



Long-term application of the organic and inorganic pesticides in vineyards: Environmental record of past use



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ABSTRACT

Areas such as Douro Demarcated Region (Portugal), where vineyards are frequently located on steep slopes of narrow valleys, can be particularly sensitive to runoff and erosion processes. These particular conditions are expected to enhance the transport of pollutants, acting as a potential source of contamination to freshwater systems. The intense vine cultivation in this region includes decades of pesticides application, that have resulted in the accumulation of these chemicals and its degradation products in the vineyards soils and sediments. Residues of several pesticides related to agricultural activities were found in soils, with older vineyards showing higher levels of Cu and banned insecticides (such as DDT). The metabolite 4,4-DDE was the compound found at higher levels in soils and in sediments. The relatively high levels in more recent sediments suggest that soils are still a source of contamination. Levels of currently used pesticides were low, which is related with their physicochemical properties, the application period, and climatic conditions.

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1. Introduction

The viticulture and wine tourism represent an important economic add value and a cultural significance in many countries. Wine is part of the culture of many countries, an element of well-being either as a form of convivial or by its health benefits, at least in the opinion of many of its defenders (Bisson et al., 2002). In Portugal, viticulture stands for approximately 7% of the national agricultural sector (Meneses et al., 2014), therefore, an important contributor to the national economy of a small country like this.

Notwithstanding, a large number of inorganic and synthetic organic pesticides are frequently applied in viticulture. These pesticides belong to different chemical classes, which means that

physicochemical properties and, consequently, its behavior (transport, mobility, and fate) in the environment, can be considerably different. Therefore, the potential hazards posed by their use are highly variable and the intensive use of pesticides in vineyards is currently a cause of public concern, mainly due to the adverse health effects, which can be found in water and wine products used for human consumption (Rabiet et al., 2010).

The century-old practice of organic and inorganic (especially Cu-based) pesticides use for control and protective measure against grapevine diseases, insect damage, and weed competition in vineyards has led to long-term accumulation of Cu and other chemical substances in vineyard soils and other environmental compartments (Besnard et al., 2001; Hildebrandt et al., 2008;

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Komárek et al., 2010). It was estimated that less than 0.1% of the pesticide applied to crops actually reaches the target pest, whereas the remnant easily enters into the environment, contaminating soil, water and air, where it can poison or otherwise adversely affect non-target organisms (Pimentel and Levitan, 1986). For example, levels of herbicides and fungicides higher than the EU regulatory limit set for surface waters, have been reported nearby vineyard areas from Spain (Hildebrandt et al., 2008) or France (Rabiet et al., 2010).

Since the end of the 19th century, Cu-based fungicides have been intensively used in Europe to control vine fungal diseases. Contrarily to synthetic organic fungicides that are banned in European organic viticulture, Cu-based fungicides, such as $\text{Cu}(\text{OH})_2$, copper oxychloride $3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2$, CuSO_4 , and Cu_2O , are allowed and indispensable for organic vine cultivation (EC regulation 473/2002). Due to the non-degradable character, Cu accumulation in vineyard soils exclusively depends in the amount applied in the agroecosystem, which is related to climatic conditions, and well correlated with vineyard ages. Although, Cu accumulation in soils is greatly affected by physicochemical conditions, which influence its solubility and sorption to soil particles. Copper in soils is mostly associated with soil organic matter (SOM), Fe- and Mn-(hydr)oxides, and to a lesser extent with clay minerals through specific and non-specific adsorption (Parat et al., 2002; Bradl, 2004; Fernández-Calviño et al., 2009). Copper can easily reach other compartments (water and sediments) by particle dispersion due to soil erosion, which is favoured in areas with more pronounced reliefs, or solubilized, particularly when low pH conditions ($\text{pH} < 6$) prevail in soil system (Adriano, 2001; Celardin et al., 2004; Boudesocque et al., 2007; Nóvoa-Muñoz et al., 2007). Management practices can also affect Cu mobility, as for example the use of organic amendments, which had a direct effect on the retention of Cu in soil (Besnard et al., 2001).

On the other hand, many of the highly toxic and persistent organic substances have been progressively banned as their hazard has been proven (e.g.: DDT, endosulfan, simazine), while others are being subject of European regulation (European Commission, 2006). Persistent and mobile pesticides can be transported in the environment over long distances to places far from the points of release, turning this issue a global environmental problem. Moreover, these persistent pesticides (or their degradation products) can remain in soils for several years, or even decades, long after their use. Through various dynamic processes they can enter directly in the food chain, or percolate down and reach groundwater reservoirs (Gavrilescu, 2005; Gaw et al., 2006). Indeed, some pesticides are still detectable in surface waters 20 years after their use had been banned (Larson et al., 1997). Nevertheless, the long-term environmental fate of pesticides has been poorly studied (Bundschuh et al., 2014; Sabatier et al., 2014).

In vineyards, such as the ones from Douro region where vines are located on steep slopes, soil erosion has also an important role on the dispersion of pollutants, especially to the nearby aquatic systems. Indeed, sediments are an important sink of contaminants and, whenever the sedimentation conditions permit, sediment cores can be used to evaluate and reconstruct historical contaminant trends in aquatic environments. In particular, dam reservoirs are interesting sites to study the presence and accumulation of pollutants because contaminated particles can eventually become trapped and buried.

Therefore, in order to evaluate the fate of organic and inorganic (Cu-based) pesticides three vineyard areas, with different plantation ages, were studied and the levels of banned and currently used pesticides were assessed. Moreover, with the aim of understanding the legacy left by the long-term pesticides application in this area, the distribution of contaminants in a sediment core from an

adjacent dam reservoir was assessed.

2. Materials and methods

2.1. Study area

The Douro Demarcated Region, where the famous Port wine is produced, covers an area of approximately 250,000 ha in north-eastern Portugal, and is considered the oldest demarcated wine-making region in the world (Andersen et al., 2004). Since December 2001, this region is considering an UNESCO's World Heritage Site due to its cultural landscape of outstanding beauty.

The studied area is a small catchment located in the municipality of Lamego, Viseu district. The area englobing the three vines sampled has about 500000 m², while the entire area, including the core sediment, has about 1400000 m². The climate of this region is characterized by a mean annual rainfall of 900 mm and an average temperature of 18 °C. The rainfall variation between the years of 1974 and 2012 are report in Fig. 1, where it is possible to delimit longer periods with high rainfall prevailing condition (1976–1979; 1983–1985; 1987–1989; 1995–1997; 1999–2003; 2006 and 2009–2010). The lowest values were obtaining for the years of 1980, 1982, 1990–1994, 1998, 2005, 2007 and 2012. The drainage basin discharges into an important water reservoir, the Varosa Dam, which collects water from two main rivers, the Varosa and the Balsemão Rivers (Fig. 2). This is an undisturbed reservoir, resulting in more than 40 years of accumulated sediments.

The geology of this area is characterized by a low-grade meta-sedimentary complex unit, composed by interstratified schists and grauwwacks. Locally this metasedimentary unit was intruded by granitic rocks evidencing high kaolinization of feldspars (Teixeira et al., 1969). The most dominant feature of the landscape in this region, with slopes at over 15%, is the terraced vineyards that blanket the countryside. Soils have been created literally by breaking up rocks and are classified as anthrosols (FAO–UNESCO, 1974).

2.2. Sampling

Forty-nine soil samples (0–15 cm) were collected, during September and October 2012, from 3 vineyards with different ages: one recently planted/replanted (V1); other with more than 15 years (V2); and one with more than 50 years (V3) (Fig. 2). Each soil sample is a composite of 2 sub-samples (one collected in the middle of the terrace, near the vine, and the other in the outmost area of terrace). A representative sample of the background of this region, without vine cultivation was collected.

Several sediment cores were collected in the reservoir. The deepest sediment column was obtained at 50 cm. Samples were sliced at each 1 cm in the first 10 cm, and at each 2 cm in the remaining. In order to have sufficient amount of sample for the different analysis, a composite sub-sample was obtained by mixing the sediments of the same depth from the different cores. Thus, 31 sub-samples were obtained.

2.3. Chemical and physicochemical characterization

Soil and sediment samples were air dried, sieved through a 2 mm nylon sieve, and well homogenized in order to obtain representative samples for analytical determinations. For chemical analysis, the samples were ground in an agate mortar. For organic pesticides analysis, samples were immediately frozen, lyophilized, sieved through a 2 mm stainless-steel sieve, and kept at –20 °C until the analysis were performed.

The grain size distribution of sand, silt and clay fractions were

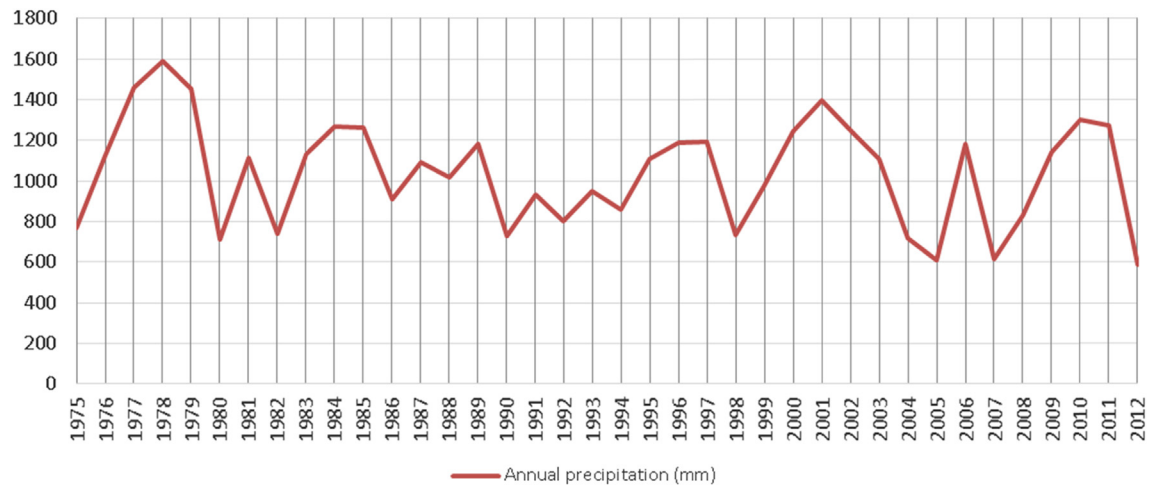


Fig. 1. Mean annual rainfall for studied region for the period of 1975–2012 (Source: <http://snirh.pt/>).

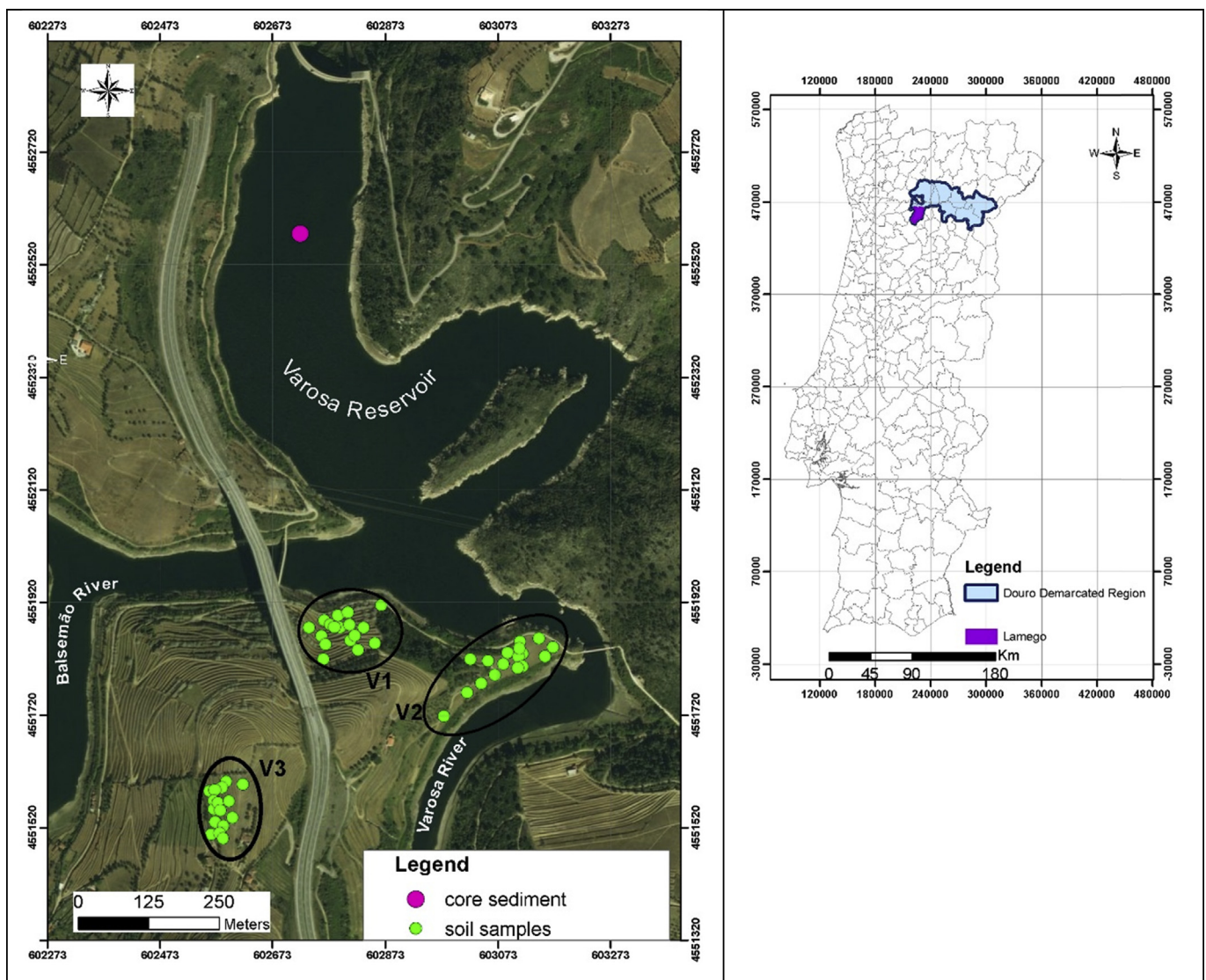


Fig. 2. Study area location and soil sampling site, Douro Demarcated Region - Lamego, Portugal.

determined only in vineyard soils, using an X-ray grain size analyzer (Sedigraph 5100). All the other physicochemical parameters were determined in both matrixes. The pH for was measured in a solid:water (1:5) suspension after 24 h of contact time. The organic carbon (OC), N and S were determined using an elemental analyzer Eurovector - EA3000, based on the principle of dynamic flush combustion. Total P (P_{total}) was extracted using H_2SO_4 1 N after incineration at 550 °C during 2 h, while available P (P_{avail}) was extracted using NH_4Cl 1 M, followed by P colorimetric determination as described by [Murphy and Riley \(1962\)](#). The concentration of Cu was determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), after an *aqua regia* digestion, at the ACME Analytical Laboratories of Canada (ISO 9002 Accredited Lab).

The pesticides under analysis were selected according to a survey of the most important and commonly applied to the vineyards of the region. The selection included fungicides (boscalid, folpet, metalaxyl, penconazole, tebuconazole), herbicides (terbutylazine and its degradation product desethylterbutylazine), and insecticides (chlorpyrifos, deltamethrin). Some pesticides currently banned were also included because they are considered priority substances under the scope of Water Framework Directive, and they were commonly used in this region during decades: endosulphan (α and β), DDX (4,4' DDE, 2,4 DDT, 4,4' DDD, 2,4 DDD, 4,4 DDT), and simazine. Regarding the core sediment samples, only the pesticides considered persistent and immobile (endosulphan and DDTx) were analyzed, as these are the only ones that could give a record of the past use.

Depending on the polarity of the compound, a mixture of hexane:acetone or methanol:water were used for the extraction of pesticides from 15 soil (5 in each area) and 18 sediment samples. Extracts were then cleaned-up by Solid Phase Extraction, using Florisil® for hexane:acetone extracts and C18 for methanol:water extracts ([Caetano et al., 2012](#); [Gonçalves and Alpendurada, 2005](#)). Compounds were quantified by GC-MS, using a ZB-5MS column, and an internal standard calibration.

2.4. QA/QC methodology

The accuracy and the precision of the analytical methods were performed by including replicates, procedure blanks, and available certified reference materials (for Cu and persistent pesticides) or fortified samples in each analytical batch. Regarding major and trace elements, replicate analysis of the soil and sediment samples gave an uncertainty of <10%. The results of blanks analysis were always below detection limit, and recoveries of reference material were within the certified value. For pesticides, replicate analysis of the soil and sediment samples gave an uncertainty of <25% for each individual compound. Also for these compounds, results of blanks analysis were always below detection limit, which ranged between 0.2 e 1.0 $\mu\text{g kg}^{-1}$. Recoveries of certified reference material and fortified samples were within the acceptable range: 60–117%.

2.5. Enrichment factors

Enrichment factors (EF) are frequently used to assess the degree of metal pollution in sediments ([Rahman and Ishiga, 2012](#); [Yao et al., 2013](#); [Islam et al., 2015](#)). The specific metal enrichment can be distinguished based on the relationship between its concentration and suitable concentrations of conservative elements ([Rahman and Ishiga, 2012](#); [Yao et al., 2013](#); [Islam et al., 2015](#)).

In this study, EF was calculated for Cu by normalizing its distribution in the core sediments to a conservative element as pointed by the following equation:

$$EF = \frac{[(C_{\text{Cu-sed}})/(C_{\text{R-sed}})]}{[(C_{\text{Cu-bk}})/(C_{\text{R-bk}})]} \quad (1)$$

where, $C_{\text{Cu-sed}}$ and $C_{\text{R-sed}}$ are the Cu and reference element concentrations in the sediment sample, respectively, whereas $C_{\text{Cu-bk}}$ and $C_{\text{R-bk}}$ are the local background concentrations for Cu and reference element, respectively.

In this case, Cu was normalized to Al, since the last is a lithogenic conservative element and a major constituent of clay minerals (main components of schists), and that has been successfully used in numerous studies to distinguish natural and anthropogenic sources of metals ([Loska and Danuta, 2003](#); [Franco-Uria et al., 2009](#); [Rahman and Ishiga, 2012](#)). The values of 33900 mg Al kg^{-1} and 16.6 mg Cu kg^{-1} of soils from the region without influence of vine cultivation were used as reference concentrations for this calculus.

2.6. Statistical analysis

Since data did not show a normal distribution (Shapiro-Wilk test), Spearman correlations were used to describe the interactions between the solid phase distribution of physicochemical parameters and Cu. In addition, principal component analysis (PCA) was performed for core sediments samples in order to understand the pattern of interrelationships among selected sediment parameters. The data was log transformed before PCA analysis.

3. Results and discussion

3.1. Physicochemical characterization of vineyard soils

The vineyard soils from this region result, as previously mentioned, by the schists breaking by man, which result in a high heterogeneity in the particle size distribution, mainly composed by two main groups: the rather coarse particles (gravel size) and the fine particles. These last ones are the most important regarding the soil texture as well as its influence on contaminants dispersion. Thus, despite the slightly higher silt content in the oldest vineyard, few differences were observed between soils samples, being all classified as silt loam. Contrarily, a high variability of physicochemical and chemical parameters was observed in the entire area ([Table 1](#)) and within each vineyard ([Fig. 4](#)). Such large inter- and intra-site variability could be attributed to management practices (e.g.: the number of vineyard treatments and the spraying methods used).

Although the soils from this region can be considered acidic (pH = 5.40, in the background sample), in vineyard soils pH values indicate the prevalence of very acidic conditions for the majority of samples (pH < 5) ([Table 1](#)). The pH values changes seem to be related with the vineyard's age ([Fig. 3](#)), since a slight decrease in these values is observed with the increasing age of vineyards. Several processes can promote soil acidification, as the leaching of basic ions from the soil profile, microbial activity, and the addition of agrochemicals. In the particular case of vineyards, an important contribution for soil acidification can result from the applications of elemental sulfur (S^0) in vines ([Klikocka et al., 2015](#)). In fact, S has been used extensively since long time as a protective measure against crop diseases, especially in the growing season ([Griffith et al., 2015](#)). The decrease of soil pH is mainly observed immediately after S application, because a quite fast oxidation of S^0 to SO_4^{2-} promotes the neutralization by salts precipitation ([Hinckley et al., 2011](#)). Indeed, recent studies have shown that the majority of the S applied oxidizes in the first half-hour, with complete oxidation to SO_4^{2-} occurring within 7 days after application ([Hinckley et al., 2011](#); [Hinckley and Matson, 2011](#)).

Table 1
Univariate statistical description of physicochemical and chemical properties of soil vineyard samples.

	pH	S (mg kg ⁻¹)	OC (g kg ⁻¹)	N (%)	C/N	P _{total} (mg kg ⁻¹)	P _{avail} (mg kg ⁻¹)	Cu (mg kg ⁻¹)
Min	3.18	100	1.9	0.015	5.8	27.1	bdl	17.8
Max	6.56	550	53	0.350	21	420	35	211
Mean	4.41	224	10.5	0.095	10.9	274	9.6	79.4
Median	4.84	200	8.5	0.082	10.5	282	6.7	55.9
CV (%)	10.8	44	79	62	21	32.6	102	70.5

bdl – below detection limit.

The concentrations of S in vineyard soils (mean value of 224 ± 125 mg kg⁻¹; Table 1) are slightly higher than the background levels (150 mg kg⁻¹) found for soils of this area. These concentrations are similar to those found in other regions, as the case of the Napa Valley vineyard, where S concentrations range between 275 and 300 mg kg⁻¹ (Hinckley and Matson, 2011), but lower than the levels (326–496 mg kg⁻¹) found in four Apulian organic vineyard (Provenzano et al., 2011). Several factors can affect local vineyard S budgets, as the management practices (S applications, type and irrigation strategies), soil properties and rainfall. Typically, S is not expected to accumulate in soils, since it is easily leached, particularly during the wet season, when almost all S applied is removed from soils (Hinckley and Matson, 2011). Therefore, though higher S levels were observed in the oldest vineyard soils (Fig. 3), this is not probably related to accumulation processes but with a greater frequency in S applications on vines. Nevertheless, the particle size and formulation of the S product may have some influence on the fate of this element (whereas fungicidal S consists of small particles with a large surface area favouring a rapid volatilization, the S-containing fertilizers are prepared to slow up S oxidation).

Soils from the studied areas are in general poor in organic carbon (OC) and N (Table 1). The behavior of OC and N are quite similar and below the background levels of the area, with the higher values found at the oldest vineyard, and the lower ones in the new vineyard (Fig. 3). The lower levels observed in the youngest vineyards are probably a result of tillage-based management of the soil surface, which limited the potential for organic matter (OM) accumulation.

The mean value of soil C/N ratio is 11 ± 2.36 across the whole area (Table 1) and very similar between each vineyard (Fig. 3). This is in agreement with the values found for topsoil of arable land, which typically ranges from 10 to 12 (Osman, 2013), and increase in the subsoil. Also, identical C/N values have been reported by other authors for tilled vineyards on sloping land, and under different soil and climate conditions (Stevanato et al., 2014). This indicates that runoff and the conventional tillage-based managements, which limit the input of fresh organic residues and enhance mineralization of existing soil OM, are probably the main factors contribution to the low C/N ratios in these soils.

Phosphorus (P) is a macronutrient for plants, with a great impact on agriculture production. The increasing application of P-fertilizers in the recent years has significantly improved soil P status in most regions of the world (Mejías et al., 2013; Rubaek et al., 2013), but has been caused P accumulation in some soils (Cordell et al., 2009; Maguire et al., 2009; Tóth et al., 2014; Wang et al., 2014). The accumulation of P in soil also has negative consequences since the accumulated fraction is an unnecessary cost to the farmer; phosphates are non-renewable resources; it may cause negative environmental impacts, because even small amounts of P leaching into watercourses can cause eutrophication processes (Elser and Bennett, 2011).

In acidic soils, P can be predominantly adsorbed by Al/Fe-

oxyhydroxides (Parfitt, 1989). Furthermore, in such conditions, P become available at extremely slow rate, which may cause nutritional deficiencies for plants. Total (P_{total}) and available (P_{avail}) P content in studied soils were higher than the background value (Fig. 3), and no significant correlation was found between both. The higher and lowest amounts of P_{total} were found in the vineyard with an age between 15 and 50 (Fig. 3), which is probably related with the type of P-fertilizers used and with the application rates as demonstrated by Kang et al. (2011).

3.2. Cu in the vineyard soils

The total Cu contents (18–211 mg kg⁻¹, Table 1) are high when compared with the mean level of 15.5 mg kg⁻¹ for agricultural soils in Europe (Oorts, 2013). Also, these concentrations are high when compared with the background value of the area (16 mg Cu kg⁻¹, Fig. 3). These data clearly demonstrate that the source of Cu in the studied vineyard soils is attributed to the application of Cu-based fungicides, as the historical use of Bordeaux mixture [CuSO₄+Ca(OH)₂]. The Bordeaux mixture has been widely used since the end of 19th century in several countries (McBride, 1981; Romić et al., 2014), however the exact period time that this compound started to be used in the studied region is not known. Moreover, there is no available data about the number of applications and the amount of Cu applied.

Previous studies conducted in vineyard topsoils from other European countries reported Cu contents ranging from 14 to 945 mg kg⁻¹ (Komárek et al., 2010), exceeding the limits of 50–140 mg kg⁻¹, set by the EU Council Directive 86/278/EEC. Slightly lower values were reported in Australian vineyard soils, ranging between 6 and 249 mg kg⁻¹, probably due to the lower average annual usage of Cu-based fungicides, which is estimated to be 5–13 kg ha⁻¹, in contrast to the typical annual usage of 10–50 kg ha⁻¹ in some European regions (Wightwick et al., 2008). Levels as high as 3200 mg kg⁻¹ were found in Brazilian vineyard soils (Mirlean et al., 2007), whereas in the Champagne region (France) the maximum level of Cu found was 1500 mg kg⁻¹ (Besnard et al., 2001). Such high levels as the ones found in Brazil reflect the impact of the climate, since high volumes of fungicides are needed in areas with greater humidity and precipitation for diminishing downy mildew attacks (Komárek et al., 2010). For example, Deluisa et al. (1996) studied vineyards cultivated in distinct climatic conditions [humid (rainfall > 1200 mm y⁻¹), plain zone (rainfall: 800–1000 mm y⁻¹), and drier (rainfall: 400–800 mm y⁻¹)] and found that the mean Cu levels gradually decreased from 297 mg kg⁻¹, to 200 mg kg⁻¹, and 75 mg kg⁻¹, respectively. On the other hand, Wightwick et al. (2008) found no apparent link between Australian climatic regions and annual Cu usage, and suggested that individual vineyard management practices, rather than climate, influence the extent of Cu use in viticulture.

It is interesting to note that Cu contents of the surface soils varied widely, as shown in Table 2. Such large variability could be

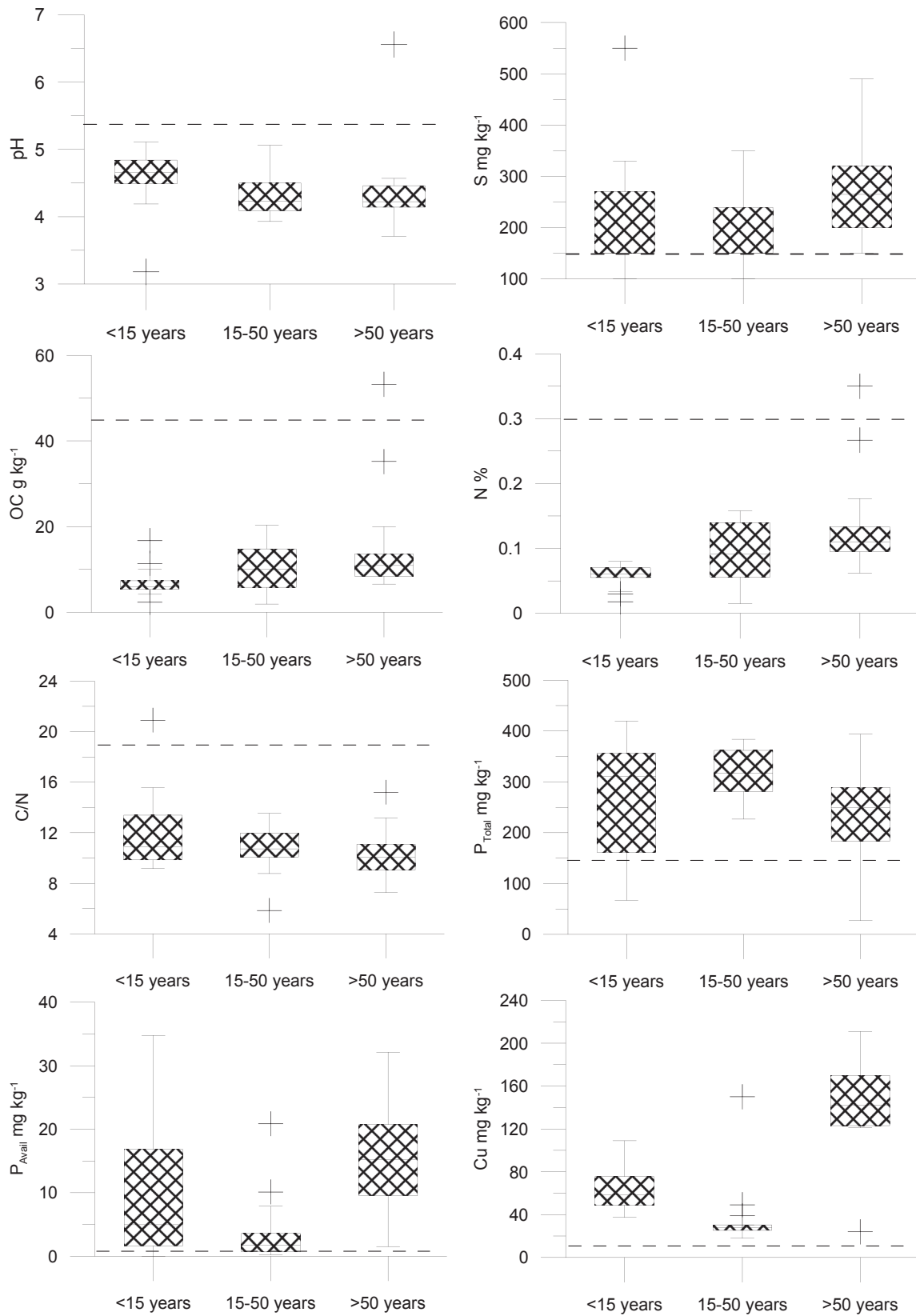


Fig. 3. Boxplots of main physicochemical and chemical parameters within different vineyards (dash line represents the geochemical background levels determined in soils of this area).

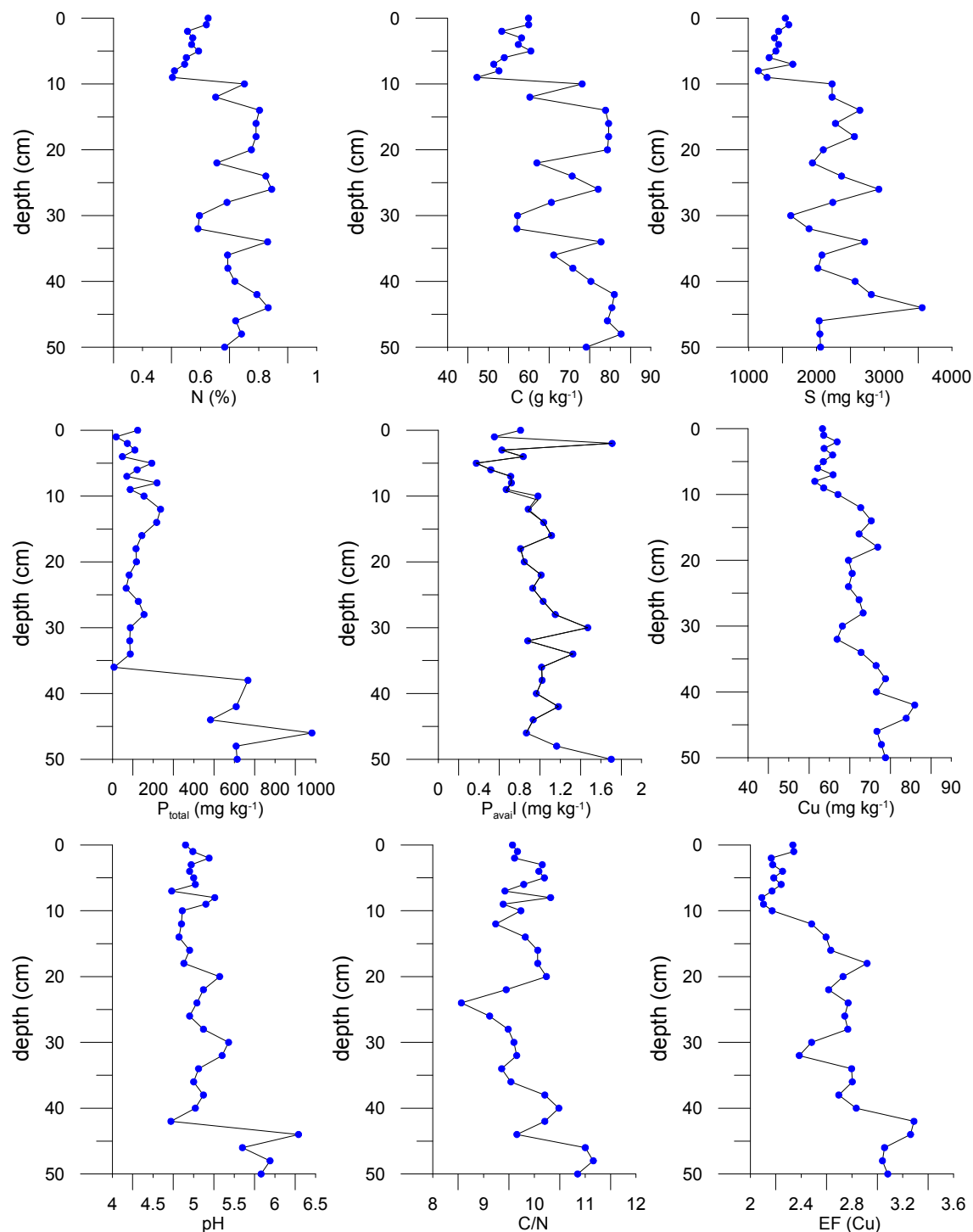


Fig. 4. Nitrogen (N), organic carbon (OC), sulfur (S), total phosphorus (P_{total}), available phosphorus (P_{avail}), copper (Cu), pH, C/N ratio and enrichment factor of Cu (EF) distribution as a function of sediment core depth.

attributed to the number of Cu applications. Moreover, Cu retention and, consequently, its accumulation in the surface soils within the same region could be influenced by several factors, such as: the soil's physicochemical parameters (e.g.: OC content, cation exchange capacity, and pH); the local topography; the history of Cu-based fungicides applications; and different management practices (e.g.: tillage, OM incorporation) (Wightwick et al., 2008; Fernández-Calviño et al., 2009).

Previous studies demonstrated that prolonged periods of fungicide treatments result in a more pronounced Cu accumulation in soils (Romić et al., 2014; Rusjan et al., 2007). Nevertheless, other studies did not found a significant relationship between vineyard age and Cu accumulation (Wightwick et al., 2008). Data obtained for Douro region did not allow to establish a correlation between the amount of Cu in soils and the age of vineyards, despite the highest Cu contents were found at the oldest vineyard (mean

Table 2
Spearman correlations between soil physicochemical and chemical properties.

	N	C	pH	P _{total}	P _{avail}	S	Cu
N	1.00	0.94	−0.61	−0.01	0.41	0.51	0.40
C		1.00	−0.52	0.02	0.28	0.44	0.32
pH			1.00	0.17	−0.36	−0.50	−0.18
P _{total}				1.00	−0.11	−0.07	−0.27
P _{avail}					1.00	0.40	0.68
S						1.00	0.56
Cu							1.00

Values in bold correspond to significant correlations to $p < 0.01$ level of significance.

144 mg kg^{−1}). Although, the lowest Cu contents were found at the middle age vineyard (mean 35.4 mg kg^{−1}). In addition, the lack of relationship between the age and the Cu content may also be related to management practices such as ploughing and/or remobilization of soils during the new vine plantation.

Considering the influence of soils properties on Cu contents, no strong correlations were found between the analyzed soil parameters and Cu levels (Table 2). The strongest correlations were found between Cu and P_{avail} and with S. The correlation between Cu and P_{avail} can be explain due to the fact that the application of P-fertilizer could also contribute to the accumulation of Cu in surface soil since Cu²⁺ can form an insoluble salt (CuHPO₄) with HPO₄^{2−} (Shuman, 1988).

3.3. Levels of synthetic organic pesticides in vineyard soils

Herbicides were detected only in one sample (located in the old vineyard) at levels below 8.5 µg kg^{−1}. Herbicides are normally applied in spring (February–May) and, due to their physicochemical properties (high polarity, low K_{OC} values, and low half-live values), they do not tend to persist in soils for a long time, being easily leached to groundwater or to nearby aquatic systems. Thus, since sampling was performed at the end of summer, the results obtained are not surprising.

Regarding the five fungicides analyzed, folpet was not detected in any sample, and tebuconazole was detected in less than 50% of samples, whereas penconazole was detected in all samples (Table 3). Previous studies, found similar results for folpet once even during the application period this fungicide was not detected in soil samples due to its rapid degradation (Bermúdez-Couso et al., 2007; Schreck et al., 2008). Tebuconazole and penconazole have similar solubility in water (0.036 and 0.073 g L^{−1}, respectively) and the same log K_{OW} value (3.7), but a different K_{OC} (769 and 2205 L kg^{−1}, respectively) and soil half-life (40–170 and 133–343 days, respectively). Thus, the higher frequency of detection of penconazole is likely to be related to its lower mobility and higher persistence.

Considering the median concentration of all samples, metalaxyl was the most abundant (22 µg kg^{−1}), followed by boscalid

(9.6 µg kg^{−1}), and penconazole (3.6 µg kg^{−1}). Metalaxyl has a short half-live (10–40 days), it is soluble (8.4 g L^{−1}), and very mobile (log K_{OW} = 1.8; K_{OC} = 30–300 L kg^{−1}), thus, it is not expected to be retained in soils (Bermúdez-Couso et al., 2007; Komárek et al., 2010; Schreck et al., 2008). However, these higher levels observed for metalaxyl, as well as for boscalid, are probably related to their application period, since they are applied latter in the summer. Moreover, they are also the most commonly used in this area.

Levels of fungicides found in the vineyards at Douro region are low, but similar to that observed in other vineyard areas. For example, in the Rias Baixas vineyards (Spain) a survey, which included the analysis of metalaxyl, penconazole, and tebuconazole, was performed 1 and 9 months after the last application and only tebuconazole was detected (12 µg kg^{−1} in one sample, 1 month after the last application) (Rial-Otero et al., 2004). In the nearby region of Ourense, Bermúdez-Couso et al. (2007) found levels of metalaxyl and penconazole similar to the ones from the present study, with exception of samples collected during the application period, which showed levels higher than 100 µg kg^{−1}. In vineyard soils from France, metalaxyl was found at levels of 50 µg kg^{−1}, one day after application (Schreck et al., 2008). Therefore, the lower levels found in the studied area can be related to the sampling period (1 month after the last application). Moreover, this was a dry year (Fig. 1), resulting in low application rates of fungicides due to the low incidence of diseases.

With exception of metalaxyl, which shows higher levels in the older vineyard, for the other fungicides there is no trend between age of vines and levels of fungicides. Penconazole showed similar median values in the three areas, whereas median levels of boscalid and tebuconazol were similar in the two older vineyards, and they were not detected in the youngest one. Thus, differences in the levels of fungicides found in the three areas are more likely to be related with management practices (different timing and mode of application) than with its accumulation in soils caused by successive applications. Indeed, only boscalid showed a significant correlation with OC, which is one of the most important properties regarding sorption of these compounds in soils (Komárek et al., 2010). Moreover, the high range of values observed in the oldest vineyard is related to a hotspot observed for metalaxyl, penconazol, and boscalid, which it is suspected to be related with the local of storage and preparation of pesticides.

Regarding insecticides currently applied, chlorpyrifos was not detected in any sample and deltamethrin was detected at very low levels. These results are in line with other studies, since insecticides are not commonly used in vines and they are applied only sporadically (Schreck et al., 2008). On the other hand, insecticides that were used in the past, but due to their persistence, lower mobility, and toxicity, monitorization of their levels in the environment is still need, only ΣDDX showed significant levels. Endosulfan was detected at very low levels, and no differences were observed between the three areas, which may indicate that levels

Table 3
The frequency of detection (%) and levels (µg kg^{−1}) of fungicides and insecticides detected in soils from the three studied vineyards.

	V1 (<15 years)			V2 (15–50 years)			V3 (>50 years)		
	Freq detection	range	median	Freq detection	range	median	Freq detection	range	median
Metalaxyl	40	bdl–0.34	–	100	10–40	22	100	25–70	39
Penconazol	100	2.9–34	3.6	100	1.9–4.6	3.5	100	2.6–127	4.7
Tebuconazol	0	–	–	60	bdl–11	3.5	80	bdl–13	4.2
Boscalid	0	–	–	100	3.8–84	13	100	8.7–145	11
Deltamethrin	100	1.2–2.4	2.0	40	bdl–24	–	100	3.2–15	7.5
Endosulfan	80	bdl–2.6	1.4	80	bdl–3.4	1.5	100	0.6–3.1	1.3
ΣDDX	100	0.24–5.8	1.0	20	bdl–0.31	–	100	11–40	24

bdl - below detection limit.

are related with global background contamination. DDX, banned in Portugal in 1988, showed very high values in vineyards with more than 50 years. Indeed, the pattern of the DDX mixture is dominated by the metabolite 4,4-DDE, ranging from 53 to 100%, which indicates that it is a legacy of the past (Neitsch et al., 2016). Levels of DDTx found in the studied area are slightly lower than the typical residual levels found in southwestern Germany (20–60 $\mu\text{g kg}^{-1}$), where this pesticide was banned 40 years ago (Neitsch et al., 2016). However, these values are similar to the ones found in vineyard soils from the Ebro River basin, in north-eastern Spain (27.8 $\mu\text{g kg}^{-1}$ for 4,4-DDE), where this pesticide was banned in 1977 (Hildebrandt et al., 2009). On the other hand, these values can be considered high when comparing with the ones found in vineyards from another agricultural region in Spain (range of 0.08–0.62 $\mu\text{g kg}^{-1}$, median of 0.60 $\mu\text{g kg}^{-1}$) (Muñoz-Arnanz and Jiménez, 2011). Considering some of the existing guideline values for soil quality (e.g. Dutch, USEPA), the area corresponding to the older vineyard can be considered contaminated with DDX, and thus, the potential risks to the environment should be assessed. Moreover, the effect of modern pesticide, which typically contain high levels of surfactants, on the mobilization of DDX should be assessed (Neitsch et al., 2016).

As observed for Cu and for the more persistent compounds such as deltamethrin (Table 3), the higher levels of the ΣDDX were observed in the in old vineyard, followed by the youngest one and the less contaminated was the medium age vineyard. Indeed, there is a significant relationship between DDX and Cu levels ($r^2 = 0.7198$). The higher levels of contaminants found in the older vineyard reflect the accumulation and persistence of some pesticides used in the treatment of vines over time. The higher levels found in the youngest vineyard compared with the one with intermediate age are probably related with management practices such as ploughing, reflecting the importance of such practices in the mobilization of contaminants.

3.4. Distribution of physicochemical parameters in sediment core samples

The sediment column that was deposited over the years in dam reservoirs are an important record of the geogenic sources, as well as of the human activities exerted on environment. Despite the relevant information that these sediments contain, they are not widely studied, comparing with natural lakes, probably due to the complex sedimentation patterns caused by changes in water levels and in the discharges of input streams, in a relatively short period of time (Shotbolt et al., 2005; Tibb et al., 2010).

Favoring by the proximity of vineyards to the Varosa dam and by their slope, the sediments that were and are being deposited in the Varosa Reservoir certainly have a significant contribution from vineyard soils. Thus, in order to understand the contribution of vineyard soils to the sedimentation rate, but especially the changes

operating along the years in the agriculture management in this region, element fluctuation in the core sediments was studied.

Fig. 4 shows the vertical distributions of some chemical and physicochemical parameters (N, OC, S, P_{total} , P_{avail} , Cu, pH, C/N) in the sediment core samples, as well as the EF for Cu. The N, OC and S concentrations range between 0.50 and 0.85% (mean of $0.68\% \pm 0.11$), 47.2–82.7 g kg^{-1} (mean of $67.2 \pm 10.9 \text{ g kg}^{-1}$) and 1140–3560 mg kg^{-1} (mean of $2034 \pm 567.2 \text{ mg kg}^{-1}$), respectively. In general, levels are lower in the first 10 cm, with a tendency to increase with depth. Also, these three parameters show similar trends with depth, which are reinforced by the significant positive correlations between them (Table 4), suggesting a common origin. When comparing these values with that one's determined in soils is possible to verified the big differences between both compartments, where the higher levels in sediments reflect the accumulation of these macronutrients coming from upstream draining basin, which preservation are favoured due to prevailing reduction conditions below the water column.

The first 20 cm of core sediments profile do not reveal major shifts in C/N ratios, suggesting a rather constant OM source. In addition, these values are close to the mean value found in vineyard soils, which may indicate a direct contribution from the soils of this area. At deeper layers, the C/N values are slightly higher compared to the upper sediments, where major shifts were observed (Fig. 4). A significant decrease occurs between 20 and 25 cm, followed by an increase tendency with depth. Higher values may reflect preferential the preservation of OM due reduction conditions and/or increased contribution of terrestrial OM (Mügler et al., 2010).

The P_{total} concentration vary along profile (Fig. 4), showing higher concentrations in the deeper layers, most probably due to excessive nutrients (e.g. N-P-K type) input from agriculture in the past. The P_{total} distribution shows a similar pattern with pH, indicating that the increase of pH may also promote the immobilization of P in sediments (Fig. 4). The P_{avail} concentrations are very low, more or less constant along the profile (Fig. 4), and, in general, lower than the levels in vineyard soils, which may indicate that P_{avail} is readily uptake by vines.

The EF of Cu is greater than 1 in all core sections (Fig. 4), confirming the inputs of Cu into the Varosa Reservoir, with an anthropogenic origin (vine practices). Anyway, Cu content is slight higher in soils. Similar to P_{total} , the EF of Cu shows an increase in deeper layers, reflecting that in past the use of agrochemicals was more pronounced than nowadays (Fig. 4). Nevertheless, the highest values of this index were observed between 10 and 28 cm and in bottom part of the core (40–45 cm). This is probable related with more intense precipitation periods that, in addition to favour leaching processes, also conducts to more intense applications of Cu-based pesticides (e.g. Bordeaux mixture).

In order to date the geochemical historical records in sediments and associate this with major climatic events or major anthropogenic actions in the region, $a^{210}\text{Pb}$ geochronological dating was attempted. Unfortunately, the results obtained were not consistent and did not allow to establish a precise chronology of the sediments. Thus, to complement the lack of core dating, Principal Component Analysis (PCA) was performed. The data set used for PCA contained 8 variables and 31 sediment samples. The first two factors accounting 71.3% of total variance (Fig. 5a), were retained. Factor 1 accounts for 55.1% of the total variance and includes N, OC, S, P_{total} , P_{avail} and Cu on opposition to Al. Enrichments in N, OC, S, P_{total} , P_{avail} and Cu are commonly derived from agriculture activities, whereas in these environments Al are mainly related to geogenic sources. The pH, included in factor 2, accounts for 19.1% of the total variance.

Over time, sediments that were deposited in the dam are characterized by a high variability (Fig. 5b). For both factors the

Table 4
Spearman's correlation coefficient between physicochemical and chemical parameters in sediment core samples.

	pH	N	C	S	P_{total}	P_{avail}	Cu
pH	1.00	−0.08	0.01	−0.18	0.16	0.21	0.13
N		1.00	0.90	0.92	0.29	0.48	0.60
C			1.00	0.80	0.45	0.43	0.75
S				1.00	0.20	0.53	0.68
P_{total}					1.00	0.22	0.46
P_{avail}						1.00	0.61
Cu							1.00

Values in bold correspond to significant correlations to $p < 0.01$ level of significance.

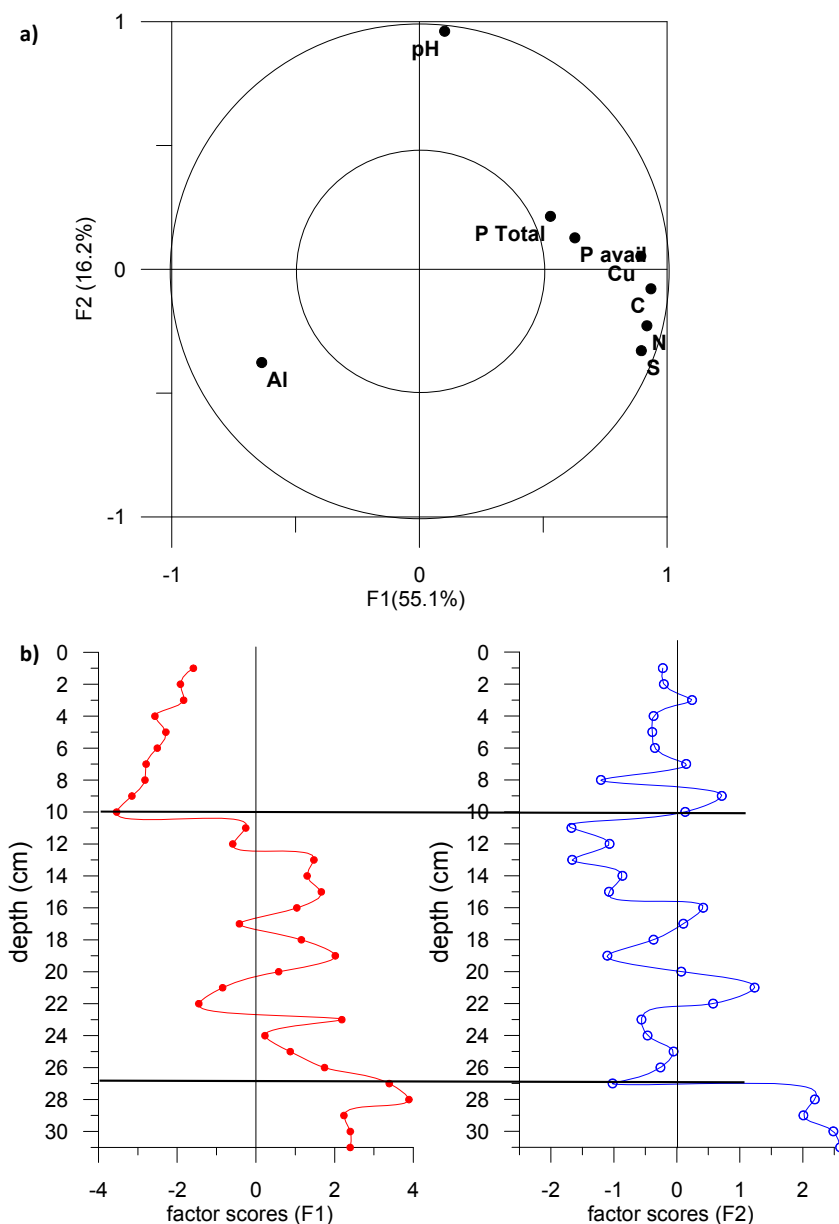


Fig. 5. Representation of the first two PCA factorial plans (F1 vs F2) according to variables association (a), and their variation over core profile (b).

most significant changes occur at 10 cm and at 27 cm. In the first 10 cm, the geogenic component is dominant in relation to the agriculture contribution. Below this depth, the contribution of agriculture practices is more evident, despite some sporadic episodes of greater geogenic contribution (Fig. 5b). The influence of pH in first 10 cm does not seem to be important, whereas between 10 and 27 cm it seems that there is a relationship between pH and agricultural contribution. Thus, in layers where the agriculture contribution is higher, the pH values are lower and on the other hand, the geogenic contribution is higher when the pH increases.

At large temporal scale, the high C-N-S-Cu-P_{total} and P_{avail} contents could result of the more intensive rain periods (Fig. 1), where application of pesticides is more intensified and the erosion processes favoured. Moreover, the loss of nutrients and other elements from the soil and their deposition on dam reservoir can be directly influenced by rainfall intensity and time. Thus, the close links

between Cu and organic fractions (C, N and S) and P of the sediments suggest a similar source. However, the punctual enrichment of Cu and P may also be associated with small erosion events (Quinton et al., 2001; Quinton and Catt, 2007). This is due to the wide range of particle sizes mobilized during intense rainy events, whereas in the lower intensity events the mobilization of fine particles is favoured, in which metals are preferably sorbed (Quinton and Catt, 2007). Likewise, the OC enrichment ratios are greater for sediments displaced by low intensity rainfall storms (Jacinthe et al., 2004; Martínez-Mena et al., 2012). In addition, as previously referred, soil erosion can also be accelerated by land use and management practices, such as tillage and intensive use of post-emergence herbicides (Poeplau and Don, 2013; Beniston et al., 2015; Labrière et al., 2015).

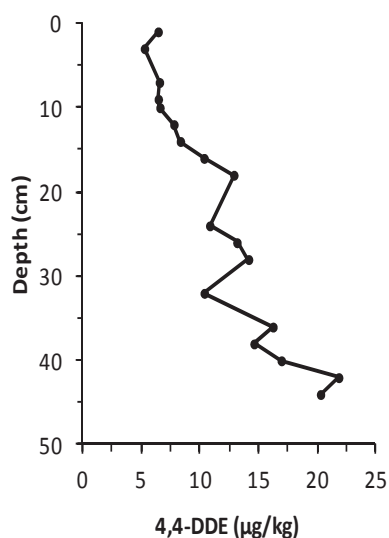


Fig. 6. 4,4-DDE distribution as a function of sediment core depth.

3.5. Levels of synthetic organic pesticides in sediment core

Regarding the profile of \sum DDX in the sediment core, and similar to soils, 4,4-DDE was the most frequently detected compound in these samples, which is in line with other studies (Thevenon et al., 2013; Bettinetti et al., 2016; Liao et al., 2017). Since 4,4-DDE is an aerobic degradation product of DDT, it means that DDT was probably degraded in soils and then remobilized into the aquatic system (Sabatier et al., 2014). Indeed, the relatively high levels found in the upper layers (around $6.5 \mu\text{g kg}^{-1}$), suggest that there is still an input. Nevertheless, the observed increase in the concentrations of 4,4-DDE levels with depth (Fig. 6), reflects the legacy of the past, and the behavior is similar to Cu. In fact, there is a significant correlation between these two contaminants ($r^2 = 0.70$). Several studies indicate that DDX residues in the sediment cores reached peak values in the late 1970s or early 1980s, which was the period of maximum use around the world and coincides with the age of the dam. The decrease in levels between 2 and 10 cm, should reflect the prohibition of this pesticide that occurred in 1988. However, other management practices can explain the continuous input of this contaminant. For example, the increase in the use of post-emergence herbicides, and the surfactants present in new pesticides formulations, have been related with remobilization of DDX (Neitsch et al., 2016; Sabatier et al., 2014). In recent years it is a common practice in Douro region the non-tillage practices, together with the application of herbicides only nearby the vine roots. Thus, these practices may result in a reduction of erosion, which can explain the more or less constant levels found in the first 10 cm, as observed in the PCA analysis (Fig. 5 b).

The median concentration observed for 4,4-DDE was $10.6 \mu\text{g kg}^{-1}$, ranging between 5.25 and $21.8 \mu\text{g kg}^{-1}$, which can be considered low when comparing with hotspots such as the Palos Verdes Shelf (levels of 4,4-DDE as high as $25100 \mu\text{g kg}^{-1}$ in surface sediments and $28400 \mu\text{g kg}^{-1}$ in a sediment core; Liao et al., 2017). In Como Lake (Italy), concentrations of 4,4-DDE in sediment cores ranged from 27 to $75 \mu\text{g kg}^{-1}$, and no significant decrease over time (since DDT was banned until to 2016) was observed (Bettinetti et al., 2016). However, levels found in Douro's sediment core can be considered high when comparing with levels found in Tagus estuary (Portugal). In Tagus estuary the most contaminated core showed a range of values between 1.4 and $250 \mu\text{g kg}^{-1}$, but despite the very high maximum value, the median concentration was just

$4.6 \mu\text{g kg}^{-1}$ (Mil-Homens et al., 2016). Similarly, in Lake Brè (Switzerland), concentrations of 4,4-DDE ranged from non-detect to $2.5 \mu\text{g kg}^{-1}$ (Thevenon et al., 2013). Nevertheless, according the Norwegian guidelines, based on ecotoxicological effects, the studied sediments can be classified as good, since most of values are between 0.5 and $20 \mu\text{g kg}^{-1}$. The upper limit for this class is based on the predicted no effect concentrations for chronic exposures to that compound (Bakke et al., 2010; Liao et al., 2017).

4. Conclusions

The vineyard soils of the studied area are, in general, acid, poor in macronutrients, and OM. In addition, a high variability of the contaminants studied was found between and in each vineyard. Residues of several pesticides (organic and inorganic) related to agricultural activities were found in soils. The levels found were in general low, with older vineyards showing higher levels of Cu and banned insecticides (such as DDT and its metabolites), evidencing the effects of accumulation and persistence of those pesticides. In addition to the physicochemical properties of pesticides, the period and rate of application, which highly depend on climatic conditions, have a great impact on the amounts of pesticides presented in the soils. Thus, the results obtained depend on the sampling period.

The landscape morphology (characterized by steep slopes) of this area promotes soil erosion and migration of pollutants. Therefore, the study of sediment core of dam reservoir proved to be a useful tool to understand the legacy of contaminants input from soils. The increase of pesticides levels with depth reflect the intensive use of these substances in the past. Although, the variability observed at small scale shows different input events, i.e. geogenic versus anthropogenic contributions. In addition, the presence of the metabolite 4,4-DDE in the upper sediment layers indicate that soils are still a source of contamination. This suggests the importance of management practices (e.g. ploughing) in the soil erosion and in the mobilization of such contaminants to other environmental compartments.

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