compulsory courses (every 5 years) foreseen by National Action Plan and in line with the contents of Directive 2009/128/EC, it was possible to start raising awareness about environmental issues of all professional pesticide users.

- The Vegetated filter strip at edge-of-field is applied in 52% of farms. However, in some cases it is used for passage of vehicles (inaccurate knowledge) while in other cases it was already present as hydraulic arrangements;
- Vegetated ditches are present in 78% of farms and are considered effective in containing runoff. In general respondents are not concerned about runoff that is perceived of moderate intensity. Respondents believe that measures taken (hydraulic arrangement, drainage channels, good field practice such as Inter-row processing and weeding on the row) are sufficient to contain the phenomenon;
- Barriers are present in 24% of farms and are considered effective in containing drift;
- A buffer strip of size (width) not less than 5 meters and not more than 15 meters is applied by 97% of respondents. Non spray buffer zone is compulsory in Italy if specifically indicated in the label;
- Air injection drift reducing nozzles are used by 52% of the respondents. In general, technical devices for drift reduction and special equipment to reduce spray drift are considered effective in reducing drift exposure although adoption is not always easy due to the widespread use of pneumatic sprayers in the area;
- Nutrient soils analysis for pH, macro elements, organic matters and C/N are performed by almost 50% of respondents and are used for fertilization planning;
- Weed control is undertaken by 44% of farmers. Of these, 73% apply a good practice of inter-row processing and weeding on the row, while the rest use permanent grassing in the inter row and weeding on the row. Grassing between rows (at least alternate) is increasingly popular and is adopted for quicker and more effective phytoiatric strategy and thus to reduce the number and use of pesticides.

3.3 Participatory monitoring, participatory training approach and demonstration farm

Based on the results from Zambito Marsala et al. (2020) and Suciu et al. (2020), that evaluated the occurrence of the 15 PPPs in groundwater and the possible contamination sources, an impact of end-users behavior on PPPs concentration in groundwater was highlighted. However, even if after three sampling campaigns, between November 2017 and September 2018, 153 occurrences of PPPs were observed in the 78 collected samples (38 values were above EQSgw), in the last two sampling campaigns, between July and September 2019, just 69 occurrences of PPPs were monitored in the 53 collected samples, with 9 values above EQSgw. Therefore, in 2019 a decrease by 44 % of PPPs occurrences and by 68% of values above EQSgw were observed. In the framework of participatory monitoring strategy, maps, results and graphs are produced and are all available on the project platform at the link: (https://water-protect.eu/en). Indeed, a GIS Platform was developed within the project, in which it is possible to consult the results of the monitoring studies. These data, together with the survey outputs, were presented during participatory training events, organized with the scope to facilitate the spread of sustainable practices, to prevent point sources contamination and, at the same time, to promote a coherent and harmonized approach that can facilitate the birth of useful collaborations and tangible synergies.

A high percentage of farmers use well water for pesticide treatments and still a fairly high percentage of farmers of the area under study don't have a dedicated area for mixing and filling the sprayers. The participatory training events were organized in a "demonstration farm" where an impermeable and mobile platform for filling and washing sprayers was implemented. Here, new technical solutions for correct management of wastewater (spillage or water resulting from the external machine cleaning) were presented and communication material prepared in the form of card games, posters and info-graphics of BMPGAPs, designed to getting farmers familiar to the problems and relative solutions, including how to use the well water without contamination risk, were prepared and distributed. The presentation of monitoring data motivated farmers to participate to these events and stimulated them to implement and to adopt the innovative and sustainable measures proposed and change behaviours. Commonly, the platforms used for washing sprayers and filling are made in concrete, often waterproofed with resin. This solution could have maintenance problems especially if located in geographical areas where temperatures in winter fall below the freezing level, as it is our case. Therefore, it has been decided the use of a mobile platform, available on the market, cheaper and very easy to use, durable (double layer UV resistant PVC) and that can be easily protected during the winter. The collected pesticide polluted water should be stored in a storage tank, transferred with a pump or gravitationally. Storage must ensure double retention, so that any leaks can always be recovered. Finally, the stored polluted water should be delivered directly to a specialized company, even if the costs are quite high for large volumes. Indeed, several alternatives were taken into account and presented, as for example the re-use of the stored water after a chemical /physical treatment for the external sprayer washing, or the installation of bioremediation systems. These solutions were not implemented in the “demonstration farm” because both are not legally approved (at the time of the project). In fact, legal contradictions restrict the application at national level of the physical/chemical/bio-purification systems, even if it could represent a BMP and a technically viable alternative MM of point source contamination, enabling the treatment of PPPs contaminated liquids directly in the farm.

In this context, the leader for water governance, Emilia - Romagna Region, was directly involved through sharing of research outputs (monitoring data, survey outputs, hydrological data), which highlighted the possible impact of end-user behaviour on groundwater contamination in the study area. This increased the awareness and sensibility of the Region to find together with the farmers and partners of the project the most suitable solution.

4. *Discussion and conclusion*

The effectiveness of engagement initiatives may depend more on how the initiative is implemented, rather than the choice of method used (Dean et al., 2016). It is generally assumed that face-to-face methods increase awareness and knowledge in attendees, facilitate the gathering of community opinion and preferences and also provide input for researchers. In our study, different consultation mechanism and strategies throughout the overall project, such as face to face meeting, direct survey, participatory monitoring and the planning of several training activities, were adopted. The low level of trust of the farmers, was the highest barrier at the beginning of the project. The involvement of key people, like representative of farmer's consultancy, of farmer's organizations or of farmer's associations, was fundamental to gain farmers trust and further involvement. Therefore, our perception, supported also by the results of the monitoring campaigns, which show a decrease trend in the contamination of the aquifer examined, is that the level of awareness of farmers, concerning water pollution in the study area, increased but we cannot say that most of them are aware of the problem. An important number of farmers, the ones that follow most the activity of the project and participate to all the face to face meetings, are now showing a high interest and are willing to take actions in order to avoid pollution.

However, some sustainable practices or innovations which could potentially match the incentives of rural development policy are discredited for several reasons because:

- are not always compatible with farmers work organisation and landscape situations;
- their impact is not ensured, farmers need more information;
- are not economically feasible;
- the legislative contradictions as for example for physical/chemical/bio-purification systems, with the result to have CAP measures inapplicable for farmers.

Furthermore, even if training is compulsory and operators need a certificate to use pesticides, and despite the quality level of the regional training system, the training is entirely theoretical and does not include demonstrative activities and sharing of experiences. A very high percentage of interviewed farmers are unaware of the existence of monitoring data on pesticides and nitrates in surface and groundwater even though 64% declare to participate regularly or have participated in training courses concerning the prevention of water contamination. Therefore, to link environment and farmers and increase their awareness, the organisation of demo farming participatory events, as proposed in this work, results as mandatory. The knowledge of the factors involved in the contamination processes and of the context monitoring data allow to adopt behaviours or structural changes aimed at limiting and controlling the contamination. There is a growing interest by farmers and operators in more “modern” communication approaches—experimental, demonstrative, and participatory (Sacchettini and Calliera, 2016). An improvement of the training system is recommended with the use a combination of lessons and group discussions, followed by practical demonstrations, which allow “learning” through practice and promote the understanding of the issues addressed.

To link back the experience we have gathered during this exercise to the effectiveness of the policy implementation in protecting water resources, we can definitely conclude that proactive provision of information on the challenges in water quality and their potential cause are essential to ensure awareness at farm level, and understanding the positive contribution farmers can make. Currently, information is often unclear, scattered or not easily accessible. In many cases farmers rely on informal channels (farmer associations, media, extension consultants, etc.) to obtain such information.

The positive contribution to sustainable water management of agriculture, including through implementing BMPs and MMs should be evaluated, recognized and communicated. Perception on costs vs. benefits of implementation of various BMPs or MMs have an important impact on the willingness of farmers to implement them. Hence, direct information, know-how and as well as support for actual investments needed for implementation of will play a key role in the future uptake of such measures by farmers.

Link environment and farmers and Demo farming participatory events. It is also important to improve the “farmer image and proudness” and restore public confidence in farmer's activities, the sensibility of farmers to social pressure, and their investments and commitments to pro-environmental actions in line with the Sustainable Development Goals (SDGs) n.6 on water. Participatory events fostered the community's understanding of the added value of the commitment of farmers that, with the application of mitigation measures and respect for good practices, contribute to collective well-being by acting on all ecosystem services and common goods.

A set of indicators that highlight the contribution agriculture has into water management (able to capture positive and/or negative trends) will help involvement of farmers and will stimulate ownership of the process.

At the end of the overall process, we can affirm that the multi-actor approach adopted was successful in increasing knowledge and improving attitudes to more sustainable water practices. The different consultation mechanisms and involvement strategies applied throughout the overall process, could be expanded to other areas with similar environmental and agricultural conditions. However, there is no evidence whether these increases in knowledge and positive attitudes can be maintained over time. Therefore, further targeted communication campaigns and actions should be taken into account in order to reach a more sustainable pesticide use, to maintain a good water status and to solve contradictions, both communicative and legislative, which make the recommended rules or MMs inapplicable.

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Chapter 5

General conclusions

Water is an essential resource for human health, agriculture, energy production, transport and nature, but securing sustainable management of water and of aquatic and water-dependent ecosystems and ensuring that enough high-quality water is available for all purposes, remains one of the key challenges of our time in Europe.

Agricultural production has become increasingly intensive, with high inputs of fertilizers and pesticides leading to the emission of large amounts of pollutant loads into the water environment.

The main object of this thesis was to evaluate the impact of viticulture on groundwater quality by PPPs and nitrates in a hilly area, situated in the North-West of Italy, investigating the contamination sources in order to develop the best management practices and mitigation measures to avoid groundwater and environmental pollution. The quality of groundwater in this area was never investigated before.

Hence, water protection is the priority of this project.

The results of monitoring studies from 2017 to 2019, showed a contamination of groundwater by pesticides and nitrate and thus an evaluation of PPPs and nitrates source contamination was carried out through isotopic studies of N and O of NO_3^-, and through hydrologic analysis by use of the model CRITERIA 3D.

The evaluation of the contamination sources was significant in order to find the best solutions to prevent groundwater contamination and consequently to protect the environment.

Furthermore, these monitoring results were presented to the farmers and all stakeholders of the study area in order to involve them into the project and to raise their awareness.

As one of the 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. Based on the results obtained, in fact, the contamination source evaluated resulted to be due to both diffuse and point-source contamination.

In this specific case, considering the particularity of the shallow aquifers where the wells are located, an increase of atmospheric temperature and decrease of precipitations can determinate a concentration rise of

PPPs in groundwater. 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.

On the other hand, the influence of nitrogen-based fertilization on nitrates occurrence in groundwater was evaluated. Moreover, in order to characterize the investigated aquifer and to evaluate the influence of nitrogen fertilization of vineyards on nitrates occurrence, isotopic and hydrochemical analyses were carried out. The results obtained showed a high vulnerability of the aquifer to external changes. Isotopic investigations showed that most of the NO_3^- detected in the groundwater samples of the wells, derived from the use of inorganic nitrogen fertilizers, in agreement with the land use and viticulture practices declared by the farmers during the interviews. Moreover, the survey results indicated a tendency of farmers to follow their own experience for fertilization and therefore, the introduction of a Farm Sustainability Tool for Nutrients, as proposed by European Commission, would increase the knowledge concerning fertilization efficiency and induce a harmonization of fertilization practices.

In this regard, the adoption of PPPs mitigation measures and innovation at farm level, represent a drivers to reach the sustainable water policy objectives. With the aim to prevent the pesticide pressure of hilly vineyards on groundwater contamination, a stepwise approach in Tidone Valley was applied by use of different consultation mechanisms and involvement strategies throughout the overall process. Furthermore, a waterproof platform for sprayer washing, equipped with wastewater recovery and disposal system implemented in a farm was successful among farmers of the area and the several demonstration activities organized showed its functionality and promoted a diffuse use in Tidone Valley. The proposed approach, moreover, could be used to assess possible effects of climate change and even transferred to other similar territorial realities.

Moreover, in this study, different consultation mechanism and strategies throughout the overall project, such as face to face meeting, direct surveys, participatory monitoring and the planning of several training activities, were adopted. The involvement of key people, like representative of farmer’s consultancy, farmer’s organizations or farmer’s associations, was fundamental to gain farmers trust and their involvement in the project. Therefore, our perception, supported also by the results of the monitoring campaigns, is that the level of awareness of farmers, concerning water pollution in the study area, increased but we cannot say that most of them are aware of the problem. The most important result of the study, however, was that at the end of the overall process, the multi-actor approach and engagement strategy adopted were successful in improving attitudes to more sustainable practices. This is supported also by the monitoring data that show in 2019 a decrease by 44% of PPPs occurrences and a fall by 68% of values above EQSgw if compared with the period 2017–2018.

Hence, we can state that the multi-actor approach adopted was successful in increasing knowledge and improving attitudes to more sustainable water practices. The different consultation mechanisms and involvement strategies applied throughout the overall process, could be expanded to other areas with similar environmental and agricultural conditions. Therefore, further targeted communication campaigns and actions should be considered in order to reach a more sustainable pesticides use, to maintain a good water status and to solve contradictions, both communicative and legislative, which make the recommended rules or MMs inapplicable. Besides, a multi-actor approach and a participatory monitoring perspective with a strictly cooperation, planning together for the right solutions, lead to the achievement of more sustainable objectives.

To conclude, actually, the sustainable water management has become a major issue in Europe. In 2000 the European Union approved the Water Framework Directive (WFD, 60/2000), the purpose of which was to provide a reference framework for water management in Europe for the coming decades. In summary, the main objectives of the WFD concern the preservation, protection and improvement of water quality, as well as a rational use of water resources by different economic sectors (urban centers, industry, agriculture and energy). It is based on the principle of preventive action, the reduction of damages, at both the source and the sink, and the ‘polluter pays principle (Viaggi et al., 2010). This objective should reflect a common objective of everyone and we must sustain it in order to preserve the environment system and particularly the Earth.

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