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Regione Basilicata
Al Presidente della Giunta Regionale
Dott. Marcello Pittella
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Ill.mo Presidente

Si ritiene opportuno informarLa che in data 10 Maggio 2016, la prestigiosa rivista scientifica Environmental Monitoring and Assessment, ha pubblicato un lavoro di un gruppo di ricercatori dell'Istituto Zoopropfilattico Sperimentale della Puglia e della Basilicata dal titolo "*Environmental monitoring of the area surronding oil wells in Val d'Agri (Italy): element accumulation in bovine organs*".

Nello specifico sono stati analizzati gli organi di accumulo di animali da reddito (ovini e bovini) che pascolano nelle aree della Val d'Agri per verificare il livello di 18 metalli pesanti.

Su un totale di 129 animali esaminati, solo 5 hanno presentato livelli superiori ai limiti indicati dalla European Commission Regulation per cadmio e piombo, mentre tutti gli altri animali avevano livelli molto inferiori.

Il lavoro (che allego alla presente), oltre a suggerire l'ovino come animale indicatore del livello di inquinamento dell'ambiente da metalli pesanti, sottolinea che nella aree di pascolo, prospicienti i pozzi di estrazione del petrolio, tali livelli sono estremamente bassi e pertanto si può affermare, su una base scientifica, che non esiste alcun pericolo per la salute umana.

Cordiali saluti

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Environmental monitoring of the area surrounding oil wells in Val d'Agri (Italy): element accumulation in bovine and ovine organs

Oto Miedico, Marco Iammarino, Giuseppe Paglia, Marina Tarallo, Michele Mangiacotti & A. Eugenio Chiaravalle

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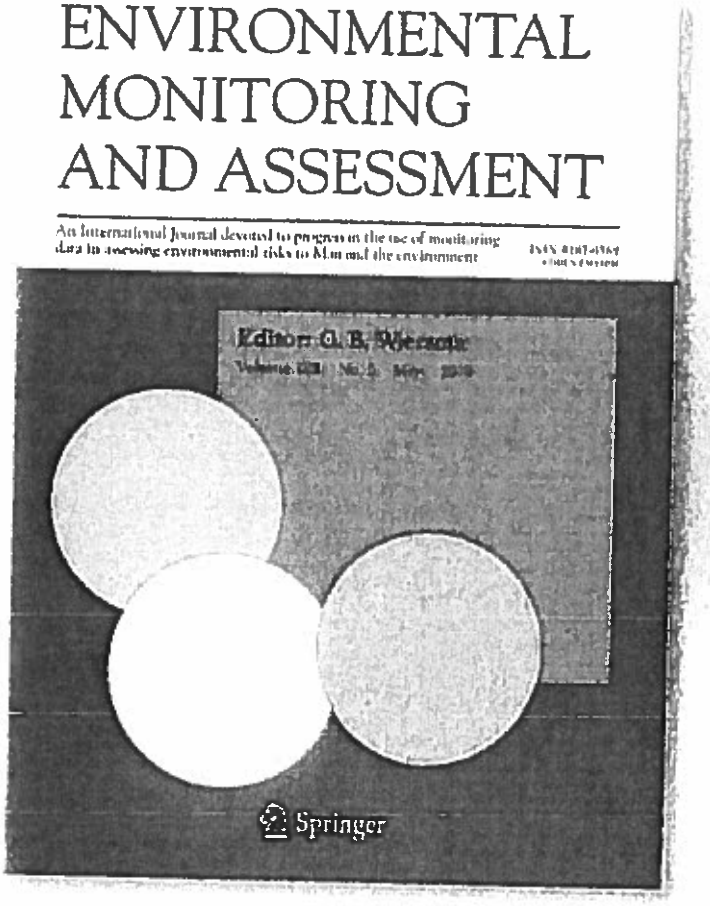

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Environmental monitoring of the area surrounding oil wells in Val d'Agri (Italy): element accumulation in bovine and ovine organs

Oto Miedico · Marco Iammarino · Giuseppe Paglia · Marina Tarallo · Michele Mangiacotti · A. Eugenio Chiaravalle

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Abstract In this work, environmental heavy metal contamination in the Val d'Agri area of Southern Italy was monitored, measuring the accumulation of 18 heavy metals (U, Hg, Pb, Cd, As, Sr, Sn, V, Ni, Cr, Mo, Co, Cu, Zn, Ca, Mn, Fe, and Al) in the organs of animals raised in the surrounding area (kidney, lung, and liver of bovine and ovine species). Val d'Agri features various oil processing centers which are potentially a significant source of environmental pollution, making it essential to perform studies that will outline the state of the art on which any recovery plans and interventions may be developed. The analysis was carried out using official and accredited analytical methods based on inductively coupled plasma mass spectrometry, and the measurements were statistically processed in order to give a contribution to risk assessment. Even though five samples showed Pb and Cd concentrations above the limits defined in the European Commission Regulation (EC) No 1881/2006, the mean concentrations of most elements suggest that contamination in this area is low. Consequently, these results also suggest that there is no particular risk for human exposure to toxic trace elements. Nevertheless, the findings of this work confirm that element accumulation in ovine species is correlated with geographical livestock area. Therefore, ovine-specific organs might be used as bioindicators for monitoring contamination by specific toxic elements in exposed areas.

Keywords Trace elements · Heavy metals · ICP-MS · Environmental contamination · Oil wells

Introduction

The chemical contamination of the environment has a pervasive effect on both human population growth and technological development. The release of chemical contaminants into the environment may be due to several types of events, such as oil or chemical spills, nuclear fallout, or incorrect management of harmful wastes (infectious, toxic, or radioactive, especially in developing countries). Global concern over the public health impact attributed to environmental chemical contamination has been increasing over the last three decades. Indeed, the World Health Organization (WHO) estimates that about a quarter of all diseases are due to prolonged exposure to environmental pollution. However, most of these diseases are not easy to detect and may be acquired during childhood and manifested only in adulthood (Kimani, 2015; Schmitt, 2015).

The majority of dangerous chemical contaminants, considered particularly harmful for humans, especially children (Velea et al., 2009), are heavy metals (particularly Pb, Cd, Hg, As), relating to water and soil contamination (Järup, 2003; Velea et al., 2009; Zhuang et al. 2008), and $PM_{2.5}$, PM_{10}, CO, SO_2, NO_2, and O_3, relating to air pollution (Zhang et al. 2015).

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Heavy metals are commonly defined as those having a density of more than 5 g cm^{-3}, and cadmium, mercury, lead, and arsenic (half-metal) are considered very dangerous due to their potential for high exposure (Denny, 1987; Jarup, 2003). Once absorbed, cadmium accumulates irreversibly in the human body, particularly in kidneys and liver, and may cause irreversible damage both to these organs and to bones and the respiratory tract (Bernard and Lauwerys, 1986; Bernard, 2008). Mercury is another highly toxic metal to human health, since it poses a particular threat to the development of the child *in utero* and, in a nursing woman, it may pass into breast milk. Mercury, mercurous, and mercuric salts and its short-chained alkyl compounds, such as methylmercury, may cause protein precipitation, enzyme inhibition, and may damage primarily the brain, where they can remain for a long time, and gut lining and kidney (Berlin et al., 2007; Risher and De Woskin, 1999; World Health Organization, 2007; Broussard et al., 2002; Bernhoft, 2012). Lead is known to interfere with several body functions, affecting the central nervous, hepatic, hematopoietic, and renal systems, producing serious disorders (Kalia and Flora, 2005; Flora et al., 2012). Regarding arsenic, the inorganic form tends to be more toxic than the organic one does. The human health effects of chronic arsenic toxicity are well known as arsenicosis, characterized by skin pigmentation and keratosis. Moreover, arsenic may interfere with cellular respiration and may develop its carcinogenicity also by direct interaction with red cell membranes (Jomova et al., 2011; Guha Mazumder, 2008; Agency for Toxic Substances and Disease Registry, 2011).

In order to monitor the pollution level in the vicinity of an industrial built-up area, the investigation of heavy metal levels in surface waters, sediments, plants, soil, and animal organs is one of the first operations to be implemented (Szarek-Lukaszewska et al., 2002; Zhuang et al., 2008; Velea et al., 2009; Akoto et al., 2014).

The main objective of this work was the environmental monitoring of the Val d'Agri area of Southern Italy, by measuring the accumulation of 18 heavy metals (U, Hg, Pb, Cd, As, Sr, Sn, V, Ni, Cr, Mo, Co, Cu, Zn, Ca, Mn, Fe, and Al) in the organs of animals raised in the surrounding area (kidney, lung, and liver of bovine and ovine species). Val d'Agri is a unique area featuring several oil processing centers which can be a significant source of environmental pollution, making it essential to perform studies that will outline the state of the art on which any recovery plans and interventions may be developed (Loperte and Cosmi, 2015).

The analysis was carried out using official and accredited analytical methods based on inductively coupled plasma mass spectrometry (ICP-MS), and the data recorded were statistically processed in order to give a contribution to risk assessment.

Materials and methods

Chemicals

Thirty percent (*v*/*v*) H_2O_2, 68 % (*v*/*v*) HNO_3 and ultrapure water were purchased from Romil Ltd (Cambridge, UK); standard solutions of the elements (U, Hg, Pb, Cd, As, Sr, Sn, V, Ni, Cr, Mo, Co, Cu, Zn, Ca, Mn, Fe, and Al) (1000 mg L^{-1}) were supplied by CPA Ltd. (Stara-Zagora, Bulgaria); ultrapure argon, anhydrous ammonia, and methane (N 55) were purchased from AIR Liquide s.p.a. (Milan, Italy).

Sampling

A total of 129 samples were collected from three different geographic areas near oil wells in Val d'Agri (Southern Italy). These areas were the following: Corleto Perticara (40° 22′ 49.584″ N–16° 2′ 29.545″ E), Grumento Nova (40° 17′ 14.851″ N–15° 53′ 25.926″ E), and Viggiano (40° 20′ 49.341″ N–15° 53′ 58.399″ E). The animal organs were collected from a slaughterhouse, under the supervision of the personnel involved in the research project, who checked that all operations were executed by avoiding any possible contamination of the samples. The samples may be considered representative of respective geographic area, since the animals were born and raised in the three areas mentioned above. The monitoring was carried out by evaluating the levels of 18 heavy metals (U, Hg, Pb, Cd, As, Sr, Sn, V, Ni, Cr, Mo, Co, Cu, Zn, Ca, Mn, Fe, and Al) in different organs (kidney, lung, and liver) of bovine and ovine species raised in these three areas. An accurate description of the sampling is shown in Fig. 1.

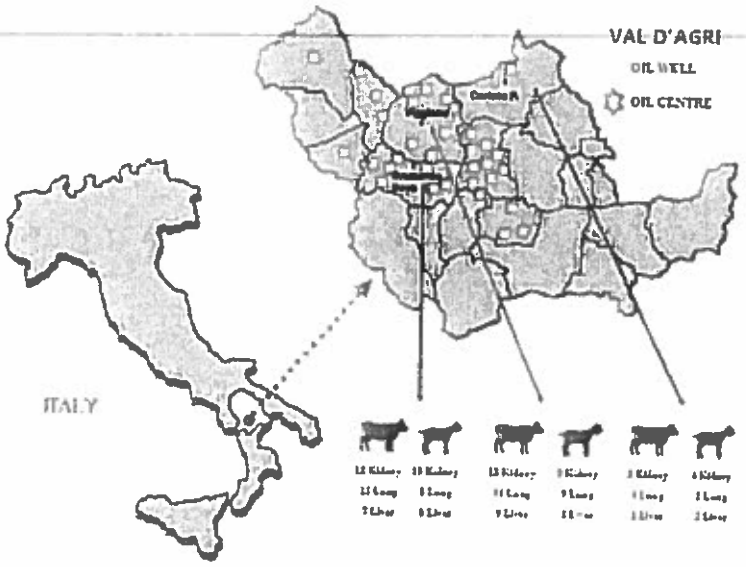

Fig. 1 Experimental design. One hundred twenty-nine samples (kidneys, livers, and lungs) were obtained from both ovine and bovine species collected in three different areas (Grumento Nova, Viggiano, and Corleto Perticara) surrounding oil wells in Val d'Agri

Apparatus and methods

This monitoring was carried out using the UNI EN 15763:2010 reference method (European Committee for Standardization, 2010). This method has been accredited by the Italian organism for laboratory accreditation, ACCREDIA, since 2010. Approximately 500 g of the sample was collected and then homogenized in a commercial blender (model HGB2WTG4, Waring Laboratory Science, Stamford, USA). The homogenized sample (1.0 ±0.0001 g) was weighed by an analytical balance (Mettler Toledo s.p.a., Novate Milanese, Milan, Italy) and then mineralized. Microwave-assisted acid digestion was carried out using an ETHOS-ONE microwave reaction system (Milestone s.r.l. Sorisole, Bergamo, Italy). The UNI EN 13805 reference procedure was adopted (European Committee for Standardization, 2002): 1.0 g of the homogenized sample was weighed inside a Teflon vessel, and then 6 mL of 68 % (*v*/*v*) HNO_3 and 2 mL of 30 % (*v*/*v*) H_2O_2 were added. The vessels were placed into the microwave reaction system and total sample digestion was obtained through the following schedule: up to 120 °C in 15 min and constant for 10 min; up to 190 °C in 15 min and constant for 20 min; cooling stage (30 min) to reach room temperature. After digestion, the pressure in the vessels was released and the resulting hydrolysate was transferred into 50-mL polypropylene tubes which were filled to the mark by addition of ultrapure water for further analysis by ICP-MS.

An inductively coupled plasma mass spectrometer (PerkinElmer Inc., model Elan DRC II, Massachusetts, USA) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a baffled cyclonic spray chamber (Glass Expansion, Inc., West Merbourne, Australia), and a quartz torch with a quartz injector tube (2 mm i.d.) was used. The analytical procedure was submitted to a validation procedure which assured all analytical performances required for this type of determination. All validation parameters which characterize the analytical procedure, together with an accurate description of operational parameters, are reported in Table 1. Two replicates of each sample were analyzed, and the heavy metal concentrations were evaluated as the mean of two measurements. Certified material (NIST 1577b—bovine liver) was analyzed at each working session for quality assurance purposes. This method has already been applied successfully for other heavy metal monitoring studies (Miedico et al., 2013, 2015).

Data analysis

Data was tested for normal distribution and since Gaussian distribution was not achieved for all parameters, before performing principal component analysis (PCA) and ANOVA test, we first normalized the dataset

Table 1 ICP-MS settings and validation parameters

Inductively coupled plasma mass spectrometer settings	
Radiofrequency generator	1000–1300 W
Gas flow	1.5 L min^{-1}
Argon nebulization flow	0.9–1.1 L min^{-1}
Pump settings/Sample flush	60 s
Sample flush speeding	−32.0 rpm
Read delay	20 s
Read delay analysis speeding	−20 rpm
Wash	45 s
Wash speeding	32 rpm
Scanning settings/dwell time	50 ms
Sweeps/reading	20
Reading/replicate	1
Replicates	3
Scanning mode	Peak hopping
Radiofrequency generator	1000–1300 W

Validation parameters

Element	Calibration range (ng mL^{-1})	Determination coefficient (R^2)	RSD (%) ($n = 10$)	LOQ (ng g^{-1})
Al	2.0–200	0.9997	7.1	59
As	0.5–50	0.9987	9.5	21
Cd	0.5–50	0.9999	5.3	2.8
Co	0.5–50	0.9981	6.4	9.9
Cr	0.5–50	0.9980	7.2	13
Cu	2.0–200	0.9987	2.1	11
Fe	2.0–200	0.9981	3.2	3.1×10^3
Hg	0.1–10	0.9986	8.4	1.4
Mn	2.0–200	0.9980	3.7	30
Mo	0.5–50	0.9992	4.1	12
Ni	0.5–50	0.9875	5.9	30
Pb	0.5–50	0.9982	5.7	5.6
Sn	0.5–50	0.9991	8.5	5.6
Sr	0.5–50	0.9995	2.1	9.9
U	0.01–1.0	0.9999	4.0	0.72
V	0.5–50	0.9891	7.8	15
Zn	2.0–200	0.9986	2.9	1.8×10^3
Ca	2.0–200	0.9975	4.9	1.5×10^3

by mean centering (the average value is calculated and then subtracted by the data), and then we scaled the data by using the unit variance scaling method (mean-centered and divided by standard deviation of each variable).

PCA was performed using SIMCA (Umetrics, Sweden). Before PCA, data lower than the limit of quantification (LOQ) was replaced with $LOQ/(2^{1/2})$. This approach was indicated by the Italian National Institute of Health, in the document "Rapporti ISTISAN 04/15", as a protective measure related to health and environment (Italian National Institute of Health, 2004). Data was scaled by using the unit variance scaling method before PCA. One-way ANOVA test was used to find elements that changed significantly between organs, locations, and species ($p < 0.05$).

Results and discussion

The overall goal of this work was to monitor the accumulation of the selected elements in farm animals raised in the area surrounding oil wells in Italy. We therefore tried to understand of which the investigated matrices was the best match for use as a bioindicator for contaminant element accumulation.

Summary of data

Samples were collected in an area of approximately 1700 km^2 surrounding the oil wells of Val

Table 2 Range and average values of the overall dataset ($n = 129$)

Element	Range (ng g^{-1})	Average ± SD (ng g^{-1})
U	0.51[a]–2.2	0.60 ± 2.1
Hg	1.0[a]–27	2.1 ± 2.6
Pb	4.0[a]–1142	56 ± 134
Cd	2.0[a]–2344	206 ± 370
As	15[a]–35	16 ± 4
Sr	7.0[a]–453	33 ± 57
Sn	4.0[a]–673	51 ± 114
V	11[a]–95	14 ± 12
Ni	21[a]–1936	163 ± 253
Cr	9.2[a]–2670	159 ± 382
Mo	69–3770	807 ± 778
Co	7.0[a]–202	44 ± 42
Cu	915–818*	37.2* ± 102*
Zn	7.53*–147*	25.7* ± 21.2*
Ca	19.3*–1540*	123* ± 241*
Mn	21[a]–7.61*	1.46* ± 1.82*
Fe	16.0*–1890*	168* ± 205*
Al	42[a]–39.3*	3.87* ± 4.82*

[a] $LOQ/(2^{1/2})$

*values to be multiplied by 10^3

d'Agri. A total of 129 samples were collected in this study, including kidneys, livers, and lungs from both ovine and bovine species (Fig. 1). For 13 of the 18 elements included in this study, over 90 % of the measurements were higher than the LOQ. For the remaining five elements (U, Hg, As, Sn, and V), more than 50 % of the measurements were lower than the LOQ. Range and average values for the overall dataset are reported in Table 2.

Element distribution in organs

PCA was used as the first step for data reduction and visualization, with the aim of highlighting any variation in the dataset. The principal components are rank-ordered by the variability that they represent in the data set, with the first principal component accounting for the greatest variability in the data and so on (Trygg et al., 2007).

As expected, we observed that different organs clustered separately along the first principal component (PC1) that accounts for 24 % of the total variance (Fig. 2). Thirteen elements changed significantly between organs as described in Fig. 2 (Table 3, ANOVA test, $p<0.05$). Both essential and toxic elements influenced the clustering in the first components. Most of them mainly accumulated in the liver, such as Mn, Co, Mo, Zn, Cu, and Pb (Fig. 2). On the other hand, Cd was found at higher concentrations in the kidney, while Al accumulated mainly in the lung (Fig. 2). Accumulation of Cd in kidney is in

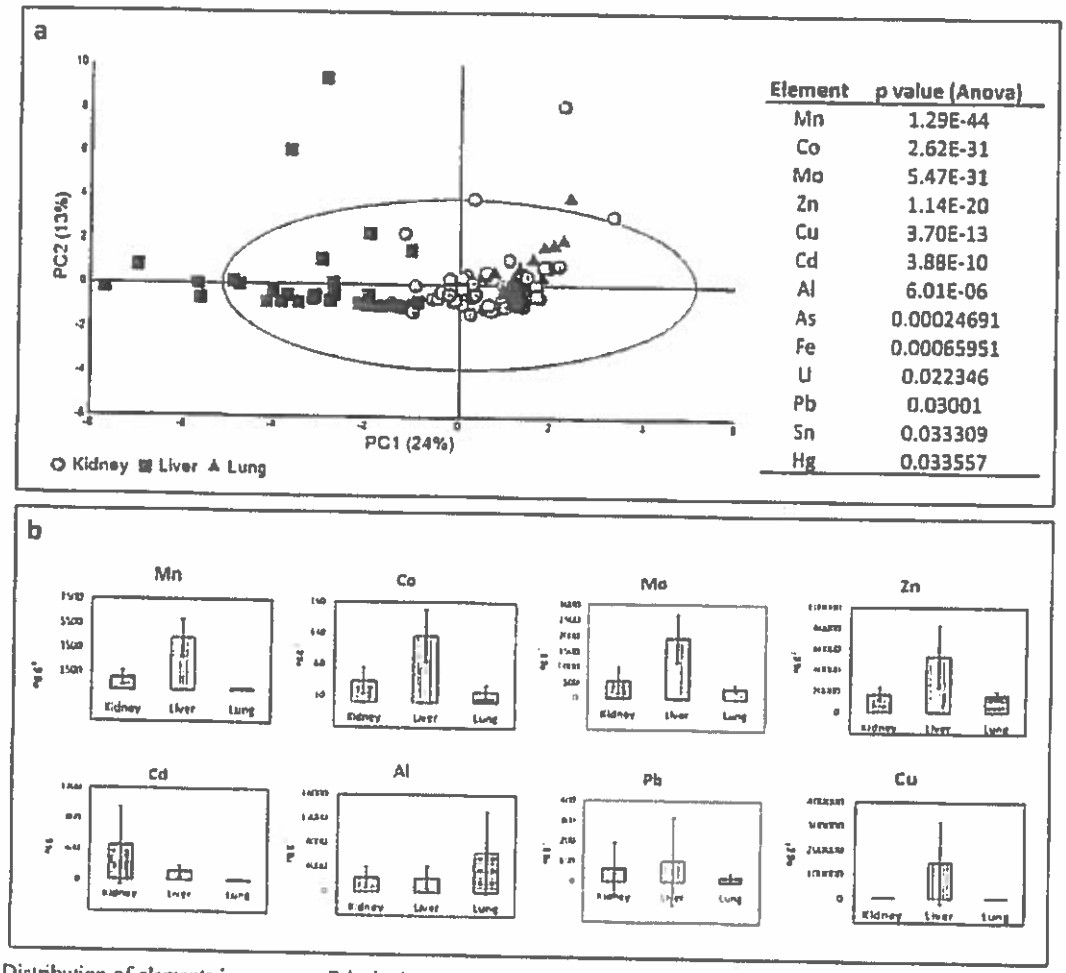

Fig. 2 Distribution of elements in organs. a Principal component analysis and p values for significant elements (samples are colored by organ). b Accumulation of selected elements in kidney, liver, and lung. *Error bars* represent standard deviations

Table 3 Element distribution in kidney, liver, and lung

Element	Kidney ($n=50$)		Liver ($n=30$)		Lung (49)	
	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})
U[b]	0.51[a]–2.1	0.7 ± 0.4	0.51[a]–1.3	0.5 ± 0.2	0.51[a]–1.1	0.5 ± 0.1
Hg[b]	1.0[a]–8.6	2.5 ± 1.8	1.0[a]–27	2.7 ± 4.8	1.0[a]–2.9	1.3 ± 0.2
Pb[b]	6.0–910	64 ± 127	16–1142	102 ± 217	4.0[a]–81	21 ± 19
Cd[b]	6.0–2345	451 ± 501	20–300	118 ± 69	2.0[a]–95	11 ± 6
As[b]	15[a]–35	18 ± 6	15[a]–23	15 ± 2	15[a]–24	15 ± 3
Sr	7.0[a]–454	46 ± 77	7.0[a]–71	16 ± 13	7.0[a]–243	32 ± 47
Sn[b]	4.0[a]–225	22 ± 45	4.0[a]–225	55 ± 128	4.0[a]–630	81 ± 145
V	11[a]–96	14 ± 13	11[a]–91	16 ± 18	11[a]–44	13 ± 6
Ni	21[a]–1940	171 ± 282	21[a]–557	117 ± 127	21[a]–1490	185 ± 281
Cr	9.2[a]–1.49*	92 ± 222	9.2[a]–1.37*	102 ± 248	19–2.67*	264 ± 535
Mo[b]	69–2.25*	577 ± 414	83–3.77*	1.95* ± 762	99–2.08*	346 ± 95
Co[b]	7.0[a]–83	34 ± 20	47–203	106 ± 42	7.0[a]–94	17 ± 11
Cu[b]	915–12.5*	3.91* ± 2.07*	3.10*–818*	149* ± 171*	1.05*–114*	2.64* ± 1.50*
Zn[b]	7.53*–28.8*	17.5* ± 6.14*	19.5*–147*	53.3* ± 29.6*	11.4*–33.2*	17.1* ± 3.33*
Ca	19.8*–1010*	133* ± 206*	19.3*–459*	61.0* ± 81.7*	31.9*–1540*	149* ± 323*
Mn[b]	174–2.16*	1041 ± 570	1.71*–7.61*	4.33* ± 1.55*	21[a]–5.49*	143 ± 104
Fe	16.0*–431*	87.2* ± 64.9*	45.2*–1890*	254* ± 377*	70.0*–525*	197* ± 98.1*
Al[b]	42[a]–6.49*	2.3* ± 1.71*	42[a]–6.10*	1.84* ± 1.79*	42[a]–39.3*	6.43* ± 6.79*

[a] $LOQ/(2^{1/2})$

[b] $p<0.05$ (one-way ANOVA test)

*Values to be multiplied by 10^3

agreement with previous studies (Akan et al., 2010; Abd El-Salam et al., 2013; Akoto et al., 2014; Alkmim Filho et al., 2014; Canty et al., 2014). No information was found to support accumulation of Al in the lungs of bovine and ovine species.

The levels of most of the elements seem to show that, at the time of this study, contamination related to the presence of oil wells is minimal. Only five samples showed concentrations of Pb or Cd which may be considered significantly higher than those of the others ($p<0.05$), taking as reference the limits established by the European Commission Regulation (EC) No. 1881/2006 (European Commission, 2006) related to these two elements in animal organs (legal limits related to Hg, Sn, and As in animal organs are not established). These were two bovine samples (one liver and one kidney) collected in the area of Viggiano, with Pb concentrations higher than 500 ng g^{-1} and three kidney samples (two ovines from around Grumento Nova and one bovine from near Corleto Perticara) with Cd levels higher than 1000 ng g^{-1}.

Element distribution by the sampling area

Even though PC1 accounts for the greatest variability in the data, we also evaluated the possibility of further clustering along the other principal components. In Fig. 3, we show the PCA performed by dividing samples based on their sampling area. We noticed that the second principal component (PC2) partly separated samples collected in the Viggiano area (Fig. 3a). Nevertheless, after performing ANOVA, none of the elements changed significantly from one sampling area to the next.

We then plotted the second and the third components (accounting respectively for 13 and 12 % of the total variance) (Fig. 3b). While PC2 provided the cluster for samples collected in Viggiano, PC3

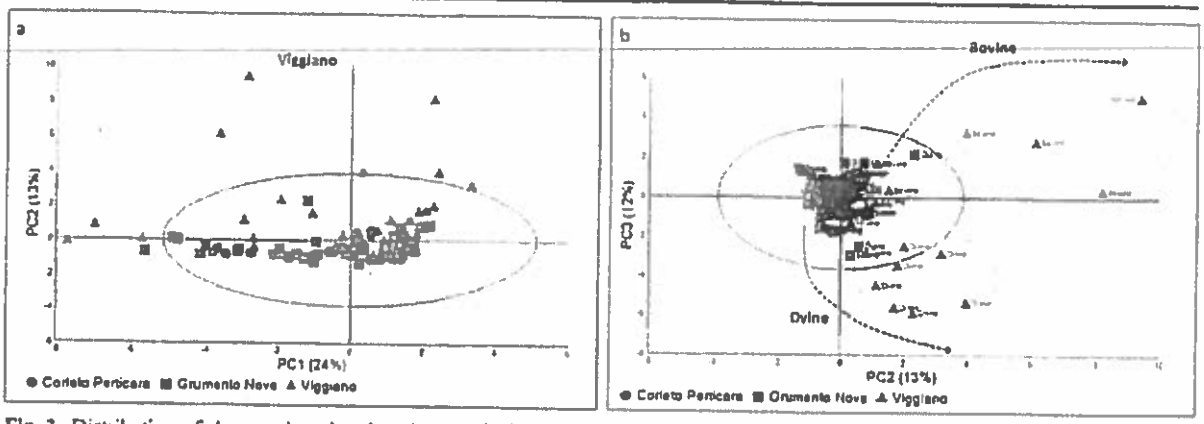

Fig. 3 Distribution of elements based on location. a Principal component analysis obtained by plotting the first and second component. b Principal component analysis obtained by plotting the second and the third components. In both a and b, samples are *colored* by location)

highlighted other useful information. Indeed, bovine and ovine samples from Viggiano provided two separate clusters (Fig. 3b). In order to better understand this finding, we performed another PCA separately on bovine and ovine samples (Fig. 4). The new analysis highlighted the fact that ovine samples separated better according to the sampling area (Fig. 4). Univariate analysis (Table 4, ANOVA test) confirmed the PCA results by showing that, in bovine samples, only three elements changed significantly among different areas (Sn, U, and Hg, $p<0.05$). On the other hand, ovine samples had 10 elements that showed significant changes among the 3 areas (Zn, As, V, U, Hg, Mo, Pb, Mn, Co, and Sn, $p<0.05$). Some of these elements, such as As, V, and Mo, have previously been associated with pollution from petrochemical areas (Nadal et al., 2004; Bosco et al., 2005; Nadal et al., 2009). In more than 50 % of the measurements, the levels of As and V were lower than the LOQ. This result seems to indicate a low environmental impact of oil wells in the investigated area. Another element often associated with pollution deriving from petrochemical plants is Cr (Nadal et al., 2004; Bosco et al., 2005; Nadal et al., 2009). In this study, we found increased levels in the area of Viggiano (Table 2), although due to the quite wide range of concentrations, this change proved to be not significant.

The Grumento Nova area was characterized by higher accumulation of Hg and Pb in ovine species (Fig. 5a). These two toxic elements accumulated in

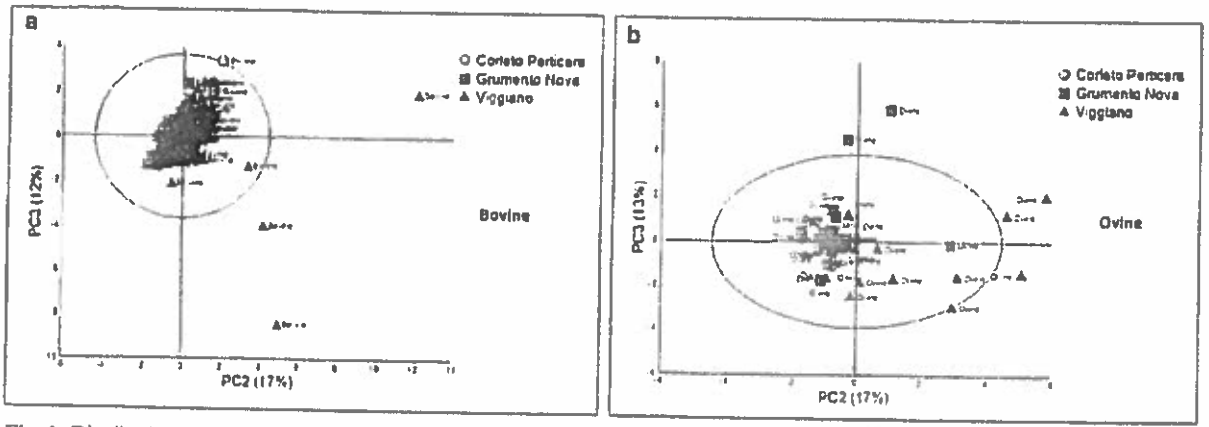

Fig. 4 Distribution of elements in bovine and ovine species based on location. a Principal component analysis of bovine samples obtained by plotting the second and the third components. b Principal component analysis of ovine samples obtained by plotting the second and the third components. In both a and b, samples are *colored* by location)

Table 4 Element distribution in ovine and bovine based on sampling location

Ovine						
Element	Corleto Perticara ($n = 8$)		Grumento Nova ($n = 21$)		Viggiano ($n = 17$)	
	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})
U[b]	n. a.	n. a.	0.51[a]–1.9	0.6 ± 0.3	0.51[a]–1.0	0.6 ± 0.2
Hg[b]	n. a.	n. a.	1.0[a]–27	4 ± 6	1.0[a]–4.3	2.1 ± 1.3
Pb[b]	10–54	23 ± 15	4.0[a]–190	56 ± 48	8.3–100	33 ± 25
Cd	2.0[a]–229	72 ± 80	6.5–2345	418 ± 697	6.1–910	146 ± 253
As[b]	n. a.	n. a.	15[a]–26	15 ± 3	15[a]–29	16 ± 4
Sr	15–39	24 ± 8	7.0[a]–195	39 ± 51	12–454	91 ± 117
Sn[b]	4.0[a]–21	6 ± 6	4.0[a]–204	25 ± 49	4.0[a]–674	172 ± 206
V[b]	n. a.	n. a.	11[a]–45	14 ± 9	11[a]–27	12 ± 4
Ni	43–321	135 ± 104	21[a]–497	97 ± 102	32–988	258 ± 304
Cr	11–122	58 ± 36	9.2[a]–1497	111 ± 320	15–2668	532 ± 885
Mo[b]	131–2.51*	948 ± 967	86–3.77*	1.29* ± 1.14*	85–2.08*	650 ± 652
Co[b]	7.0[a]–102	44 ± 39	7.0[a]–117	47 ± 29	14–133	44 ± 33
Cu	1.80*–86.4*	14.2* ± 29.3*	915–114*	159* ± 28.8*	955–818*	74.7* ± 203*
Zn[b]	9.51*–65.6*	27.3* ± 20.1*	7.53*–51.9*	24.1* ± 12.1*	10.3*–78.4*	22.0* ± 16.1*
Ca	19.8*–98.4*	44.5* ± 23.3*	24.9*–475*	112* ± 124*	44.8*–1540*	418* ± 524*
Mn[b]	132–5.71*	132 ± 2.19*	128–6.35*	1.77* ± 1.88*	74–6.26*	1.30* ± 1.91*
Fe	31.4*–110*	74.9* ± 30.4*	25.6*–431*	106* ± 91.6*	16.0*–635*	210* ± 171*
Al	639–5.05*	1.99* ± 1.77*	139–39.2*	5.01* ± 8.38*	508–6.67*	2.93* ± 2.03*
Bovine						
Element	Corleto Perticara ($n = 8$)		Grumento Nova ($n = 34$)		Viggiano ($n = 41$)	
	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})	Range (ng g^{-1})	Average ± SD (ng g^{-1})
U[b]	0.51[a]–1.2	0.8 ± 0.3	0.51[a]–0.8	0.51 ± 0.1	0.51[a]–2.1	0.7 ± 0.4
Hg[b]	1.0[a]–7	3 ± 2	1.0[a]–7	2 ± 1	1.0[a]–7	2 ± 1
Pb	4.0[a]–87	30 ± 29	4.0[a]–97	30 ± 22	6–1142	101 ± 229
Cd	19–1.19*	303 ± 425	5–884	150 ± 223	4–947	178 ± 249
As	15[a]–26	18 ± 5	15[a]–30	16 ± 4	15[a]–35	18 ± 6
Sr	7.0[a]–35	16 ± 9	7.0[a]–34	15 ± 7	7.0[a]–280	28 ± 44
Sn[b]	27–363	143 ± 111	4.0[a]–630	35 ± 114	4.0[a]–123	20 ± 32
V	11[a]–11	11 ± 0	11[a]–20	11 ± 2	11[a]–96	18 ± 21
Ni	21[a]–83	45 ± 21	21[a]–1.94*	205 ± 338	21[a]–1.49*	153 ± 238
Cr	28–187	83 ± 49	16–703	113 ± 157	16–559	103 ± 122
Mo	212–1.65*	538 ± 481	147–2.87*	739 ± 687	69–2.48*	706 ± 596
Co	7.0[a]–118	29 ± 38	7.0[a]–23	44 ± 51	7.0[a]–165	46 ± 47
Cu	2.12*–27.1*	37.6* ± 94.4*	1.25*–452*	38.9* ± 92.9*	1.05*–43.9*	35.4* ± 82.2*
Zn	11.4*–62.1*	22.0* ± 16.7*	9.14*–67.0*	23.3* ± 12.9*	8.43*–147*	30.5* ± 31.1*
Ca	57.6*–520*	137* ± 155*	19.3*–140*	49.0* ± 25.9*	20.3*–915*	78.6* ± 136*
Mn	21–4.94*	1.04* ± 1.65*	32–6.64*	1.30* ± 1.76*	49–7.61*	1.51* ± 1.85*
Fe	82.7*–238*	140* ± 56.5*	50.3*–314*	155* ± 91.9*	45.2*–1890*	215* ± 322*
Al	312–4.82*	1.26* ± 1.46*	42[a]–14.9*	4.59* ± 4.14*	42[a]–26.3*	3.95* ± 4.35*

n. a. Not applicable (All values are lower than the LOQ)

[a] $LOQ/(2^{1/2})$

[b] $p < 0.05$ (one-way ANOVA test)

*Values to be multiplied by 10^{3}

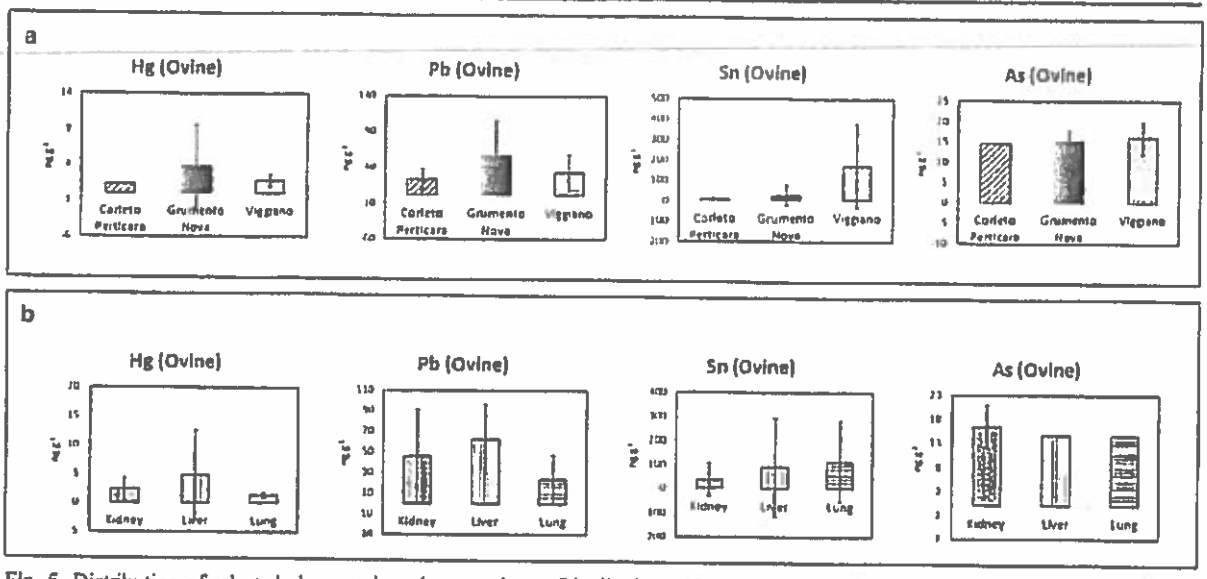

Fig. 5 Distribution of selected elements in ovine samples. a Distribution of selected elements in ovine samples based on location. b Distribution of selected elements in the organs of ovine species

ovine liver (Fig. 5b). In the Viggiano area, we recorded increased levels of Sn that accumulated mainly in the lung, while As accumulated mainly in the kidney.

Ovines are one of the few livestock animals that have rarely been raised in an intensive, confined animal feeding operation. Being a herbivorous mammal that prefers to graze on grass, it is particularly suitable for monitoring contamination in exposed areas. Moreover, considering the fact that many shepherds use managed intensive rotational grazing, where a flock is rotated through multiple pastures, ovines can be used as bioindicators of a vast area. In contrast, bovines are often raised in controlled animal feeding conditions and might be not representative of a contaminated area.

Conclusions

In this study, we monitored the accumulation of 18 elements in liver, kidney, and lung of bovine and ovine species raised in Val d'Agri. This area is characterized by the presence of several oil wells. Regarding the differences among the three sampling areas (Viggiano, Grumento Nova, and Corleto Perticara), after performing ANOVA, none of the elements appeared to change significantly. Even though five samples showed higher Pb and Cd concentrations than that allowed in the European Commission Regulation (EC) No. 1881/2006, the mean concentrations of most elements suggest very slight contamination of this area. Consequently, these results also suggest that there is no particular risk for humans from exposure to toxic trace elements.

Most trace elements, such as Mn, Co, Mo, Zn, Cu, and Pb, accumulated mainly in the liver. On the other hand, Cd was found at a higher concentration in the kidney, while Al accumulated mainly in the lung.

As regards differences between bovine and ovine organs, ovine samples had 10 elements that showed significant changes among the 3 areas (Zn, As, V, U, Hg, Mo, Pb, Mn, Co, and Sn). Consequently, the findings of this work make it clear that element accumulation in ovine species correlated with the geographical livestock area. Therefore, ovine-specific organs might be used as bioindicators for monitoring contamination by specific toxic elements in exposed areas.

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