LEAD AND CADMIUM IN SOILS OF LA RIOJA VINEYARDS, SPAIN

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ABSTRACT

Land degradation can be triggered by the abuse of chemicals that damage soil quality. Agriculture is changing the chemical and physical properties of soils, and in vineyards, those changes are due to the use of pesticides. In order to assess the Pb and Cd content, 212 soil samples from La Rioja D.O.Ca were analysed. Concentrations of Pb in soil ranged from 0·96 to 64·31 mg kg^{-1} with a mean concentration of 21·26 mg kg^{-1} in the surface layer, while they ranged from 7·97–43·93 mg kg^{-1} with a mean of 20·83 mg kg^{-1} in the subsurface layer. The mean content of bioavailable lead was 1·03 mg kg^{-1} in the surface layer and 0·76 mg kg^{-1} in the subsurface. Cd overall average concentration was 0·29 mg kg^{-1} in the surface; in the subsurface, the mean was 0·31 mg kg^{-1} and ranged from 0·10 to 1·22 mg kg^{-1}. The values in the surface layers were 0·15 mg kg^{-1} and in the subsurface layer 0·01 of Cd bioavailability. On the basis of pedogeochemical Pb and Cd distribution, balanced fertilization will be of great importance for sustainable development of agricultural wine-producers. Copyright © 2016 John Wiley & Sons, Ltd.

KEY WORDS: lead and cadmium; vineyard soils; guideline levels; spatial variability; La Rioja D.O.Ca

INTRODUCTION

The fate of the soils of the world is related to human activities that can preserve soils ecosystems or degrade them. The influence of human management is definitive as we can trigger soil degradation processes, preserve soils or even recover soil by means of rehabilitation and restorations strategies that will bring to us again the services soils offer to human societies (Keesstra *et al*., 2012; Bai *et al*., 2013; Mekuria & Aynekulu, 2013; Berendse *et al*., 2015; Brevik *et al*., 2015a). Agriculture is one of the human activities that damages soils because of ploughing, herbicide application, depletion of organic matter, soil structure degradation, fire impacts or compaction (Cerdà *et al*., 2009; Keesstra *et al*., 2014; de Oliveira *et al*., 2015; Laudicina *et al*., 2015; Zornoza *et al*., 2015), and restoration and rehabilitation is difficult and expensive as the lost soil takes millennia to reform (Giménez Morera *et al*., 2010; Jordán *et al*., 2010; Brevik & Lazari, 2014; Mekonnen *et al*., 2015; Tejada & Benítez, 2014; Mekonnen *et al*., 2015; Roa-Fuentes *et al*., 2015).

Land degradation is triggered by the abuse of chemicals that damage soil quality (Roy & McDonald, 2015; Sacristán *et al*., 2015). Agriculture is changing the chemical and physical properties of soils, and in vineyards, those changes are due to the use intense ploughing (Novara *et al*., 2011; Lieskovský & Kenderessy, 2014; Costantini *et al*., 2015; Martínez-Casasnovas *et al*., 2015; Tarolli *et al*., 2015), and

the use of of pesticides (Vaudour *et al*., 2015). Accumulation of heavy metal in soils is of concern for agricultural production due to the adverse effects on food quality, crop growth, and environmental health (Fergusson, 1990; Ma *et al*., 1994; Brevik & Sauer, 2015; Oliver & Gregory, 2015). Those elements can accumulate in soils from a range of different sources: weathering of minerals contained in soil parent material (Baker & Amacher, 1982; Pacyna *et al*., 1991), use of biosolids or disposal of municipal sewage sludge and effluent recognized as an environmentally acceptable practice (Webber & Shamess, 1987; Abdul Kashem & Singh, 1999; Manthey *et al*., 2000) and fertilizers or agrochemicals (Nziguheba & Smolders, 2008; Czarnecki & Düring, 2015). Lead and Cd are two elements released in the environment through the natural weathering of rocks or from various sources related to human activity, such as soil management practices.

Lead and Cd are some of the less abundant trace metals, with an average lithosphere abundance of around 13 mg kg^{-1} for Pb Paterson (2011) and 0·098 mg kg^{-1} for Cd Heinrichs *et al*. (1980). Ure & Berrow (1982) calculate worldwide averages for the metals discussed as 29·2 and 0·62 mg kg^{-1}. Not all trace elements are essential to plant health. These elements are not required in soils, and their accumulation can have a negative impact on soil, plant health and, in some cases, might be accumulated in the human food chain, (Brevik & Burgess, 2013), as in wine. Therefore the use of contaminants, included waste materials, agrochemical and others, must be monitored and controlled.

Wine is a complex matrix, and trace elements are among the components that contribute to its quality. The

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consumption of wine in moderate quantities contributes to the requirements of the human organism for some essential elements, such as Ca, Cu, Se and Zn; however, levels of Cd and Pb may be potentially toxic (Galani-Nikolakaki *et al*., 2002; Monaci *et al*., 2003). Environmental contamination and agricultural practices may change the multi-element composition of wine and may endanger the relationship between wine and soil composition (Taylor *et al*., 2002; Almeida & Vasconcelos, 2003; Thiel *et al*., 2004; Ettler *et al*., 2006). For example, a major source of Pb in wine may be related to anthropogenic winery equipment, vine treatment and others.

Lead and Cd content in vineyard soils of La Rioja D.O.Ca are not found in the literature. Ocio *et al*. (1987 a, b, c) focused their attention only on soil characterization and classification in a restricted area, Rioja Alavesa. The present study was undertaken to provide a general assessment of the pedogeochemical levels of Pb and Cd from several Rioja D.O.Ca vineyard soils. Based on the fact that concentrations of trace elements in soils may be influenced by agricultural use (Roberts *et al*. 1994, Longhurst *et al*., 2004; Mico *et al*., 2006; Lambert *et al*., 2007; Gaw *et al*., 2008), the specific objectives of this study were to (i) assess soil Pb and Cd pedogeochemical contents in vineyard soils and (ii) contribute to the knowledge geographic distribution of these elements.

MATERIAL AND METHODS

La Rioja D.O.Ca is among the most famous and renowned wine regions in the world. Rioja D.O.Ca, the most famous wine Denomination of Origin (D.O.) in Spain, was established in 1926, (Rioja is the oldest D.O.). It was awarded the D.O. status, and is one of only two wine-producing regions that have received the prestigious D.O. Ca title. The research area, La Rioja D.O.Ca (Figure 1a), is located on the Iberian Peninsula. The region is largely agricultural land where the main produced crops are from vineyards (63·200 Has) and orchards. This region is divided into three distinct zones: (i) Rioja Alta (upper), located in the

highlands, in the west of the region (400–500 m), has an Atlantic climate and calcareous soils; (ii) Rioja Baja (lower), in the east (around 300 m), has a Mediterranean climate, quite dry and hot, with soils developed on fluvial materials; and (iii) Rioja Alavesa, (coolest and wettest), situated in the north. There are various parent materials: calcareous sedimentary rock marls, molasses, limestones and gypsums, (in terraces, glacis, ramps, etc.), in juxtaposition with a few acidic rocks; frequently with gravel. The climate is continental with an average temperature of 12–14 °C, and the precipitation ranges between 300–600 mm, including a long and cold winter and short summer.

The territory of La Rioja D.O.Ca has a wide range of soil that reflect the different nature of each and its distinct origins, differences in soil formation by factors such as parent material, landform, vegetation, climate and age. The result is a wide spectrum of soil types: entisols, inceptisols, mollisols, alfisols, exceptionally aridisols, (Soil Survey Staff, 2006); calcisols, regosols, cambisols, fluvisols, phaeozems, leptosols and luvisols, according to the FAO-ISRIC-ISSS (2006). For vineyards purposes, many of those soils have some chemical and physical limitations (e.g. high-active limestone contents) that require careful management (García Navarro *et al*., 2011).

Random soils samples were collected. At each site, two depths were sampled using a core; one representative of the surface layer (from 0 to 30 cm) and the other from the underlying layer or subsurface (30–70 cm). The number of samples was 212, corresponding to 106 sample locations. Each sampling location was identified in the field using a Garmin (Schaffhausen, Switzerland) Trex handheld global positioning system. A schematic diagram of the research sampling locations is shown in figure 1.

After field sampling, all the soil samples were dried at room temperature to a constant weight and carefully sieved through a 2-mm mesh. The coarser material was discarded, and the remaining fine-earth fraction was gently mixed until it appeared to be homogeneous. Aliquots of this fraction were randomly taken for chemical analysis. All samples were analysed for soil texture (Day, 1965). Organic matter (OM) content was determined by dichromate digestion based on the Walkley–Black method. Soil reaction was estimated potentiometrically after equilibration with H_2O and in 0·1 M KCl using a 1:2·5 soil/solution ratio. Calcium carbonate content was determined using a Bernard calcimetre. Pb and Cd were analysed after complete dissolution using a mixture $HNO_3/HClO_4/HF$ following a procedure described in detail in previous studies (Iñigo *et al*., 2013). Atomic absorption spectroscopy with a graphite furnace and a Varian (Palo Alto, CA, USA) 220 FS device were used to analyse those concentrations. The detection limits were calculated as three times the standard deviation of 10 sample blank (Tüzen, 2003) and were: 0·48 mg kg^{-1} for Pb and 0·02 mg kg^{-1} for Cd. The content of bioavailable components was determined with the method developed by Lindsay & Norvell (1978). Duplicates were used in order to assure quality control.
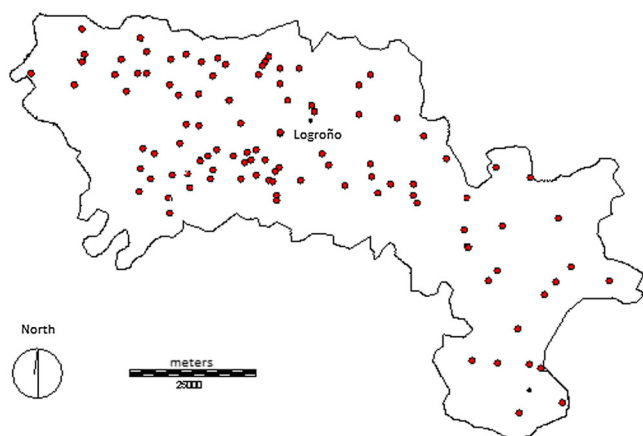

Figure 1. Location map of the study area and distribution sampling. Logroño is located in 42° 27′ 56·6″ N latitude and 2°26′ 20·4″ W longitude.

The statistical descriptors (mean, standard deviation, maximum and minimum) of the two individual trace elements were calculated using SPSS version 17 for Windows (Microsoft Corporation, Redmond, WA, USA). As a key factor to achieve the purposes outlined, we calculated the enrichment factor (EF), (top/bottom ratio), as indication of relative enrichment/depletion of elements in the uppermost soil layer. The geostatistical study was conducted with IDRISI 3·2.

RESULTS AND DISCUSSION

Table I provides the summary statistics for soil and the concentrations of Pb and Cd based on all samples (number of samples, mean, standard deviation, variance and maximum and minimum) for the soil layers at depths of 0–30 and 30–70 cm.

Observed textures were variable. The soil showed a significant pH variation and low organic matter. The vast majority of subsurface material was rich in calcium carbonate; therefore, the soil shows higher concentrations, especially in the subsurface layer. All these data showed distinct edaphic properties.

Pb and Cd Baseline Concentrations

Table I shows the mean, maximum, minimum, mean and standard deviation of the concentration of Pb and Cd in the 0–30 and 30–70 cm soil layers of La Rioja D.O.Ca vineyards soils.

Lead

Soil Pb concentrations ranged from 0·96 to 64·31 mg kg^{-1} (Table I) with a mean concentration of 21·26 mg kg^{-1} in the surface, while in the subsurface, they ranged from 7·97 to 43·93 mg kg^{-1} with a mean of 20·83 mg kg^{-1}. The mean content of bioavailable Pb was 1·03 mg kg^{-1} in the surface layer and 0·76 mg kg^{-1} in the subsurface. All these concentrations were similar to typical background concentrations found for 224 undisturbed soil samples of La Rioja soils (Iñigo et al., 2013). Those values also were generally low in comparison with concentrations found in other parts of Spain (Rodríguez Martín et al., 2006; Micó et al., 2007). The soil Pb contents are similar in both layers. Adriano (2001) found a mean concentration of 35 mg kg^{-1} in Spain, 30 mg kg^{-1} in France and 39 mg kg^{-1} in Europe. (Table II)

The mean soil Pb contents in our study were similar to those reported by Kabata-Pendias & Mukherjee (2007). Holmgren et al. (1993), found a mean concentration of 12·3 mg kg^{-1} in agricultural soils, while Zanini & Bonifacio (1992) found concentrations similar to the present study (21 mg kg^{-1}) in soils samples from agriculture sites. Our values are much lower than those reported by Onyari et al. (1991), from roadside soils in Kenya where Pb is still used as a gasoline additive, and found that concentrations within Nairobi City varied from 137 to 2196 mg kg^{-1} with a mean of 659 mg kg^{-1}.

Lead contents found in this study were lower than the European Union upper limit of 300 mg kg^{-1} (European Commission (EC), 1986); therefore, higher mean concentration has been found in European soils than in La Rioja D.O. Ca soils. Lead content values in this study were well below the soil guidelines that have been established for several countries (Morgan, 2013). Moreover, concentrations in the area did not exceed recommended guidelines for environmental soil health 86/278/CEE in agricultural soils with pH > 7·3 (European Commission (EC), 1986).

Table I. Trace element concentrations (mg kg^{-1}) and some properties at the soil quality.

	N	Minimum	Maximun	Mean	Standard Deviation	Variance	EF	RV
pH (S)	106	5·04	8·83	8·12	0·64	0·41		
pH (SU)	106	5·24	8·85	8·21	0·50	0·25		
CO$_3$Ca (S)	106	0·00	51·75	20·37	14·55	211·93		
CO$_3$Ca (SU)	106	0·00	54·32	20·98	14·39	207·33		
OM (S)	106	0·10	3·24	0·90	0·54	0·29		
OM (SU)	106	0·00	3·49	1·0	0·82	0·68		
Clay (S)	106	1·62	49·34	20·09	9·30	86·65		
Clay (SU)	106	0·00	45·93	18·34	9·70	94·25		
Pb total (S)	106	0·96	64·31	21·26	8·98	80·65		
Pb total (SU)	106	7·97	43·93	20·83	6·90	47·6		
Pb Bio (S)	106	0·3	10·72	1·03	1·40	1·97		
Pb Bio (SU)	106	0·4	4·03	0·76	0·67	0·46		
Cd total (S)	106	0·10	0·65	0·29	0·11	1·23		
Cd total (SU)	106	0·10	1·22	0·31	0·18	3·25		
Cd Bio (S)	106	0·01	0·03	0·15	6·27	3·94		
Cd Bio (SU)	106	0·0	0·40	0·01	8·67	7·52		
Pb total							1·02	39·22
								34·63
Cd total							0·93	0·51
								0·67

Soil properties (pH, organic matter %, calcium carbonate % and clay contents %) and descriptive statistics (median, standard deviation, etc.) of total and plant-available Pb and Cd contents in 212 vineyard soil samples. Also pedogeochemical baselines (RV) and enrichment factor (EF) of Pb and Cd in the D.O.Ca Rioja region
S, surface horizon; SU, subsurface horizons; Bio, bioavailable; EF, enrichment factor; RV, reference value.

Table II. Correlation matrix (surface horizons)

	pH	CO$_3$Ca	OM	Clay	Pb
pH					
CO$_3$Ca	0·296				
OM	0·002	0·095			
Clay	0·132	0·267	0·007		
Pb	0·030	−0·297	−0·036	0·046	
Cd	−0·114	−0·128	−0·130	−0·071	0·467

Significative correlation at 0·01 level (bilateral)

Cadmium

The concentration ranged from below the detection limit to 0·65 mg kg^{-1} (Cd was not detected in 34 surface layer, because they were below the detection limit <0·02 mg kg^{-1}). The overall average concentration was 0·29 mg kg^{-1} in the surface; in the subsurface, the mean was 0·31 mg kg^{-1} with a range from 0·10 to 1·22 mg kg^{-1}.

The concentration range for total Cd was higher than the concentration range of 0·07–0·3 mg kg^{-1} reported by Agbenin *et al.* (2009). Soil Cd levels found in this study were well below acceptable soil limits established by many countries (Morgan, 2013).

Soil contents found in this study are in line with what has been found in other soils of La Rioja (Iñigo *et al.*, 2013). The average Cd levels are below values established as excessive (5 mg kg^{-1}) by Adriano (1992), who found mean soil contents of 1·70 mg kg^{-1} for Spain, 1·76 mg kg^{-1} for Holland, 0·95 mg kg^{-1} for Norway and 1·0 mg kg^{-1} for Sweden.

Cadmium concentrations are comparable with those reported by Bowen (1979): 0·1–2·0 mg kg^{-1} in agricultural soils. In relation to other agricultural soils Holmgren *et al.* (1993) reported an average of 0·26 mg kg^{-1} in USA, and Chen *et al.* (1997) reported 0·8 mg kg^{-1} in Hong Kong. In general, concentrations in our study were below the 1–3 mg kg^{-1} limit recommended by the European Union and did not exceed recommended guidelines for environmental soil health 86/278/CEE on agricultural soils with pH > 7.

Statistical Correlations

Strong relationships ($p < 0.05$) were found Pb for surface/Pb subsurface and Cd surface /Cd subsurface, as found by Kumad *et al.* (1989). It should be stressed that both total Pb and Cd content showed negative relationships with calcium carbonate content (Bini *et al.*, 1988). These trends in the concentrations described seem to be related to the calcium carbonate of neoformation, because Cd can be fixed as CdCO$_3$ (Barona & Romero, 1996; Ramos *et al.*, 1994; Moreno *et al.*, 1996). Significant positive correlations were observed between Cd and clay contents in subsurface layer. The clay provides Cd with protection from water leaching and the Cd is made available in the soil as a plant nutrient. Bioavailable Cd positively correlated with the amount of organic matter. Therefore, clay content and organic matter content modified the Cd properties, (Angelone *et al.*, 1988; Bini *et al.*, 1988; Basta *et al.*, 1993; Ramos *et al.*, 1994; Alvim & Lourenco, 2000; Lafuente *et al.*, 2008).

Variability in Pb and Cd across Rioja D.O.Ca

Soil Pb and Cd in the sampling area are dependent on the soils and topography. In the present study, soil sampling reflected mainly soil type (including slope characteristics), recent soil amendments and field boundaries tillage. The multivariate statistical and GIS-based approach has been used by Facchinelli *et al.* (2001) and Lin (2002) to identify variations of heavy metal sources in soils. The maps presented in Figures 2 and 3 demonstrate the variability in Pb and Cd across the Rioja D.O.Ca vineyard region and represent the pedogeochemical baseline. These concentrations show a large scale pattern, with the highest values in the southern areas and decreasing concentrations towards the north.

Lead

A heterogeneous distribution of total Pb was found (Figure 2a), attributable to differences in parent materials contents and soil processes, whereas the bioavailable Pb contents showed a homogenous distribution (Figure 2c). Rioja Alta sector showed a greater level of total Pb in surface and subsurface layers while it was relatively low in Rioja Baja.

Frequency concentration in front of intervals showed three surface layer Pb populations: the first with an average of 20·02 mg kg^{-1}, (pertaining to 95% of the soil samples); the second with a 41·15 mg kg^{-1} concentration (3% of the soil samples within this area); and the third with a mean concentration of 101· mg kg^{-1} (2% of the soil samples). In the subsurface, there were three populations: the first with an average of 11·62 mg kg^{-1} (corresponding to 15% of the soil samples), the second with 21·47 mg kg^{-1} (80% of the soil samples) and the third 38·13 mg kg^{-1} (5% of the soil samples). Nearly 100% of the soil samples ranged between 11·62–41·15 mg kg^{-1}. We can infer a geological origin by comparing surface and subsurface maps. We take into account that the soil processes are of low intensity by the abundance of carbonate and low rainfall; also, hydrolytic weathering and the current pedoclimatic conditions exercise its influence on weathering processes and the geochemical pathways. So many times, the soils morphology is very simple: Ap-C or Ap-Bw-C. Pb distribution content shows, in the frequency concentration / intervals, a strongly skewed distribution with a mean value of 20·02 mg kg^{-1}.

Cadmium

Heterogeneity of Cd contents is displayed in the maps (Figure 3). Some soils of La Rioja Alta and Rioja Baja show higher concentrations, whereas relatively low values are
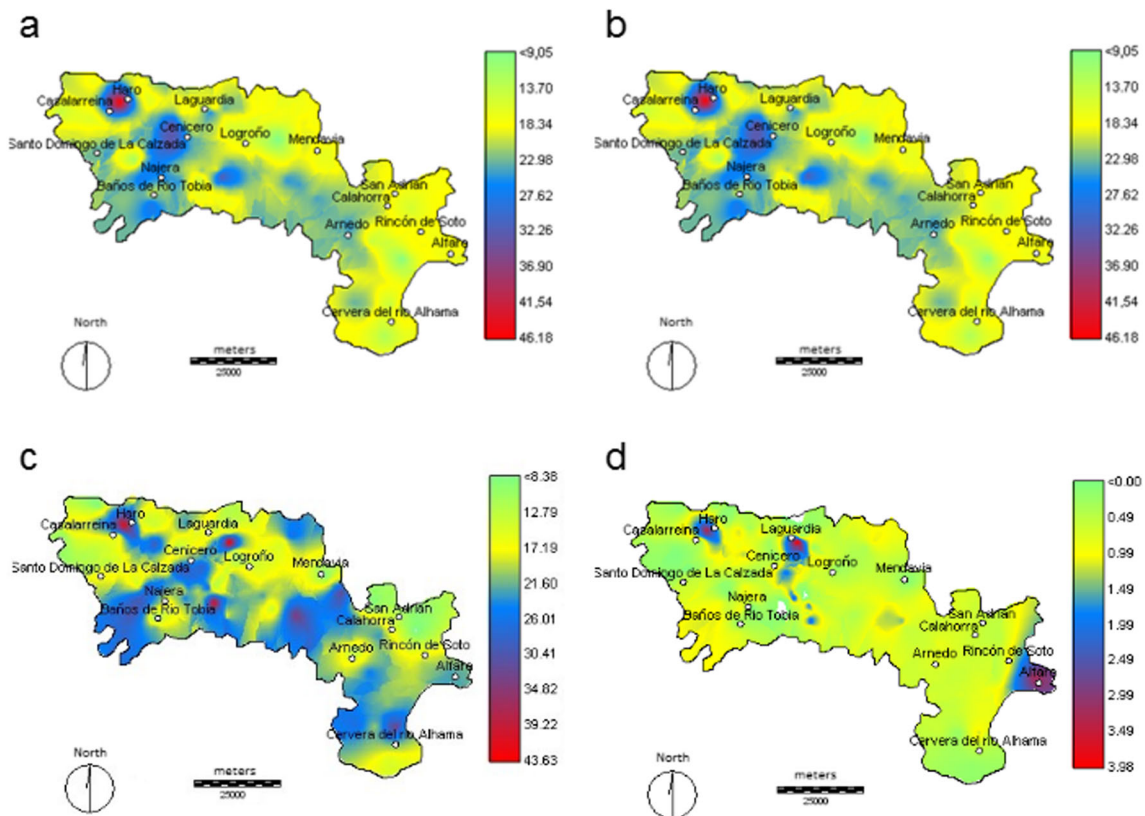
Figure 2. Spatial Pb content (values in mg kg^{-1}) observed in the vineyard soils of La Rioja (D.O.Ca). (a) Surface Pb content that reflects baseline levels. (b) Surface bioavailable Pb content. (c) Subsurface Pb content. (d) Subsurface bioavailable Pb content.

observed in some zones (Figure 3a). Cadmium bioavailable contents are also heterogeneous in the region (Figure 3c). Cadmium may be derived from the parent material (Cook & Freney, 1988) or have an anthropogenic origin (Czarnecki & Düring, 2015).

In the surface layer, almost all Cd values were below 0·2 mg kg^{-1}. Five Cd populations were identified: the first with an average of 0·05 mg kg^{-1}, (corresponding to 15% of the soil samples); the second with a 0·061 mg kg^{-1} concentration (5% of the soil samples within this area); the third with a mean concentration of 0·149 mg kg^{-1} (60% of the soil samples); the fourth with a 0·317 mg kg^{-1} mean concentration (10% of the soil samples); and finally, the fifth with 0·479 mg kg^{-1} (10% of the soil samples). There were four Cd populations in the subsurface layer: the first with an average of 0·134 mg kg^{-1} (corresponding to 30% of the soil samples); the second with 0·261 mg kg^{-1} (corresponding to 60% of the soil samples); the third with 0·489 mg kg^{-1} (8% of the soil samples); and the fourth with 0·840 mg kg^{-1} (2% of the soil samples).

Reference Values

Over the last decade, there has been a significant amount of research conducted in Spain having the goal to develop baseline values for trace elements (Junta de Andalucía, 2004; Jiménez Ballesta *et al*., 2010, etc.). Several approaches have been documented in the literature for determining the background TRACE METAL levels in soils

and sediments (Matschullat *et al*., 2000; McIlwaine *et al*., 2014). Because anthropogenic contamination can be present, background concentrations must be derived from statistical analyses applied to a dataset 'clean' of outliers. Basic statistics providing 'baseline values' (Reimann *et al*., 2005; Mrvić *et al*., 2011) and geostatistical predictions (Saby *et al*., 2009, 2011) are various methods for estimating the natural levels of TMs in a studied soil dataset.

The Pb and Cd baseline levels were determined after removing the outliers. Figure 4 (a and b) show the range of Pb and Cd contents in soil samples in the studied area as box plot diagrams. We used the following formula:

$$\text{Reference} \quad \text{value} = \text{mean} + 2 \times \text{SD} \qquad (1)$$

(Gil *et al*., 2004; Micó *et al*., 2007; Jiménez Ballesta *et al*., 2010). The final reference values were 39·22 mg kg^{-1} for Pb and 0·37 mg kg^{-1} for Cd.

Implications

Trace elements in agro-ecosystems may be inherited from soil parent materials or result from human activity-related inputs. The results show that Rioja D.O.Ca soils display a wide variety of elemental Pb and Cd contents. In a previous study, Iñigo *et al*. (2013) reported Pb and Cd contents in undisturbed soils of this region (La Rioja) almost identical those found in the vineyard soils of this study. In comparison with agricultural soils of Spain, (Rodríguez Martín *et al*., 2006 and Rodríguez *et al*., 2008), soils in the
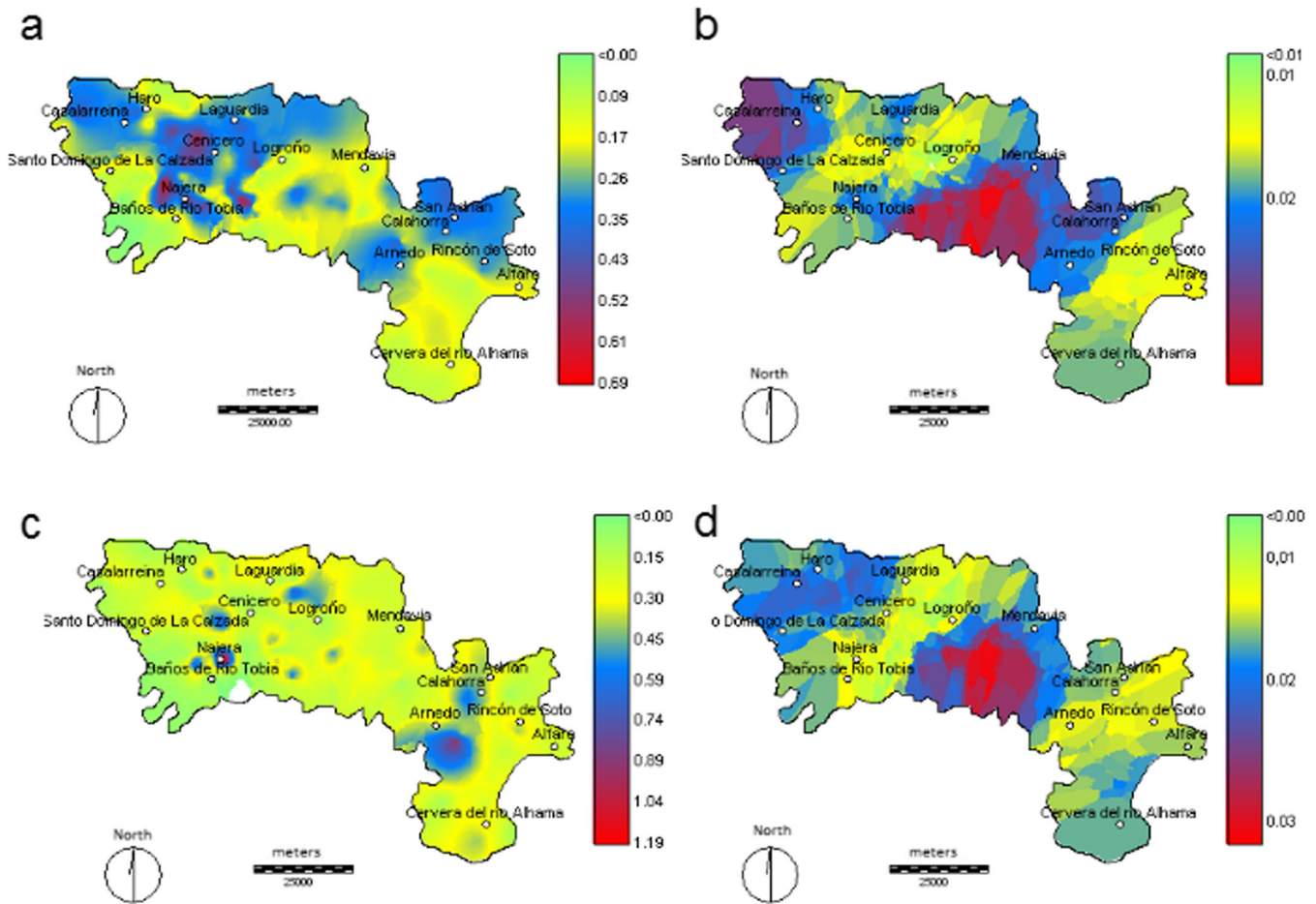
Figure 3. Spatial Cd content (values in mg kg^{-1}) observed in the vineyard soils of La Rioja (D.O.Ca). (a) Surface Cd content that reflects baseline levels. (b) Surface bioavailable Cd content. (c) Subsurface Cd content. (d) Subsurface bioavailable Cd content.
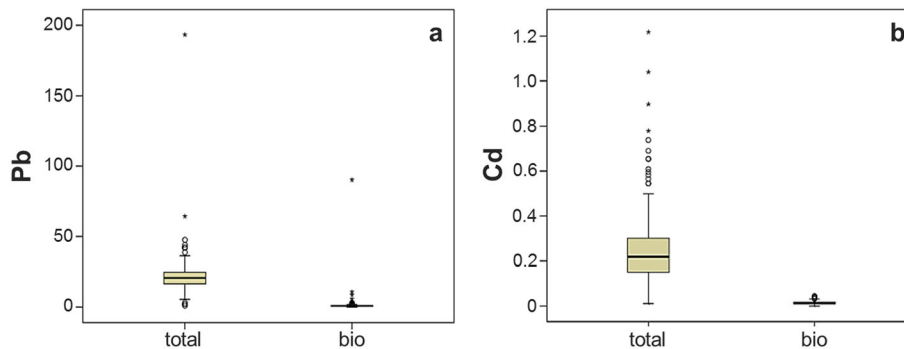

Figure 4. (a) Boxplot of Pb concentrations (mg kg^{-1}) in vineyard soils from La Rioja D.O.Ca. Outlier concentrations were mainly associated with agricultural practices (fertilizers and agrochemicals application) and with traffic from surrounding areas. (b) Boxplot of Cd concentrations (mg kg^{-1}) in vineyard soils from La Rioja D.O.Ca. Probably the source of outlier concentrations is the use of phosphate fertilizer, which contains cadmium as an impurity.

presentstudy have low or similar concentration values of Cd and Pb.

Asadi *et al*. (2012) and Ibáñez *et al*. (2015) found that the integrated effects of topography and land use determined soil properties. Topography is a relevant factor controlling soil erosion processes through the redistribution of soil particles and soil OM (Cerdà & García-Fayos, 1997). The range of soil erosion rates in vineyards is diverse because of the different land managements, climate conditions, parent material and soil properties, but generally, the soil and water losses are high and non-sustainable (Novara *et al*., 2013). The topographic factor has been traditionally included in the study of the spatial distribution of soil properties (Ozgoz *et al*., 2013; Wang & Shao, 2013; Brevik *et al*., 2015b). Some Pb concentration values could be ascribed to Pb deposition (from vehicles emissions rather than from fertilizers and pesticides).

The pedogeochemical baseline concentration summarized provides a baseline value for assessing soil quality and can be

used as screening levels to determine if naturally occurring Pb and Cd are present at ambient concentrations at the vineyard site. The study showed that Pb and Cd concentrations of the soils in the study area varied from one soil type to another.

CONCLUSIONS

Results of this research revealed that Pb and Cd concentrations in the vineyard soils of La Rioja D.O.Ca were similar with background concentrations found in other soils around the world. These concentrations show a large scale pattern, with the highest values in southern areas and decreasing concentrations towards the north. However, there is a considerable local variation. Cadmium and Pb mean values were 0·29 and 21·26 mg kg^{-1}, respectively. This data provides a reference for the status of Pb and Cd in vineyard soils for La Rioja D.O.Ca and will therefore be particularly useful for the evaluation of anthropogenic inputs as a result of land use activities. To evaluate the potential negative repercussions on the quality of agricultural soils by the presence of Pb and Cd, the spatial variability maps could help the understanding of potentially hazardous areas for agricultural crops (human and livestock).

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