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Lead isotopic fingerprint in human scalp hair: The case study of Iglesias mining district (Sardinia, Italy)

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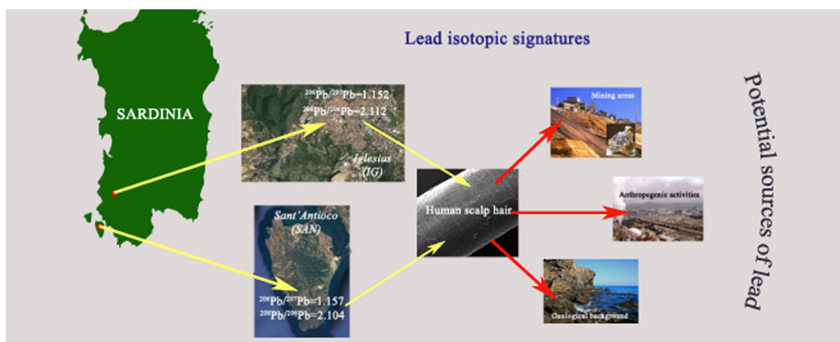
HIGHLIGHTS

- Lead isotopes data pointed to a mixing among lead derived from geogenic and anthropogenic sources.
- We measured lead isotopes in human hair and road dust samples to trace the potential sources of Pb in Iglesias district.
- High concentrations of lead in hair from children living close to the mining site were observed.

GRAPHICAL ABSTRACT



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ABSTRACT

The Sulcis-Iglesiente district (SW Sardinia, Italy) has been, until recently, one of the most important Italian polymetallic mining areas for the extraction of lead. Epidemiological studies conducted over several decades have indicated this site at high risk of environmental crisis with possible adverse effects on the public health. In the present paper we discuss Pb isotope signatures in human scalp hair and road dust collected from the Sulcis-Iglesiente area in order to trace the exposure of populations to potential Pb sources. A total of 23 determinations (20 on hair samples and 3 on road dust samples) of lead isotope ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb) were carried out. The obtained results were integrate with literature data regarding the total content of Pb in hair samples from the same study area. Hair from children living in Sant'Antioco exhibited lead isotope ratios in the ranges 1.152–1.165 for ^{206}Pb/^{207}Pb and 2.101–2.108 for ^{208}Pb/^{206}Pb, while hair samples from Iglesias resulted less radiogenic: ^{206}Pb/^{207}Pb ~ 1.147–1.154 and ^{208}Pb/^{206}Pb ~ 2.106–2.118. These values pointed to a multi-source mixing between the less radiogenic sources, corresponding to the Pb ore deposits, and the more radiogenic sources identified in local background.

1. Introduction

Mining areas are environmental sites raising great health concerns because of the release of a variety of harmful metals and metalloids into soil, air and water causing potentially deleterious effects on the

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populations living nearby. Such an environmental hazard lasts throughout the mine exploitation period, and may continue years after it has been shut down. The Sulcis-Iglesiente district (SW Sardinia, Italy) has been, until recently, one of the most important Italian polymetallic mining areas, where Pb and Zn were extracted since the time of Phoenician, Carthaginian and Roman domination. The polymetallic mineralised occurrences mainly contain galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and barite ($BaSO_4$) (Boni et al., 1996; Boni et al., 2002).

The industrial activity peaked with the industrial revolution and ended in the 1990s. Nowadays, the remaining wastes, still present, deliver heavy metals into the local environment.

Located close to the town of Iglesias, the San Giorgio area constitutes a dramatic example of an area affected by intense mine pollution. There are 17 million cubic metres of open pit excavations and 12 million cubic metres of dump and tailings (RAS, 2003; http://www.sardegnaambiente.it/index.php?xsl=612&s=169247&v=2&c=4807&idsito=18). Southern and western winds can easily transport metal-enriched particulate matter from the mining wastes to the densely populated town of Iglesias, located only a few hundreds of metres away. Pollution can also reach the local rivers, ponds and sediments through runoff, even though some natural abatement processes exist (De Giudici et al., 2017).

Epidemiological studies regarding the mining areas of Sardinia have indicated the Sulcis-Iglesiente as a typical example of how dispersion of metal can affect human health. As pointed out by Biggeri et al. (2006), the district of Sulcis-Iglesiente, and more particularly the towns of Iglesias and Arbus, are characterized by statistically significant excesses of i) mortality of males, largely caused by non-neoplastic respiratory conditions; ii) deaths from pneumoconiosis and iii) lung cancer of males. These authors also highlighted that, in relation to the closure of mines, there was a time trend (1981–2001) towards a decrease of mortality due to respiratory conditions, which nevertheless remain largely higher than the regional average, even in the most recent periods. Relevant to metal dispersion health threats, studies of multiple sclerosis epidemiology in southwest Sardinia suggested that this disease is related to the environmental influence exerted by geology and the occurrence of mine wastes (Cocco et al., 2011).

Among the metals to which the people living near Sulcis-Iglesiente district is particularly exposed, lead is certainly the one that causes most concern because of its high toxicity. High levels of Pb in other local environmental matrices are well documented in literature. For example, the low quality of waters in the study area, with high dissolved Pb, Zn and Cd was already reported by Cidu et al. (2001, 2007, 2009, 2012) and Medas et al. (2012a, b) and De Giudici et al. (2017). Contaminated waters are often discharged directly into local creeks facilitating the dispersion of contaminants in the environment. Boni et al. (1999) carried out a stream sediment survey in southern Iglesiente and observed high contents of Pb, Zn and Cd in samples collected along the carbonate ridges bordering the mining district of Iglesias. Furthermore, Leita et al. (1989) reported that soil and vegetation samples had Pb levels exceptionally high with concentration of 71,000 μg/g and 4000 μg/g, respectively. Recently, Cidu et al. (2012) confirmed lead anomalies values in soil reporting mean concentration of 492 mg/kg.

Human biological matrices, such as blood (Sanna et al., 2007, 2011; Forte et al., 2011; Gil et al., 2011; Madeddu et al., 2013), hair (Sanna et al., 2007, 2008, 2011; Varrica et al. 2014a); urine (Sanna et al., 2011) and adipose tissue (Vallascas et al., 2013) also revealed exceptionally high levels of metals and metalloids in people living close to the mining sites, with respect to other parts of Sardinia. As an example, Madeddu et al. (2013) asserted that subjects living closed to sardinian dismissed mine exhibited higher Pb concentrations in blood (geometric mean: 41.4 μg/L) than controls (geometric mean: 26.5 μg/L). Similar findings were obtained by Sanna et al. (2008) who employed human scalp hair as biomonitoring matrix. These authors reported that lead levels in children living from two towns in the Sulcis-Iglesiente area (Carbonia and Gonnesa) were significantly higher than those in children living in the unexposed town of Sinnai (southern Sardinia), with mean values of 1.86 and 0.91 μg/g in male and 2.21 and 2.03 μg/g in female respectively, compared to 0.68 μg/g in Sinnai male and 0.50 μg/g in Sinnai female.

We decided to use Pb isotope ratios to identify the main sources of lead contamination in this peculiar area. The feasibility of the method was ensured by the large body of literature describing how lead isotope ratios measured in different environmental matrices such as soil, streams and groundwater, house dust, sediments, airborne particulate matter, ore deposit, human hair and blood (Barton et al., 2000; Bollhofer and Rosman, 2001; Duzgoren-Aydin and Weiss, 2008; Gulson, 2008; Komarek et al., 2008; Cheng and Hu, 2010; Font et al., 2012; Félix et al., 2015; Vautour et al., 2015; Brewer et al., 2016; Cicchella et al., 2016; Cuvier et al., 2016; Witt et al., 2016; Mil-Homens et al., 2017; Rezza et al., 2017; Vázquez Bahéna et al., 2017) can be reasonably used to discriminate Pb derived from geogenic or anthropogenic sources.

In the present paper we present and discuss the results of 23 determinations of lead isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$), carried out on 20 hair samples and 3 road dust samples, along with literature data (Varrica et al., 2014a) regarding the total content of Pb in hair samples from the same study area.

2. Material and methods

2.1. Study area

A simplified geological sketch map of the study area (SW Sardinia) is shown in Fig.1. The town of Iglesias is located near the mining – waste of San Giorgio area. In addition to the release of harmful elements from mine wastes other potential local pollutants are limited to emissions from vehicular traffic. The area of Sant'Antioco Island is not affected by intense mine activity and the pyroclastic volcanic rocks, outcropping in this site, are not characterized by metal mineralisation events. The city is affected by anthropogenic impact due to the proximity to the metallurgical plants of Portovesme Harbour that were active until a decade ago.

2.2. Hair samples

A total of 20 hair samples from Sant'Antioco (10 samples) and Iglesias (10 samples) were collected and analysed for lead isotope ratios. Donors were randomly selected and considered eligible if they belonged to these categories: Caucasian ethnicity, age between 11 and 13 years, living in the selected area for >5 years, absence of diseases, recent surgery or orthodontic treatment, non-smokers and natural hair colour. According to the EU and national legal and ethical requirements, children's legal representatives signed consent forms authorising sample collection. The procedure for hair sampling may be found in Varrica et al., 2014a.

2.3. Roadway dust samples

Three roadway dust samples were also collected; two close to the mining area, more precisely one at Monteponi (RD_{MT}), and another one within the urban area of Iglesias (RD_{IG}). A third sample was collected at Sant'Antioco (RD_{SAN}), an area outside the mining site, but affected by industrial activities. Samples were collected from several points of the road edges using a plastic brush and stored in small self-sealing plastic bags.

2.4. Sample treatment

In the laboratory of Dipartimento di Scienze della Terra e del Mare (DiSTeM), University of Palermo, hair samples were reduced into smaller fragments, repeatedly washed with 2-propanone and water, dried at

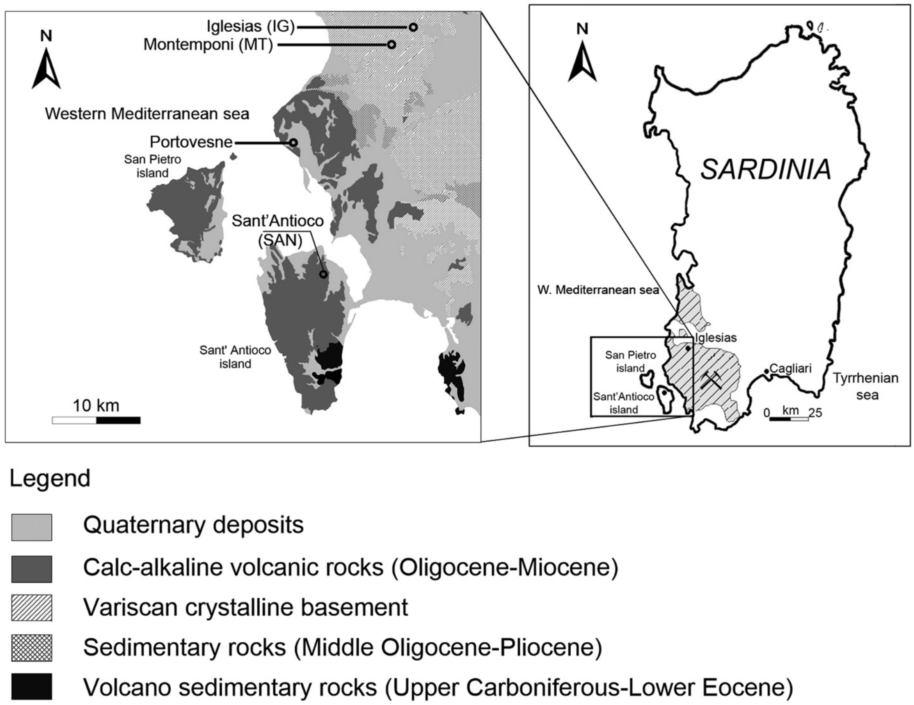

Fig. 1. Simplified geological sketch map of the study area (SW Sardinia), as proposed by Carmignani et al., 2012 and Oggiano & Mameli, 2012. The shaded area indicates the mining areas.

low temperature (40 °C) for 24 h, and weighed. Digestion of about 150 mg of washed hair samples started with 3 mL of concentrated HNO_3 of Suprapur grade (Merck) for 24 h. It was completed for a further period of 24 h, by adding 0.5 mL of H_2O_2 of Suprapur grade (Merck). The obtained solution was then diluted with 18 MΩ·cm demineralised water.

Road dust samples were initially sieved through a 500 μm sieve to remove matter as debris, pebbles, stones, and grass. Afterwards, a further screening through a 20 μm mesh sieve was necessary to select a finer fraction to be analysed. About 0.1 g of dried material, weighed precisely, was totally digested in a mixture 3:2:1 of HNO_3–$HClO_4$–HF in a Teflon vessel and heated in microwave system (CEM). Quantification of lead was performed by inductively coupled mass spectrometry. The analytical procedure for road dust analyses was checked by using the NIST standard reference material Road Dust, SRM 1648. The mean metal recovery rate of certified element in the reference material was 86% (Certified value: 6550 μg/g; found 5657 ± 407 μg/g).

2.5. Lead isotopes

Lead isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) in hair and road dust samples were measured at the Institut de Physique du Globe de Paris, University of Paris 7 Denis Diderot, by a Quadrupole-based ICP-MS (Agilent). Instrumental mass bias was corrected by sample-standard bracketing techniques, using a NBS 981 lead solution as standard every four unknown samples. The intensity ratio correction factor never exceeded 4‰. Solutions were adjusted to produce a signal of about 400,000 cps on the ^{208}Pb isotope (Monna et al., 1998; Monna et al., 2000). Precisions are typically of 3 and 4 at the third decimal place for the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, respectively. The confidence interval of the mean is provided at a 95% level.

2.6. Statistical data analysis

Data were analysed statistically using the free R software (https://www.r-project.org/). To compare Pb concentrations of independent samples coming from several sites, the Kruskal-Wallis test was first used as a non-parametric alternative to the one-way ANOVA. If the Kruskal-Wallis test appeared to be significant ($\alpha < 0.05$), all pairwise comparisons between groups were then made using the Conover-Inman test (Conover, 1999) implemented in the conover.test R package. The Conover-Inman procedure corresponds to a Fisher's least significant difference method performed on ranks. To examine the possible differences in terms of lead isotopic compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) between the two main sites studied, a nonparametric test for one-way multivariate data based on permutation ($n = 10{,}000$), was applied. Unlike the traditional MANOVA, such an approach does not require the multivariate normality of the data. More information can be found in the npmv package (Ellis et al., 2017).

Table 1
Lead isotope ratios measured in hair and road dust samples from Iglesias (RD_{IG}), Monteponi (RD_{MT}) and Sant'Antioco (RD_{SAN}). The errors for isotopic measurements are given at a 95% confidence level.

Samples	$^{206}Pb/^{207}Pb$			$^{208}Pb/^{206}Pb$		
Hair sample IG	1.153	±	0.004	2.111	±	0.007
Hair sample IG	1.154	±	0.002	2.106	±	0.006
Hair sample IG	1.154	±	0.003	2.110	±	0.006
Hair sample IG	1.147	±	0.004	2.118	±	0.003
Hair sample IG	1.149	±	0.003	2.114	±	0.005
Hair sample IG	1.152	±	0.004	2.112	±	0.007
Hair sample IG	1.153	±	0.001	2.114	±	0.003
Hair sample IG	1.153	±	0.004	2.110	±	0.008
Hair sample IG	1.151	±	0.003	2.114	±	0.006
Hair sample IG	1.166	±	0.005	2.111	±	0.010
Hair sample SAN	1.152	±	0.004	2.108	±	0.007
Hair sample SAN	1.156	±	0.004	2.101	±	0.008
Hair sample SAN	1.157	±	0.003	2.104	±	0.007
Hair sample SAN	1.158	±	0.004	2.103	±	0.006
Hair sample SAN	1.165	±	0.003	2.102	±	0.010
Hair sample SAN	1.157	±	0.004	2.104	±	0.005
Hair sample SAN	1.158	±	0.002	2.106	±	0.004
Hair sample SAN	1.154	±	0.004	2.106	±	0.009
Hair sample SAN	1.158	±	0.005	2.103	±	0.010
Hair sample SAN	1.159	±	0.003	2.102	±	0.004
Road dust sample from Iglesias (RD_{IG})	1.150	±	0.002	2.116	±	0.005
Road dust sample Monteponi (RD_{MT})	1.151	±	0.002	2.117	±	0.004
Road dust sample Sant'Antioco (RD_{SAN})	1.162	±	0.002	2.097	±	0.005

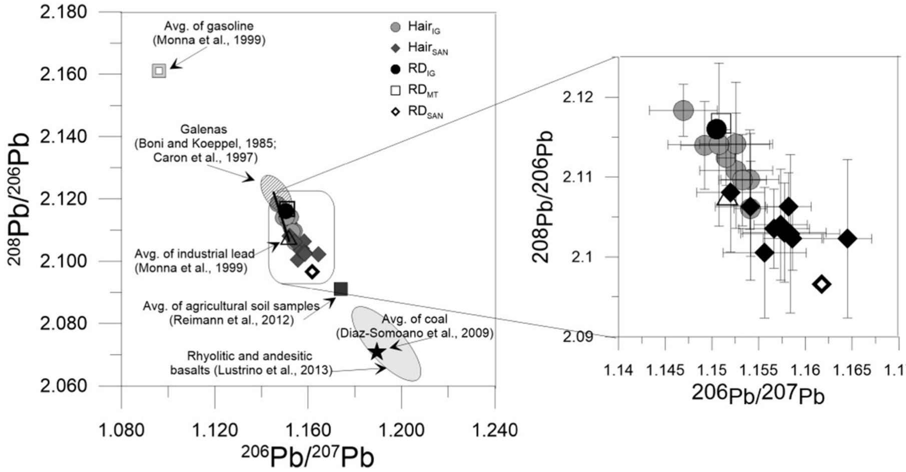

Fig. 2. ^{206}Pb/^{207}Pb vs ^{208}Pb/^{207}Pb plot. The diagram shows lead isotopic ratios measured in: 1) hair samples from Iglesias (IG) and Sant'Antioco (SAN); 2) three road dust samples collected at Iglesias (RD_{IG}), Monteponi (RD_{MT}) and Sant'Antioco (RD_{SAN}); 3) volcanic deposits from Sant'Antioco (Lustrino et al., 2013); 4) galena's domain from Iglesias (Boni and Koppel 1985; Caron et al., 1997); 5) average value of samples from industrial plants and gasoline (Monna et al., 1999); 6) average value of samples from agricultural soil (Reimann et al., 2012); 7) average value of coal from Europe (Díaz-Somoano et al., 2009). The error bars represent confidence level of 95%.

3. Results and discussion

Table 1 reports lead isotope ratios measured in the collected hair samples. Those from SAN varied in the ranges 1.152–1.165 (average 1.157) and 2.101–2.108 (average 2.104) for ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb, respectively. Samples from IG varied in the ranges 1.147–1.154 (average 1.152 excluding the outlier value of 1.166) and 2.106–2.118 (average 2.112) for ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb, respectively. Both groups of samples yielded homogeneous lead isotopic compositions, and the hair from Sant'Antioco resulted statistically more radiogenic than that of Iglesias (permutation test, $p \langle 10^{-3}$).

Fig. 2 displays, on the conventional ^{206}Pb/^{207}Pb versus ^{208}Pb/^{206}Pb plot, the lead isotope data measured in human scalp hair, in the three road dust samples collected at Iglesias (RD_{IG}), Monteponi (RD_{MT}) and Sant'Antioco (RD_{SAN}), in several galenas from Iglesias (Boni and Koppel, 1985; Caron et al., 1997), in volcanites from Sant'Antioco (Lustrino et al., 2013) and in agricultural soil (Reimann et al., 2012). Average isotopic values of former leaded gasoline, industrial sources (Monna et al., 1999) and coal (Díaz-Somoano et al., 2009) are also shown on the plot for comparative purposes. The position of the data points representing road dust samples from Iglesias and Monteponi are close to that of galenas, whereas the SAN road dust sample is closer to the more radiogenic volcanites outcropping around Sant'Antioco. It may be observed that lead isotope data regarding the analysed hair samples belong to a linear trend indicating a multi-source mixing in which the less radiogenic sources consist of former leaded gasolines, together with galenas, whereas the more radiogenic sources are volcanites, soils, and likely coal. Interestingly, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios measured in hair of children from Iglesias overlap the isotopic signatures measured in the RD_{IG} and RD_{MT} samples, almost reaching the galenas' domain. These isotopic values are likely the result of a mixing between lead derived from local rocks and anthropogenic materials, as industrial activities. Conversely, lead isotope ratios in hair samples from Sant'Antioco reflect, along with local volcanites, an important contribution from industrial lead, likely from the nearby Portovesme industrial area.

According to Varrica et al. (2014a) hair lead concentrations measured in 144 human scalp hair samples from children residing in the same study area ranged from 0.07 μg/g to 14.8 μg/g. The concentration range was almost entirely covered by the samples from Iglesias (IG), whereas lead concentrations in children residing in the town of Sant'Antioco (SAN) were limited to the range 0.07–3.27 μg/g (Table 2). Hair lead content of hair in children from IG were statistically higher than those from SAN (median Pb_{IG}: 1.56 μg/g, median Pb_{SAN}: 0.30 μg/g).

We have compared the lead concentrations in hair from adolescents living in the study sites with those measured in Sicily (Dongarrà et al., 2011, 2012; Varrica et al., 2014b, 2015) because they belong to cohorts of donors of the same age and because the results come from the same lab that employed exactly the same sampling and analytical procedures. We wish to underline this point as it represents a critical point in the interpretation of data from hair analysis.

Fig. 3 shows that the lead concentration range observed in samples from Iglesias ($IG_{5th–95th}$: 0.18–5.91 μg/g) is remarkably wider than that one regarding adolescents living in Sant'Antioco ($SAN_{5th–95th}$: 0.10–1.42 μg/g) or within the urban area of Palermo ($UA_{5th–95th}$: 0.32–2.94 μg/g), the volcanic area around Mt. Etna ($VA_{5th–95th}$: 0.002–2.44 μg/g), and a site characterized by the presence of petrochemical and power plants, near Messina (northeastern Sicily) ($IA_{5th–95th}$: 0.13–3.39 μg/g). The distributions of median values of lead concentrations for these sites are also statistically different, except between IA and VA. The Kruskal Wallis test appeared to be highly significant ($p < 10^{-15}$), meaning that at least one site is different from the others. Pairwise comparisons between groups indicate significant differences for all pairs, except between IA and VA ($p = 0.06$). When sites are ranked from the highest to the lowest values, the following order is obtained: IG > UA > VA ~ IA > SAN. The higher Pb levels found in hair of adolescents from Iglesias reflect the environmental exposure of this population to the environmental impact of the mining activities and their related wastes.

Table 2
Summary statistics of Pb contents (μg/g d.w.) in human scalp hair (Varrica et al., 2014a). Please note: number of analysed samples (n); mean; standard deviation (Std. Dev); geometric mean (GM); median; minimum (MIN) and maximum (MAX) values; 5th – 95th percentile; Kurtosis and skewness describe, respectively, the shape and the asymmetry of the distributions.

	n	Mean	Std.Dev.	GM	Median	Min	Max	5th	95th	Skewness	Kurtosis
Pb SAR	144	1.15	1.67	0.59	0.51	0.07	14.7	0.12	3.62	4.52	31.1
Pb IG	59	2.16	2.18	1.48	1.56	0.17	14.7	0.18	5.91	3.63	18.9
Pb SAN	85	0.45	0.51	0.31	0.30	0.07	3.27	0.10	1.42	3.29	13.5

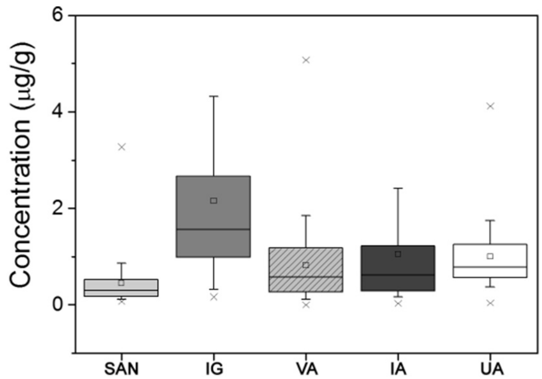

Fig. 3. Box and whisker plot of lead concentrations in human scalp hair from Sant'Antioco (SAN), Iglesias (IG) (data from Varrica et al., 2014a); data are expressed in μg/g. We report also for comparison data from volcanic area (VA), industrial area (IA) and urban area (UA) (data from Dongarrà et al., 2011; Varrica et al., 2014b, 2015). Boxes indicate interquartile range (25th – 75th) with median (solid line), whiskers that delineate 10–90 percentile range and star as minimum and maximum.

We shall not further discuss lead effects on human health because the topic has already been widely discussed in literature (Bornschein et al., 1985; Garza et al., 2006; Flora et al., 2012; Mason et al., 2014), being this element a potent toxicological agent capable of damaging the human central nervous system, kidney and skeletal system. It may be more useful to remember that the principal paths through which lead is incorporate into the human body are breathing, absorption through the skin and ingestion of contaminated food and water. However, it is difficult to establish which of these assimilation pathways might be most effective. According to World Health Organization (2011), more than 80% of the daily intake of lead derives from food and from respiration. Blood, in particular hemoglobin, is the principal transport vehicle for Pb in the human body.

4. Conclusions

The present study used the Pb isotopic signature to provide information about the exposure to lead in the adolescents living within the mining district of Sulcis-Iglesiente (Sardinia, Italy). The IG group is characterized by a significantly less radiogenic lead signature than the SAN group because a notable proportion of total lead is derived from galenas, which were locally exploited; the SAN group is less exposed to mining derived pollution, so its lead isotopic signature is more radiogenic, and closer to local geological background and industrial lead.

Hair lead concentrations of adolescents living in the mining area of Iglesias (IG) are significantly higher than those living at Sant'Antioco (SAN), located outside the mining district.

Such findings are in perfect agreement with data reported by other authors who have undertaken biomonitoring studies using human scalp hair in mining contexts.

These data confirm the real danger of mine wastes in terms of lead exposure, and consequently to other metal and metalloids, for subjects living near the mining sites of Sardinia, so that it would be appropriate to implement a continuous control of the level of Pb and other metals in the inhabitants of the cities of Iglesiente.

Finally, although in the past some doubts have been raised about the use of lead isotopes to identify potential sources of contamination in biological matrices, our data indicate that the Pb isotopes in human scalp hair constitute an effective tool to identify the Pb source in people from the Sulcis-Iglesiente area.

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