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Contents and Spatial Distribution of Arsenic in Vineyard Soils in Mediterranean Environment

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Abstract This study presents the contents and spatial distribution of arsenic (As) in vineyard soils from the Valdepeñas Protected Designation Origin (PDO) in central Spain. As content varies within the 108.40–0.03 mg·kg^{-1} range in surface horizons, and within 151.00–0.03 mg·kg^{-1} in subsurface horizons. The mean value of both horizons is similar: 4.25 and 4.88 mg·kg^{-1}, respectively. Based on optimal spatial interpolation, the spatial distribution of As in soils was mapped by the IDV method. A simple data and map analysis suggests that pedogeogenic sources are the main sources for As (the As distribution tends to match the lithology and soil types), which indicates minor anthropogenic sources, mainly by agricultural sector activities. Only a high As concentration appears in the NE area, where sporadic moderate contamination is estimated based on Dutch criteria. The data obtained from the study area provide a broader view of the concentration, distribution, enrichment, sources, and the potential environmental contamination by As in the vineyard soils of this large wine-growing zone. The assessment of the results indicates that As does not affect agriculture (vineyards) in the study area because its concentrations are low in the soil types used by agriculture. These data can be employed as a guide to learn the range of values in vineyard soils in the European Mediterranean Region that are relatively unpolluted from industrial sources to make comparisons to more polluted areas.

Keywords Agriculture · La Mancha · Land use · Vineyard soil · Total arsenic · Variability · Geochemical baseline value

1 Introduction

A series of essential micronutrients is required for the functioning of living beings but, at the same time, excess amounts of these elements produce cellular and tissue damage, which leads to a variety of adverse health effects on humans, plants, animals, and the environment. One element associated with micronutrients is As (a metalloid that occurs in the Earth's crust and, therefore, in soils), which is a non-essential nutrient that interferes with plants and can endanger crop growth.

Arsenic is a widely extended element in soil (Mandal & Suzuki, 2002). The total As content in soil varies between 0.1 and 50–80 mg·kg^{-1} worldwide (Adriano, 2001; Alloway, 1995; Bohn et al., 2001; Kabata-Pendias & Mukherjee, 2007), with a mean of about 7.2 mg·kg^{-1} (Bowen, 1979).

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According to Wedepohl (1995), Rudnick and Gao (2003), and Kabata-Pendias and Szteke (2015), As varies from less than 0.1 to 67 mg·kg^{-1}. Arsenic concentrations greater than 600 mg·kg^{-1} have also been reported (Adriano, 2001, Doubts, 1984).

Studies have shown that excess As allows agricultural products to enter the body, which can cause a series of health problems (Garg & Singla, 2011, Shi et al., 2017). Although As is beneficial for plants at very low concentrations, it is known for its environmental toxic effects. Thus, excess As can cause abnormal plant growth and disrupt the ecological balance (Mir et al., 2007; Yamaji et al., 2008; Yang et al., 2018). The consequence of all this is that As is present in food and beverages, which is a matter of concern because this element is classified as carcinogenic in humans.

Arsenic is present in soils that derive from both natural and anthropogenic sources. Thus, As appears in soils not only through the natural processes of mineral weathering, but also through anthropogenic activities like industry and some agricultural practices, which can lead to the contamination of soil and water. In vineyards, As contamination can be induced by applying pesticides, which have been forbidden since the end of the twentieth century (Huzum & Sirbu-Radasanu, 2021). Therefore, in recent decades, concern about the improper usage of hazardous agrochemicals has grown.

Since the Bronze Age, the Mediterranean Region has been home to many civilizations (Pérez-Lambán et al., 2014) and diversified agroecosystems of high ecological value have been developed (Aguilera et al. (2020). One of the most valued in the Mediterranean Region is vineyards. In vineyards, adding fertilizers and controlling certain diseases, such as mildew or powdery mildew, with pesticides are common practices. As has been habitually employed for pesticides, which means that its content in many soils has increased. However, given its toxicity, the amount of As in pesticide has been reduced, but it is still a dominating element in pesticides (Deschamps & Matschullat, 2011). This study aims to conduct fieldwork and laboratory analysis to map As distribution and to provide baseline data in vineyard soils from the extensive Valdepeñas Protection Designation Origin (PDO) in central Spain.

2 Materials and Methods

2.1 Overview of the Study Area

The study area (the center of a grape-growing district) is seated on a plateau that is surrounded by hills, on the southern edge of the Castilian South Submeseta, in the geographical context located in the connection zone between Campo de Montiel and Campo de Calatrava. The terrain is a practically flat or curved backed physiographic configuration and it is interrupted by residual reliefs in the form of island mountains (inselberg) as well as alluvial deposits (Fig. 1). The area is occupied largely by carbonated materials (limestones, marls, etc.) and, to a lesser extent, by quartzite, phyllite, argillite, basalts, and schist rocks. The annual average temperature and rainfall are 12–14 °C and 450 mm, respectively (AEMET, 2011). Its climate is semi-arid (BSh class according to Koppen, 1984) with a marked dry summer. Its low pluviometric and high evapotranspiration values coincide with the highest temperatures. Isolated patches in the entire area are occupied by inselberg or areas with mountainous relief. Of all the territory, 53% are human settlements, mainly with vineyards, olive trees, and cereals, and the remaining area is covered by Mediterranean forests.

2.2 Soil Sampling and Analytical Procedure

During June 2017 to February 2018, 90 soil profiles were described (according to FAO, 2006 guidelines) and sampled (gradually, profile by profile); two subsamples (two replicates) were collected for cross-check analysis purposes (Fig. 1). Soil samples were air-dried and passed through a 2-mm sieve before the chemical analysis. All the analyses were performed by X-ray fluorescence (XRF) (PHILIPS PW 2404) in the solid mode in a powdered aliquot of each sample. The pearls' procedure was as follows: about 5 g of sample powder (−200 mesh) was spread in the aluminum cup (40 mm diameter) over boric acid powder and pressed into a pellet by applying pressure (approx. 20 tons) with the help of a hydraulic press pellet machine to obtain a uniform pressed pellet. Quality control was evaluated by running a duplicate analysis of certified soil reference materials (NIST 2710 and CRM 039).

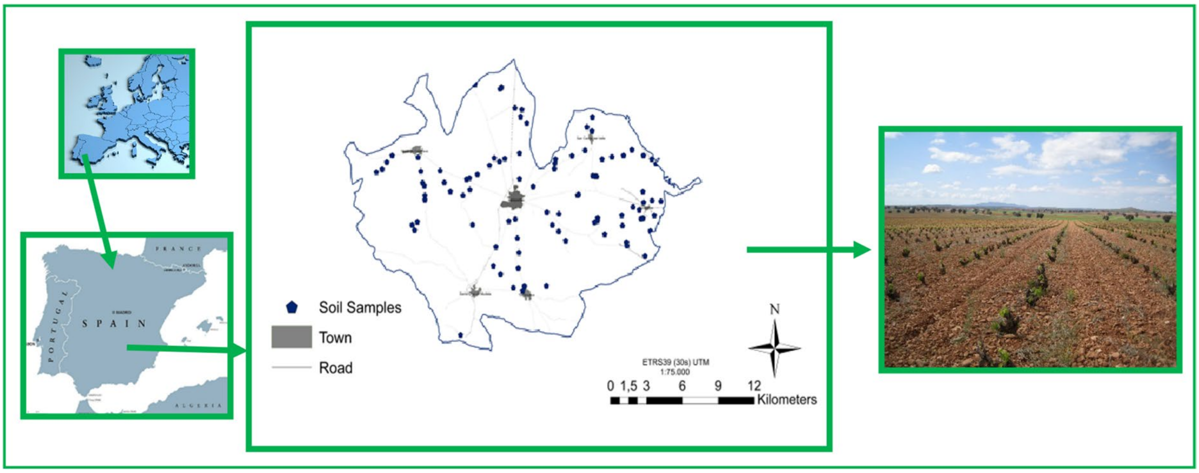

Fig. 1 Overview location map of the study area and sampling points. On the right, typical landscape with red soils showing petrocalcic horizons

To evaluate the magnitude of potential contamination, according to the criteria for contaminated land (Dutch List, 2013), the following As concentrations in soils were established (expressed as mg·kg^{-1}): uncontaminated < 20; medium contaminated 20–50; heavily contaminated > 50.

2.3 Statistical Analysis

Mathematical calculations were done using the Microsoft Excel 2013 software and the Statistical Package for Social Science computing package (SPSS 19.0 for Windows, SPSS Inc., IL, USA), both with an institutional license for the University of Castilla-La Mancha (Spain). Predictive maps of spatial variability were produced by processing data by the IDW (inverse distance-weighted) algorithm.

3 Results and Discussion

The descriptive statistical parameters (Table 1) were minimum, maximum, mean, percentile, and coefficient of variation. The total As content markedly varied within the 108.40–0.03 mg·kg^{-1} range on surface horizons and within the 151.00–0.03 mg·kg^{-1} range on subsurface horizons. The mean varied from 4.25 mg·kg^{-1} on upper horizons to 4.88 mg·kg^{-1} on deeper ones. As occurs in the Earth's crust at levels between 0.5 and 2.5 mg·kg^{-1} (Kabata-Pendias & Szteke, 2015), or 1.5 mg·kg^{-1} according to Bowen (1979). Therefore, As appears in soils as moderately enriched compared to the average upper crust. Taking into account the proposals of Alfaro et al. (2015) and Bocardi, et al. (2020), who propose that the reference value is defined as the 75th percentile (after excluding outliers), the geochemical baseline value for As in this PDO is set at 4.55 mg·kg^{-1}.

Table 1 Descriptive statistics of the studied metalloid (As)

Parameter	Surface horizon As (mg·kg^{-1})	Subsurface horizon As (mg·kg^{-1})
N	90	89
Mean	4.25	4.88
CV	2.64	3.14
Maximum	108.40	151.00
Minimum	0.03	0.03
75th percentile	7.25	5.85

N, number of samples

As abundance worldwide in soil is 7.2 mg·kg^{-1} (Bowen, 1979). However, the literature about the occurrence of soil As reveals widely disparate As concentrations with no apparent spatial pattern (Table 2). Thus, the mean As values in natural soils range between 0.1 and 80 mg·kg^{-1} worldwide for Alloway (1995), Adriano (2001), Bohn et al. (2001), and Kabata-Pendias and Mukherjee (2007). Other authors, such as Mench et al. (2009), state that

Table 2 Total As concentrations (in mg·kg^{-1}) according to different authors

Authors	Country or area	As concentration (range or mean)
Bowen, 1979	World	7.2
Alloway, 1995; Adriano, 2001; Bohn et al., 2001; Kabata-Pendias & Mukherjee, 2007	World	0.1–80
Wedepohl, 1995 and Rudnick & Gao, 2003	World	0.1–50
Burt et al., 2003	USA	7.2
FOREGS, 2005	Europe	11.6
Román-Villegas et al., 2012	Italy	3.7–283
Kabata-Pendias & Szteke, 2015	World	< 0.1–67
Mench et al., 2009	World	< 10
Jiménez-Ballesta et al., 2010	Castilla-La Mancha (Spain)	7.4
De Carlo et al., 2013	Hawaii	0.28–740
Marchant et al., 2017	France	18
Reimann et al., 2014	Europe	7
Smith et al., 2014	USA	Hor A* 5.2; Hor C* 5.7
Zuzolo et al., 2020	Italy	62.2
The present study	Valdepeñas PDO (Spain)	Hor A 4.25; Hor B* or Hor C 4.88

*Hor A, Hor B, and Hor C, horizon A, B, and C, respectively

concentrations in natural soils are generally below 10 mg·kg^{1}. Kabata-Pendias and Szteke (2015) provide values from less than 0.1 to 67 mg·kg^{-1}, with the lowest in light sandy soils and the highest in heavy loamy and organic soils. For Wedepohl (1995) and Rudnick and Gao (2003), the total As content in soil varies from 0.1 to 50 mg·kg^{-1}, with a mean of about 6 mg·kg^{-1}. The mean content calculated for topsoils in the USA is 7.2 mg·kg^{-1} (Burt et al., 2003), whereas this value for European soils is estimated at 11.6 mg·kg^{-1} (FOREGS, 2005). Soil As concentrations have been examined by Tarvainen et al. (2013) in Europe by means of a literature review: The soil baseline for As is only 20–40 mg·kg^{-1}, but the highest concentrations in soil go up to 5000 mg·kg^{-1}.

In Europe, soil As concentrations have been investigated in the European-wide FOREGS (Forum of European Geological Surveys) geochemical baseline mapping program (Salminen, 2005). As distribution in European agricultural topsoil can be explained mostly by geology (Tarvainen et al., 2013). The median As concentration in topsoil in France is 18 mg·kg^{-1} (Marchant et al., 2017). When studying the total As concentration in European agricultural soils, Reimann et al. (2014) found a median value of 7 mg·kg^{-1}. This is 1.23-fold higher than the As abundance in the Earth's upper crust, which is 5.7 mg·kg^{-1}.

By means of Smith et al. (2014), the USGS (United States Geological Survey) has investigated As concentrations throughout the conterminous USA and found a median value of 5.2 mg·kg^{-1} on the A horizon and one of 5.7 mg·kg^{-1} on the C horizon. In China, the baseline soil As concentration mainly depends on parent material, and varies between 1.06 and 31.2 mg·kg^{-1}. The mean value of 7.42 mg·kg^{-1} comes close to the European mean As concentration in agricultural soil (Hu et al., 2016).

Therefore, from all this, it can be deduced that the range of As content values is variable in the vineyard soils of the study area, which are somewhat lower in a non-negligible proportion in relation to other soils in the world on a global scale, and only one point can be considered a hot spot of As.

A clear spatial distribution pattern is observed on the map of As in the Valdepeñas PDO. The spatial distribution mapping of As (Fig. 2) matches lithology and soil types, which suggests a minor anthropogenic origin. Only a significantly high As value appears in the NE parts of the study area, which overlaps the area where a stony phase frequently develops. Indeed, a higher As concentration (150 g·kg^{-1}) prevails in the NE part of the study area near the San Carlos del

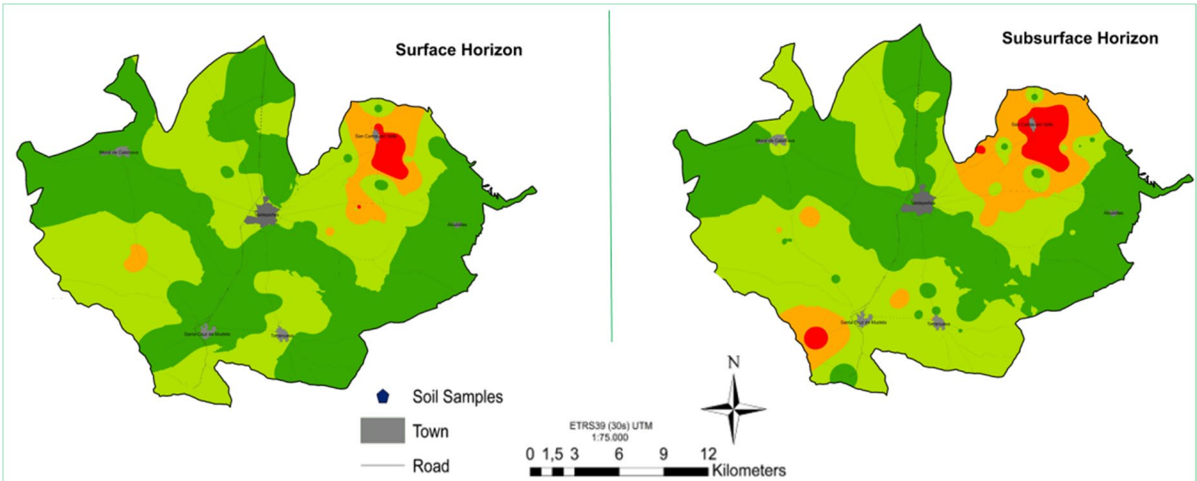

Fig. 2 Spatial patterns of the soil As contents in surface and subsurface soil layers; **a** surface horizons; **b** subsurface horizons

Valle municipality, and is probably of anthropogenic origin. These soils, which develop mainly on Plio-quaternary materials (raña or rañizo types), derive from a Paleozoic crystalline stratum (quarcite, shales, etc.), and are old red soils.

As is a potentially harmful metalloid that can enter the environment from both natural and anthropogenic sources. According to Mandal and Suzuki (2002), anthropogenic sources of As exceed the natural sources in the environment by 3:1. High toxicity often threatens human health, and even global ecosystems (Nriagu et al., 2007). The literature describes some areas with severe topsoil As contamination, such as the old open-burning grounds in Western Flanders (Belgium) (Bausinger & Preuss, 2005) and in France near Verdun (Bausinger et al., 2007). This mechanism does not apply to our study area, but the excessive application of pesticides and fertilizers to produce bigger crop yields, to protect from diseases, plus extensive groundwater pumping for irrigation purposes, could in the future result in As enrichment.

Depending on the state in the USA, the cleanup guidelines for As in soils for unrestricted use range from 7 to 40 mg·kg^{-1} (Teaf et al., 2010). The soil guideline values in the UK for residential/allotments is 20 mg·kg^{-1} and 500 mg·kg^{-1} for commercial/industrial use (DEFRA, 2002). In Andalusia (S Spain), a preliminary approximation for establishing these levels sets the total As thresholds for agricultural soils, natural parks, and industrial areas at 50, 100, and 300 mg·kg^{-1}, respectively (Aguilar et al., 1999). The most restrictive reference values are established for agricultural soils, with large differences between countries: 10 mg·kg^{-1} in the UK (Barth & L'Hermite, 1987) and 19 mg·kg^{-1} in Belgium (BWRHABT GG, 1995).

Regarding the criteria for contaminated land (Dutch List, 2013), the following As concentrations in soils are established (in mg·kg^{-1}): uncontaminated < 20; medium contaminated 20–50; heavily contaminated > 50. Based on these criteria, only one sample is heavily contaminated, only 2 samples are medium contaminated, and the rest are, therefore, uncontaminated.

The results assessment indicates that As does not affect agriculture in the study area because the As concentrations are low in the soil types used for agricultural purposes. The following have been cited as possible anthropogenic sources of As: (1) landfills and other disposals, especially sludge; (2) chemical and allied products; (3) lumber and various wood products. Agricultural and orchard practices have also been cited as a significant source of As because their contents are usually high in pesticides, fertilizers, sewage sludge, and manure. As-rich pesticides and punctual groundwater overexploitation are the probable anthropogenic sources of As in our area.

Smith et al. (1998) reported the highest As concentrations in orchard soils of the Washington State to fall within the 106–2553 mg·kg^{-1} range. Obviously, these results are very far from those herein identified, whose maximum value is 151 mg·kg^{-1} at only one point. The application of sewage sludge is a potential anthropogenic source of As (Tarvainen et al., 2013), but certainly, the application of such residue is practically non-existent in our area.

Soil As accumulation from agricultural pesticide applications has been reported at, for example, sites across the USA (Belluck et al., 2003; Yang & Donahoe, 2007). As-rich pesticides and groundwater overexploitation are, therefore, possible sources of As contamination in soils. So, it should be noted that depending on the prevailing semi-arid conditions, bigger vineyard areas are irrigated every day. Therefore, As anomalies will be primarily attributed to the use of pesticides in the Valdepeñas PDO.

The As concentration in vineyard soils was studied by considering Valdepeñas to be one of the most extensive areas in Europe in which to grow vine. Bertoldi et al. (2013) found that the soil As concentration ranged from 3.7 to 283 mg·kg^{-1} in vineyards situated in an old mining area. Senesi et al. (1999) reported that the As content in mineral and synthetic fertilizers ranged from 2.2 to 322 mg·kg^{-1} with triple superphosphate at the highest level. The values provided in this study are much lower than the level cited by the above authors. As contamination can be induced by the use of pesticides (Huzum & Sirbu-Radasanu, 2021). Fertilizer overuse is a major driver of soil contamination, particularly in irrigated cropping systems (e.g., Sanz-Cobena et al., 2017). However, our analysis performed to identify As sources reveals mainly a pedogeogenic source, although anthropogenic sources can be possibly contributed by As-rich pesticides and groundwater overexploitation for irrigation purposes. Nevertheless, near mining areas, Román-Villegas et al. (2012) found high As content in soils, although this content (in berries and wines) is very low and does not represent a risk for human health.

Based on our results, 99% of soils in the study area can be described as uncontaminated by As. Only one point showed heavy contamination (Fig. 3), which means 1% contaminated. So, only this point needs to be paid attention. Therefore, anthropogenic sources of contamination, such as use of pesticides, fertilizers, automobile emissions, and groundwater overexploitation, do not need to be reduced in this PDO. However, it is necessary to consider what Fiket et al. (2011) indicate: that wines are influenced not only by the mineral composition of the soil, but also by the geochemistry of the water used in irrigation management.

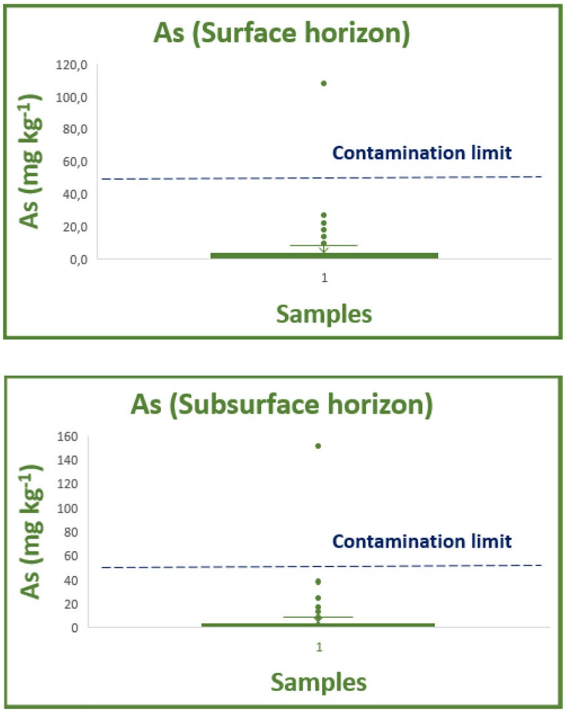

Fig. 3 Box plot diagram of As contents. The mid-line of the box indicates the limit of the criteria for heavily contaminated > 50 (mg·kg.[1]) in soil (RIVM, 2000, Dutch List, 2013)

In summary, it can be concluded from the observed results that most vineyard soils in the Valdepeñas PDO study area are free of As contamination.

4 Conclusions

In this study, the field sampling data from the Valdepeñas PDO were analyzed to characterize the As content and spatial distribution in soils at different soil depths and to also decipher the level of potential contamination. The findings of the study are as follows: the average concentration of the studied metalloid is moderately higher than the mean in crusts, which falls in line with many world regions. It is evident that the topsoil samples in the studied region do not exhibit significant to very high As enrichment, but quite the opposite: minimum As enrichment. Some points show higher As concentrations around the NE part of the study area, which coincide with the presence of the Paleozoic crystalline stratum (quarcite, shales, etc.) and derived soils on plio-quaternary surfaces (red soils). Following international criteria, low or moderate As contents in nearly 99% of the study area do not pose environmental contamination, with slight to medium environmental contamination in the rest of the area (~1%). These data can be used as a guide to know the range of values in vineyard soils of the European Mediterranean Region that are relatively uncontaminated by industrial sources to allow a comparison to be made to more contaminated areas.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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