

Human and animal health risk assessment of metal contamination in soil and plants from Ait Ammar abandoned iron mine, Morocco

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Abstract The goal of this paper is to investigate metal pollution in food chain and assess the resulting health risks to native citizens in Ait Ammar village. The results showed that cadmium (Cd), lead (Pb), and copper (Cu) concentrations in animal organs were above the metal concentration safety limit. Nevertheless, soils and plants from mining area were contaminated with iron (Fe), chromium (Cr), zinc (Zn), and Cr, Cu, Zn respectively. Cd concentrations in almost animal organs were higher than the acceptable daily upper limit, suggesting human consumption of this livestock meat and offal may pose a health risk. The estimated intake of Pb and Cd for Ait Ammar population could be a cause of concern because it exceeded the Provisional Tolerable Weekly Intake (PTWI) proposed by Joint Expert Committee on Food Additives (JECFA) in this area. Thus, conducting regular periodic studies to assess the dietary intake of mentioned elements are recommended.

Keywords Heavy metal · Health risk · Dietary intake · PTWI · Ait Ammar mine

Introduction

Morocco keeps varied and important mineral resources. There are diversities of mineral resources in Morocco. Moreover, Morocco is one of the greatest universal producers of phosphate (26.4 million tons in 2013) and other elements as baryte (1.1 million tons), iron (0.3 million tons), manganese (0.1 million tons), zinc (0.08 million tons), copper (0.046 million tons), lead (0.043 million tons), and cobalt (0.02 million tons) (The National Office of Hydrocarbons and Mines (ONHYM) 2015) (Fig. 1). Mineral resources represent the key material foundation for socioeconomic progress. However, mineral extraction has caused dangerous ecological damage, particularly in the domain of heavy metal contamination (Acosta et al. 2011).

To evaluate the impact of elevated metal concentrations in ecosystems, an important difference would be formed in dangers/consequences of metals interconnected to (i) the soil ecosystem and (ii) health of gents or animal health subsequent from bioaccumulation. The last consequence is associated to the phenomenon that a chemical accumulates in plants via diverse trophic contents in a food chain, or resultant poisoning. Trace metal accumulation in the food chain is specially considered central with respect to Cd and Pb (de Vries et al. 2007). Cu, and Zn.

These heavy metals are moved via the food chain to animals and man. The metal toxicity depends on the dosage, the chemical form of the metal distributed to the animal, the way of distribution, and the frequency and time interval of distributing the metal to the livestock (Gough and Shacldette 1976; Underwood 1977). In

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Fig. 1 Localization of sampling site in Ait Ammar iron mine (N° 29)



addition, many essential elements when given in excess are also toxic to animals.

Including the environmental pollutants, a numerous metals grouped into a class of substances that may make serious disability in humans and thus necessitate strict supervising. Essential illustrations of diseases generated by toxic elements comprise mental retardation in children that is created by lead, and kidney disease and anemia generated by Pb and Cd. Therefore, several elements cannot be counted harmless, and obligatory contact to them from nutriment must be maintained at a minutest (Mahaffey 1977).

General concern about the impact on human health of exposure to environmental pollution has led to increasing attention over the last decades to the presence of toxic substances in the human diet. However, a very restricted number of health risk assessment researches have been carried out regarding soil heavy metal pollution from mines in Morocco (Sedki et al. 2003; El hamiani et al. 2010; El fadeli et al. 2014). thus, a comprehensive contamination assessment of mining areas in Morocco is immediately required. Consequently, the aim of this work is to assess the pollution levels and health risks of heavy metals in the soils of mining areas.

Materials and methods

Study site, sample collection, and preparation

The investigation was executed at Ait Ammar $(33^{\circ} 04' N; 6^{\circ} 38'W)$, located in the Khouribga Province, about

25 km northwest of the town of Oued Zem, in central Morocco. It is part of the Hercynian Central Massif. This massif is the vast plateau, which dominates the northern portion of the western Meseta of Morocco. It is bounded on the north by Miocene forward Rif region, on the south by the plateau of phosphates and east by the Middle Atlas. The Hercynian Central Massif consists mainly of land ranging from Paleozoic Ordovician to Carboniferous, structured into successions of anticlinoriums and synclinoria, and intersected by Hercynian granitic intrusions (ONHYM 2015) (Fig. 2).

The iron mine of Ait Ammar is part of the anticlinorium Khouribga-Oulmes, where it is hosted in schist-sandstone series, Ordovician (lower and middle Lladeilien). This series is topped by large sandstone lenses or sandstone-shale, sometimes transformed into true quartzite. The Fe mineralization take place as two lenticular layers of Fe oolitic, interspersed through this arranged sandstone whose space is approximated at one hundred meters (1000 to 1500 m). The mine deposit begins with black chloritic schist (ONHYM 2015).

The mine was utilized for iron mining for numerous decades but was abandoned in 1964 (ONHYM 2015). Nowadays the majority of the area is unproductive soil or scarcely vegetated and is utilized as grazing zone for livestock owned by the residents of a proximate small village.

The study area displays a Mediterranean climate: rainy in winters and warm in summers (Nouri et al. 2013). In 19 July 2010, a total number of 20 surface (0-20 cm) soil samples were collected within Ait Ammar iron mine area (Nouri et al. 2014). The soil



Fig. 2 Regional geological setting of Ait Ammar sector (ONHYM 2015)

samples were sieved to <2 mm fraction. The soil fraction was selected for chemical analyses. Moreover, 12 vegetable species (Table 1), representing the most abundant species grown in the study area (Fig. 1), were collected from the same sites where the soil samples were collected (Nouri et al. 2013). All samples were put in polyethylene bags and transported to the laboratory on the day of sampling. In the laboratory, all fresh vegetable samples were washed with tap water and rinsed with distilled water to remove airborne pollutants. The samples were kept in the oven at 80 °C until completely dry. Dried vegetable samples were powdered using a pestle and mortar sieved and then stored in polyethylene bags at room temperature until analysis.

Chemical determinations

Chemical analyses for the soil and plants samples were performed at the accredited National Centre for Scientific and Technical Research (NCSTR) Laboratories, Rabat, Morocco. Soil sample preparation for bioavailable metal analysis was determined using the 0.01 M CaCl₂ extraction procedure (Houba et al. 1990).

 Table 1
 Plant species collected in the study area (see also Nouri et al. 2013)

| Family | Species |
|---------------|--------------------------------------|
| Apiaceae | Eryngium ilicifolium Lam. |
| | Eryngium triquetrum Vahl. |
| Asteraceae | Carlina acaulia subsp caulescens |
| | Carthamus lanatus L. |
| | Cladanthus arabicus (L.) Cass. |
| | Echinops spinosus L. |
| | Leontodon hispidilus (Delile) Boiss. |
| | Scolymus hispanicus L. |
| Poaceae | Bromus hordeaceus |
| | Bromus rubens L. |
| | Lamarckia aurea L. (Moench). |
| | Stipa capensis Thunb. |
| Ranunculaceae | Ranunculus peltatus Schrank. |

Following agitating for 2 h on a tabletop agitator, decantation of the extracts was employed and 60 mL were centrifuged ($2000 \times g$), and metal contents were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Jobin Yvon ULTIMA 2) (Nouri et al. 2014). For vegetable samples, 1 g of dried sample was digested with nitric and hydrochloric acids (Nouri et al. 2013). The soil and plants digests were analyzed for metals (Cd, Pb, Cr, Cu, Zn, and Fe) (NCSTR). The description of the methods applied to determine soil pH, conductivity, water content, organic matter (OM), total organic carbon (TOC), total Kjeldahl nitrogen (TKN) was published by Nouri et al. (2013).

Data analysis

Daily intake (DI)

The metal intake by animals combines together feed consumption and soil ingestion (Smith et al. 2009). According to Rodrigues et al. (2012). the DI of metals by animals was given by:

$$DI_{animal} = [Metal]_{feed} \times I_{feed} + [Metal]_{soil} \times I_{soil}$$

where:

 DI_{animal} daily intake of a metal for animals (mg d⁻¹);

 $[Metal]_{feed}$ and $[Metal]_{soil}$, concentration of the metal in feed and soil, respectively, (mg kg⁻¹);

 I_{feed} and I_{soil} , daily intake of feed and soil, respectively, by animals (kg day⁻¹) (Table 2).

Metal concentrations in animal organs

The concentration of metals in animal organs can be determined by (de Vries et al. 2007; Rodrigues et al. 2012):

$$= ([Metal]_{feed} \times I_{feed} / (I_{feed} + I_{soil}) + [Metal]_{soil} \\ \times I_{soil} / (I_{feed} + I_{soil})) \times BAF_{feed-animal}$$

where:

 $[Metal]_{animal-organ}$ concentration of the metal in an animal organ (mg kg⁻¹);

 $BAF_{feed-animal}$ bioaccumulation factor which is the ratio of the content of a metal in an animal organ divided by the content in feed ((mg kg⁻¹ in animal organ)/ (mg kg⁻¹ in feed)) (Table 3).

Animals' metals acceptable daily intake (ADI)

A grouping of DI_{animal} and [Metal]_{animal-organ} was utilized to determine the acceptable daily intake (ADI) for animals in view of food safety and animal health standards for animal organs (de Vries et al. 2007; Rodrigues et al. 2012):

$$\begin{split} \text{ADI}_{\text{animals}} &= \left([\text{Metal}]_{\text{limit-animal-organ}} \times \ (\text{I}_{\text{feed}} + \ \text{I}_{\text{soil}}) \right) \\ & / \ \text{BAF}_{\text{feed-animal}} \end{split}$$

 $ADI_{animals}$ acceptable daily intake of each metal for animals (mg day⁻¹);

[Metal]_{limit-animal-organ} limit concentration of the metal in an animal organ (mg kg^{-1});

The ADI indicates the maximum daily intake of a specified metal so that the concentration of that

Table 2 Daily intake (DI) parameters used in animal and human exposure calculation (Rodrigues et al. 2012)

| Cow | Sheep | Source |
|---|---|--|
| $16.9 \text{ kg day}^{-1} \text{ d.w.}$ | $2.5 \text{ kg day}^{-1} \text{ d.w.}$ | de Vries et al. (2007) |
| $0.41 \text{ kg day}^{-1} \text{ d.w.}$ | $0.10 \text{ kg day}^{-1} \text{ d.w}$ | de Vries et al. (2007) |
| Humans 50 mg day ⁻¹ | ^l d.w. | Brand et al. (2000) |
| $156.4 \text{ g day}^{-1} \text{ f.w.}$ | | INE (2006) |
| $37.8 \text{ g day}^{-1} \text{ f.w.}$ | | INE (2006) |
| | $6.8 \text{ g day}^{-1} \text{ f.w.}$ | INE (2006) |
| $16.4 \text{ g day}^{-1} \text{ f.w.}$ | | INE (2006) |
| | Cow 16.9 kg day ⁻¹ d.w. 0.41 kg day ⁻¹ d.w. Humans 50 mg day ⁻¹ 156.4 g day ⁻¹ f.w. 37.8 g day ⁻¹ f.w. 16.4 g day ⁻¹ f.w. | Cow Sheep $16.9 \text{ kg day}^{-1} \text{ d.w.}$ $2.5 \text{ kg day}^{-1} \text{ d.w.}$ $0.41 \text{ kg day}^{-1} \text{ d.w.}$ $0.10 \text{ kg day}^{-1} \text{ d.w}$ Humans 50 mg day^{-1} \text{ d.w.} $156.4 \text{ g day}^{-1} \text{ f.w.}$ $37.8 \text{ g day}^{-1} \text{ f.w.}$ $6.8 \text{ g day}^{-1} \text{ f.w.}$ $16.4 \text{ g day}^{-1} \text{ f.w.}$ $6.8 \text{ g day}^{-1} \text{ f.w.}$ |

d.w. dry weight, f.w. fresh weight

| | | Critical limit (food safety) (mg kg ⁻¹) | | | Critical limit (| Critical limit (animal health) (mg kg ⁻¹) | | | | |
|-------|----|---|-------|--------|------------------|---|--------|--|--|--|
| | | Kidney | Liver | Muscle | Kidney | Liver | Muscle | | | |
| Cow | Pb | 0.5 | 0.5 | 0.1 | 3.0 | 2.0 | _ | | | |
| | Cd | 1.0 | 0.5 | 0.05 | 5.0 | 1.4 | 0.02 | | | |
| Sheep | Pb | 0.5 | 0.5 | 0.1 | 5.0 | 5.0 | 0.1 | | | |
| | Cd | 1.0 | 0.5 | 0.05 | 4.0 | 2.0 | - | | | |

 Table 3 Heavy metal critical contents in animal products (de Vries et al. 2007)

metal in animal organs (muscle, liver, or kidney) does not exceed the organ maximum concentrations assumed by food safety and animal health standards presented in Tables 4 and 5.

Metals DI for humans and dietary intakes of vegetables and animal products

Human intake of metals in this analysis depends on intake by (i) soil ingestion; (ii) food crops; and (iii) animal organs (Rodrigues et al. 2012).

The DI of metals for humans was determined for five toxic elements (Cd, Cr, Cu, Pb, and Zn). The human DI was evaluated corresponding to the formula (de Vries et al. 2007; Rodrigues et al. 2012):

$$\begin{split} DI_{humans} = & \left[Metal \right]_{soil} \times & I_{soil-humans} \\ & + & \left[Metal \right]_{leaf-vegetables} \times & I_{leaf-vegetables} \\ & + & \left[Metal \right]_{animals-organ} \times & I_{animals-organ} \end{split}$$

where:

 DI_{humans} , daily intake of a metal for humans (mg day⁻¹);

[Metal]_{leaf-vegetables}, concentration of a metal in leaf vegetables (mg kg^{-1});

 $I_{soil-humans}$, $I_{leaf-vegetables}$, and $I_{animal-organ}$, human daily intake of soil, leaf vegetables, and animal organs, respectively, by humans (kg day⁻¹) (Table 2).

Meanwhile, maximums for human tolerable intakes for non-essential metals offered from literature are presented on a weekly basis and per kilogram of body weight (bw) (provisional tolerable weekly intake, PTWI); the determined DIs were multiplied by seven to find the respective weekly intakes and supposed a body weight of 70 kg (adult).

Results and discussion

Metal concentrations in soil and plant samples

The concentrations of Cr, Cd, Cu, Pb, Zn, and Fe in soils and plants are shown in Tables 6 and 7, respectively. All soils were acidic (mean pH 5.56, range 5.06-6.13). The soils of the study area were poor in OM (mean content 1.8 %). TKN showed percentage below 0.091 %, resulting in high C/N ratios (17.17-45.04). In general, soil metal content was high, especially for Fe, Cr, and Zn. Soil metal contents were extremely unrelated between sites, possibly due to the nature of mining processes (mineral extraction, mechanical dispersion, storage, degree of mineral weathering, presence of overburden materials, etc.) (Barrutia et al. 2011). Soil Fe, Cu, Zn, and Cr in the study area are mainly originated from natural sources, and Cd and Pb is mostly derived from anthropogenic sources (Nouri and Haddioui 2015). In addition, the enrichment factor (EF) values in the mining soil ranged from 0.10 (T.4.4) to 9.79 (T.2.4) (mean at 1.25), and most of the EF values were <5, except for two soil samples with EF values close to 5 (i.e., 5.17 and 9.79), in which relatively high Pb concentrations were observed. These results indicated that the mining soils were less affected by anthropogenic activities (data not shown). These heavy metal concentrations are lower than the reference levels of Pb and Zn but higher than Cd, Cr, and Cu reference levels reported by Gutiérrez-Ginés et al. (2015).

Table 7 shows Cr, Cd, Cu, Zn, Pb, and Fe concentrations in the crop species based on their dry weight. According to Padmavathiamma and Li (2007) and Kabata-Pendias and Mukherjee (2007). all of the collected plant species showed concentrations lower than these phytotoxic levels for Cd and Pb. By comparing the values obtained with the toxic concentrations above, which toxicity effects are possible, the critical

| | | Cow | | | Sheep | | |
|---|--------|----------|---|-------------|-----------|----------|---------|
| | | Kidney | Liver | Muscle | Kidney | Liver | Muscle |
| Cd (ppm) | Normal | 0.05-1.5 | 0.02-1 | 0.004-0.024 | 0.06-0.48 | 0.02-1.4 | _ |
| Co Kii Cd (ppm) Normal 0.0 High 5 Toxic 10 Cr (ppm) Normal 0.5 High Toxic 15 Cu (ppm) Normal 4 High 5 Cu (ppm) Normal 4 High 5 Pb (ppm) Normal 0.2 High 3 7 Zn (ppm) Normal 18 High 50 7 Zn (ppm) Normal 13 Fe (ppm) Normal 30 High 49 7 Toxic - 7 | 5-36 | 1.4–9 | 0.02 | 4–12 | 2-20 | - | |
| | Toxic | 100-250 | 50-160 | _ | 50-400 | 50-600 | _ |
| Cr (ppm) | Normal | 0.5-6.2 | 0.04-3.8 | < 0.02 | _ | _ | _ |
| | High | _ | _ | _ | _ | _ | _ |
| | Toxic | 15 | 30 | _ | _ | _ | - |
| Cu (ppm) | Normal | 4–6 | 25-100 | 1.2-1.5 | 4-5.5 | 25-100 | 1-1.3 |
| | High | 5–7 | 15 50 $ 4-6$ $25-100$ $1.2-1.5$ $4-5.5$ $25-100$ $5-7$ $200-550$ $ 4-10$ $100-500$ $10-122$ $250-800$ $ 18-260$ $250-1000$ $0.2-2$ $0.1-1$ $ 0.1-0.8$ $0.03-0.8$ | 100-500 | 1.1-1.6 | | |
| | Toxic | 10-122 | 250-800 | _ | 18-260 | 250-1000 | - |
| Pb (ppm) | Normal | 0.2–2 | 0.1-1 | _ | 0.1-0.8 | 0.03-0.8 | < 0.06 |
| | High | 3–20 | 2-10 | _ | 5-100 | 5–25 | 0.1-0.3 |
| | Toxic | 5-700 | 5-300 | _ | 5-200 | 10-100 | - |
| Zn (ppm) | Normal | 18–25 | 25-100 | 30–69 | 20-40 | 30-75 | 75–130 |
| | High | 50-140 | 300-500 | _ | 50-1000 | 100-400 | - |
| | Toxic | 130-480 | 120-500 | _ | 240-1600 | >400 | 80-130 |
| Fe (ppm) | Normal | 30-150 | 45-300 | 45–54 | 30-200 | 30-300 | 10-20 |
| Fe (ppm) | High | 49–300 | 53-700 | _ | _ | _ | _ |
| | Toxic | - | 1700 | _ | - | _ | _ |

Table 4 Concentrations of metals in the animal organs (Puls et al. 1988)

levels in this range are as follows: Cr for *C. arabicus* (L) Cass, Cu for *E. ilicifolium* Lam., *C. lanatus* L., *E. spinosus* L., and Zn for *E. spinosus* L.

Cd concentrations in shoots are not generally high. In a study investigating Cd accumulation in native species from mine sites, Zhang et al. (2012) also revealed limited amounts of Cd in vascular plants. In general, the metal concentrations determined here in native plants from Ait Ammar iron mine site were similar than those reported by Gutiérrez-Ginés et al. (2015).

Table 5 Plant-animal bioconcentration factors and evaluated ADI of heavy metals in animals (Rodrigues et al. 2012)

| | | ADI _{animal} (f | ood safety) | $(mg day^{-1})$ | ADI_{animal} (animal health) (mg day ⁻¹) | | | | BAF _{plant-animal} (mg kg ⁻¹ f.w./mg kg1 d.w.) | | | |
|--------|----|--------------------------|-------------|-----------------|--|--------|--------|-----------|--|--------|--------|--|
| | | Kidney | Liver | Muscle | Kidney | Liver | Muscle | | Kidney | Liver | Muscle | |
| Cow | Pb | 101 | 214 | 1332 | 604 | 857 | _ | | 0.086 | 0.0404 | 0.0013 | |
| | Cd | 5.80 | 16 | 262 | 29 | 44 | 105 | | 2.99 | 0.554 | 0.0033 | |
| | Zn | 8655 | 5193 | _ | 7790 | 20,772 | _ | | 0.3 | 0.5 | 0.4 | |
| | Cu | 2164 | 618 | _ | 325 | 618 | _ | | 0.8 | 2.8 | 0.1 | |
| | | Kidney | Liver | Muscle | Kidney | Liver | Muscle | Uspesific | Kidney | Liver | Muscle | |
| Sheep | Pb | _ | - | _ | _ | _ | _ | 60–100 | - | - | | |
| | Cd | 1.25 | 0.70 | 45.00 | 5.00 | 2.80 | | | 2.08 | 1.85 | | |
| 0.0029 | | | | | | | | | | | | |
| | Zn | _ | - | _ | _ | _ | _ | 150 | - | - | | |
| _ | | | | | | | | | | | | |
| | Cu | _ | - | _ | _ | _ | _ | _ | - | - | | |
| - | | | | | | | | | | | | |

Table 6 Physicochemical characterizations of Ait Ammar iron mining area (see also Nouri et al. 2013)

| Samples | T.1.1 | T.2.1 | T.3.1 | T.4.1 | Average |
|-------------------------------------|-------------|-----------|-----------|-----------|-----------|
| pH (KCl) | 6.13 | 5.60 | 5.44 | 5.06 | 5.56 |
| pH (water) | 7.20 | 6.94 | 7.11 | 6.84 | 7.02 |
| Conductivity (µS cm ⁻¹) | 151.77 | 75.57 | 55.37 | 70.10 | 88.20 |
| OM Content (%) | 2.69 | 2.68 | 1.07 | 0.77 | 1.80 |
| Water content (%) | 2.11 | 1.51 | 1.75 | 2.18 | 1.89 |
| TOC (%) | 1.5593 | 1.5565 | 0.6216 | 0.4447 | 1.0455 |
| TKN (%) | 0.0908 | 0.0489 | 0.0138 | 0.0140 | 0.0418 |
| C/N Ratio | 17.17 | 31.83 | 45.04 | 31.76 | 31.45 |
| Total metal concentration (mg | (kg^{-1}) | | | | |
| Cd | 1.37 | 0.91 | 3.06 | 0.55 | 1.47 |
| Cr | 108.38 | 119.74 | 136.97 | 156.50 | 130.39 |
| Cu | 28.78 | 36.19 | 51.97 | 62.67 | 44.90 |
| Zn | 76.24 | 65.56 | 145.32 | 129.90 | 104.25 |
| Pb | 12.46 | 0.91 | 0.82 | 14.76 | 7.24 |
| Fe | 228030.00 | 199330.00 | 373790.00 | 313080.00 | 278557.50 |

In addition, the concentrations of Cd and Cu in all plants and Zn in almost all plants samples were higher than the maximum levels permissible for forage (Table 7). The maximum chromium concentration has

Table 7 Concentrations (mg kg⁻¹ dry weight (d.w.)) of metals in the shoot tissues of the different study species (see also Nouri et al. 2013)

| Family | Species | Cd | Cr | Cu | Fe | Pb | Zn |
|-------------------------------------|---------------------------------------|--------------|-------------------|--------------------|---------|--------|---------------------|
| Apiaceae | Eryngium ilicifolium Lam. | 0.83 | 1.09 | 25.48 ^a | 565.22 | 0.73 | 63.79 |
| | Eryngium triquetrum Vahl. | 0.84 | 1.52 | 18.77 | 336.14 | 0.37 | 61.59 |
| SAsteraceae | Carlina acaulia subsp caulescens | 0.93 | 0.67 | 18.70 | 204.82 | _ | 71.72 |
| | <i>Carthamus lanatus</i> L. | 0.89 | 0.94 | 20.63 ^a | 892.08 | 1.04 | 72.96 |
| | Cladanthus arabicus (L.) Cass. | 0.88 | 9.24 ^a | 17.24 | 636.57 | 2.48 | 90.40 |
| | Echinops spinosus L. | 0.99 | 0.73 | 29.19 ^a | 297.78 | _ | 175.35 ^a |
| | Leontodon hispidilus (Delile) Boiss. | 0.84 | 2.51 | 19.01 | 1522.84 | 5.95 | 85.52 |
| | Scolymus hispanicus L. | 0.83 | 2.53 | 15.60 | 346.01 | 1.08 | 58.32 |
| Poaceae | Bromus hordeaceus | 0.83 | 4.51 | 14.63 | 417.14 | 1.92 | 39.38 |
| | Bromus rubens L. | 0.87 | 4.58 | 15.99 | 357.57 | 1.63 | 58.66 |
| | Lamarckia aurea L. (Moench). | 0.84 | 4.04 | 17.15 | 930.87 | 1.57 | 66.85 |
| | Stipa capensis Thunb. | 0.83 | 3.95 | 12.42 | 371.07 | _ | 33.52 |
| Ranunculaceae | Ranunculus peltatus Schrank. | 0.68 | 2.35 | 5.33 | 2459.66 | 16.40 | 67.86 |
| Kabata-Pendias and Mukherjee (2007) | Normal range (mg kg ⁻¹) | 0.01– 0.2 | 0.1–0.5 | 5–30 | | 5–10 | 25–150 |
| | Toxic range (mg kg^{-1}) | 5–30 | 5–30 | 20–100 | | 30–300 | 100– 400 |
| Padmavathiamma and Li (2007) | Normal range (mg kg^{-1}) | 0.05–2 | | 3–30 | | 0.5–10 | 10-150 |
| | Phytotoxic range (mg kg^{-1}) | 5-700 | | 20-100 | | 30-300 | >100 |
| WHO (1992, 1995), FAO (2000) | Maximum levels permissible for forage | 0.23 | | 2.9 | | 1.3 | 45 |

^a The values in the toxic range

-Below detection limit (Pb, 0.004 mg/L)

no threshold limit, but in the diverse papers suggested a concentration between 0.03 to 1 mg kg⁻¹ in samples (Csathó 1994; Güler 2006). Moreover, the amount of the Cd in species samples were higher than the highest acceptable limits tolerated by livestock according to Madejón et al. (2006) and lower for other heavy metals. Furthermore, the Fe concentrations were, in general, higher than the maximum levels tolerated for sheep reported by Madejón et al. (2006).

Animal exposure to metals in soil and plants

The DIs of metals for both cow and sheep are presented in Table 8. These levels were judged with minimal animal ADI levels presented in Table 5. DI of Cd for sheep and cows was 2.28 and 15.01 mg day⁻¹, respectively. The cow ADI for Cd regarding food safety $(5.8 \text{ mg day}^{-1})$ was exceeded, the same ADI for sheep $(0.7 \text{ mg day}^{-1})$ was exceeded. The eating of offal from livestock grazing at that place should consequently be avoided. Estimate of Cu DI for cows was $317.59 \text{ mg day}^{-1}$ and was above ADI in vision of animal health security (325 mg day^{-1}). No ADI levels for sheep were discovered in literature. DI of Pb was $59.02 \text{ mg day}^{-1}$ and 9.02 mg day^{-1} for cows and sheep, respectively. The ADI of 101 mg day⁻¹ (for cows, in vision of food safety) was not exceeded and the same ADI for sheep (60 mg day⁻¹) was not surpassed. In the case of Zn, the ADI for cows in vision of food safety $(5193 \text{ mg day}^{-1})$ was not exceeded while ADI for sheep $(150 \text{ mg day}^{-1})$ was surpassed. With the difference in results for sheep, the eating of offal from livestock grazing in this site should consequently be avoided. No animal ADI levels were attained for the remaining metals.

Table 8 presents the results attained for the essential and non-essential metals studied in soil, in plants, and in animal organs. The zinc contents were 23.78 mg kg⁻¹ in the kidney, 30.89 mg kg⁻¹ in the muscle, and 37.99 mg kg⁻¹ in the liver. The difference between zinc contents in the kidney and other organs was not significant (test t). The greatest copper content (49.46 mg kg⁻¹) was detected in the liver. The difference with other organs was significant (test t, P < 0.05). In the muscle and kidney, copper levels were 2.79 mg kg⁻¹ and 14.89 mg kg⁻¹, respectively. The lead levels were 0.45 mg kg⁻¹ in the kidney, 0.18 mg kg⁻¹ in the muscle, and 0.30 mg kg⁻¹ in the liver. The difference between lead levels in the kidney and other organs was significant. The concentrations of Pb detected in the cow organs are lower than those reported by de Vries et al. (2007) (critical limit) (Table 3). In this study, a high content of Cd was found in kidney (2.52 and 1.76 mg kg^{-1} for cows and sheep, respectively), whereas the liver Cd level was 0.5 mg kg^{-1} for cows and 1.57 mg kg^{-1} for sheep. Statistical analysis showed a significant difference (P<0.05) between Cd concentrations in the kidney and other organs. The Cd levels observed in the liver are similar to those reported by de Vries et al. (2007) (critical limit, food safety), higher in the kidney and lower in the muscle for cow. For sheep, the Cd contents in the kidney, liver, and muscle were higher than the critical limit (food safety) (Table 3). Moreover, the Cd values determined in this study were in accordance with those revealed by Franz et al. (2008) in the kidney and liver. Furthermore, the Cd levels in the muscles for cow and sheep were nearly similar with those reported by Islam et al. (2015). the same for Pb levels for cow but the Cu concentrations in this study for cow were higher.

In the present report, the Cu concentration in the kidney was toxic and the Cd content in the muscle was highest. However, other metal levels in different organs were normal or slightly higher than the normal, in comparison with the results reported with Puls et al. (1988) (Table 4).

In the current work, the results show Cd and Pb to concentrate primarily in the kidney and Cu and Zn in the liver. This unequal distribution amongst the organs is related to differences in the specific physiological functions of these elements and depends on their relative abundance in intracellular ligands able to bind metals, such as metalloproteins (Sedki et al. 2003).

In comparison to control animals obtained Sedki et al. (2003). the levels of Cd in the kidney and muscle in our study were higher. The same Cu levels in the liver and muscle were higher. Accordingly with Sedki et al. (2003). the highest Cu level was observed in the liver. Furthermore, the values of Cd and Pb in the kidney and liver were comparable to those measured with Slob (2005).

Cu levels in all organs, Zn in the kidney, and Cd in the liver and muscle were higher than the levels revealed with Falandysz (1993). The levels of Cd, Cu, and Zn detected in the different organs are lower than those of bovines grazing on the municipal wastewater spreading field of Marrakech, reported by Sedki et al. (2003). As is the case for many trace elements, metal levels in tissue

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| Table 8 M | easured concentrations | of metals in soils, | , in plants (shoots |), in animal t | tissues (mg | kg^{-1}) and | l estimates o | f daily intake | (DI) |
|-----------------|------------------------|---------------------|----------------------|----------------|-------------|-----------------|---------------|----------------|------|
| $(mg day^{-1})$ | of metals by cow and s | sheep based on mea | asured levels in cro | ps and soils | | | | | |

| | | | Cow | | | | Sheep | | | |
|--------|--------|-------|---------|--------|-------|--------|--------|--------|-------|--------|
| Metals | Soil | Plant | DI | Kidney | Liver | Muscle | DI | Kidney | Liver | Muscle |
| Cd | 1.47 | 0.85 | 15.01 | 2.52 | 0.50 | 0.04 | 2.28 | 1.76 | 1.57 | 0.06 |
| Cr | 130.40 | 2.97 | 103.72 | | | | 20.47 | | | |
| Cu | 44.90 | 17.70 | 317.59 | 14.89 | 49.46 | 2.79 | 48.75 | | | |
| Zn | 104.26 | 72.76 | 1272.44 | 23.78 | 37.99 | 30.89 | 192.33 | | | |
| Pb | 7.24 | 3.32 | 59.02 | 0.45 | 0.30 | 0.18 | 9.02 | | | |

are largely dependent on the metal content of diet (Sedki et al. 2003).

In the present study, the concentrations of heavy metals (Cd, Cu, Pb, and Zn) for the muscle were higher than the respective values for lambs observed in grassfinished of Missouri and imported grass-finished groups from New Zealand (Ikem et al. 2015). USA (nutrient database; USDA United States Department of Agriculture 2012). Iceland (pasture fed; Reykdal et al. 2011). and Australia (retail samples; Williams 2007).

The consumption of the meat, liver and kidney from livestock reared in this polluted area certainly contributes to the average daily metal intake by man. To our knowledge, in Morocco, no regulations have yet been established for heavy metals in meat or bovine organs but this issue has become important in many countries.

Human exposure to metals through diet

Estimated weekly intakes of Cd, Cu, Zn, and Pb for humans through diet are given in Fig. 3. Cd is a toxic heavy metal existent at low contents in environment and correspondingly in several nutriment. High contents of Cd, frequently related with human activity, principal contaminant of soil, water, and air and to augmented



Fig. 3 Calculated weekly intakes (mg/w) of Cd, Cu, Pb, and Zn on the basis of measured data on soils, plants, and estimated values in cow products

Cd uptake by animals and plants, certain of which are utilized and kept for human nutrition (Järup 2003). Foods are the central cause of human ingestion of Cd, for the non-smoking people (Järup 2003). For human, Cd can provoke kidney dysfunction, skeletal harm, and reproductive deficiencies (Järup 2003). In 2010, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) withdrew the PTWI_{Cd} value of 7 µg/kg bw (body weight) and determined a provisional tolerable monthly intake (PTMI_{Cd}) of 25 µg/kg bw (JECFA 2010). For Cd, the estimated weekly intake was 1.29. A PTWI of 0.49 mg week⁻¹ for a person weighing 70 kg has been recommended for Cd by the WHO according to our estimates the PTWI is exceeded.

Pb is a toxic element with no identified biological role that accumulates in the human corps and may create a dangerous danger to inhabitant's health (Stanković et al. 2012). The International Agency for Research on Cancer (IARC) classed inorganic Pb as possibly carcinogenic to humans (IARC 2006). A PTWI level of 0.025 mg kg⁻¹ bw for Pb was determined by JECFA in 2010. Estimated weekly intake of Pb was 3.77. The PTWI for Pb of 1.75 mg week⁻¹ was exceeded. These results are much more worrying if one considers that Pb moreover arrives in the human body via additional sources. Additionally, Pb is persistent, and accumulated in the human body, is hardly to be excreted; accordingly, increasing concern should be paid for the Pb in food and its daily intake (Fang et al. 2015).

Zn is an essential heavy metal in the human food. The necessitated daily intake for adult is around 15 mg day⁻¹; however, the average dietary Zn intake in adults is 14–20 mg day⁻¹ and is thus sufficient for alimentary requests (JECFA—Joint FAO/WHO Expert Committee on Food Additives 1982). Even though Zn is an indispensable metal for health, abnormal contents of

nutritional Zn can produce grave health difficulties, like stomach problems, skin irritations, vomiting, and anemia. Very excessive concentrations of Zn can destruct the pancreas, disturb the metabolism of protein and produce arteriosclerosis (Oyaro et al. 2007). In 1982, JECFA suggested a provisional maximum tolerable daily intake (PMTDI) for Zn of 1 mg kg⁻¹ bw, which is corresponding to 490 mg week⁻¹ for an adult with 70 kg (JECFA—Joint FAO/WHO Expert Committee on Food Additives 1982). A PTWI of 490 mg/week has been recommended for Zn which was not exceeded in our research site.

The content of Cu in nutriment meets the dietary needs of 2–3 mg day⁻¹ for adults and 0.5–0.7 mg day⁻¹ for infants. While, Cu is an essential heavy metal, excessive concentrations of intake can produce risky health consequences (Gorell et al. 1997). nonetheless, it is not carcinogenic to animals and humans. The JECFA determined a PMTDI for Cu of 0.5 mg kg⁻¹ bw day⁻¹ which is comparable to 3.5 mg kg⁻¹ bw week⁻¹, i.e., 245 mg week⁻¹ for an adult with 70 kg (JECFA—Joint FAO/WHO Expert Committee on Food Additives 1982). A PTWI of 245 mg week⁻¹ has been recommended for Cu which was not exceeded in our research site. The PTWIs of Cd, Cu, and Pb were higher than those reported by Cai et al. (2015) via consumption of foodstuffs, water, and soil.

Conclusions

The concentrations of cadmium, lead, copper, and zinc found in the kidneys, liver, and muscle of livestock grazing on the Ait Ammar iron mining area are high. The levels of heavy metals confirmed that the three sources were not adequate for human health. However, the provisional tolerable weekly intake of these elements in this present work were under the corresponding PTWI or proposed guideline levels for the corresponding heavy metals for Zn and Cu, but above for Cd and Pb. A moderate consumption of offal and meat is recommended to avoid any danger to the inhabitants. Additional investigation is required to more elucidate the influence of animal raising situations and the finishing types distributed to livestock before slaughter on the quality of offal and meat. With augmenting consciousness of consumers, it may become crucial in the future for livestock production systems to deliver information like the race, reproduction location, rearing condition, age, sex, and weight of livestock before slaughter on their offal and meat products.

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References

- Acosta, J. A., Faz, A., Martinez-Martinez, S., Zornoza, R., Carmona, D. M., & Kabas, S. (2011). Multivariate statistical and GIS-based approach to evaluate heavy metals behaviour in mine sites for future reclamation. *Journal Of Geochemical Exploration, 109*, 8–17.
- Barrutia, O., Artetxe, U., Hernández, A., Olano, J. M., García-Plazaola, J. I., Garbisu, C., & Becerril, J. M. (2011). Native plant communities in an abandoned Pb-Zn mining area of northern Spain: implications for phytoremediation and germplasm preservation. *International Journal of Phytoremediation, 13*, 256–270.
- Brand, E., Otte, P. F., & Lijzen, J. P. A. CSOIL 2000: an exposure model for human risk assessment of soil contamination. A model description. The Netherlands: RIVM Bilthoven; 2007. RIVM report 711701054.
- Cai, L. M., Xu, Z. C., Qi, J. Y., Feng, Z. Z., & Xiang, T. S. (2015). Assessment of exposure to heavy metals and health risks among residents near Tonglushan mine in Hubei, China. *Chemosphere*, 127, 127–135.
- Csathó, P. (1994). Heavy metal contamination of environment and agricultural production. A review. (In Hungarian) MTA TAKI Budapest, 155, 1–176.
- de Vries, W., Römkens, P. F. A. M., & Schütze, G. (2007). Critical soil concentrations of cadmium, lead, and mercury in view of health effects on humans and animals. *Reviews of Environmental Contamination and Toxicology*, 191, 91–130.
- El fadeli, S., Bouhouch, R., El abbassi, A., Chaik, M., Aboussad, A., Chabaa, L., Lekouch, N., Hurrell, R. F., Zimmermann, M. B., & Sedki, A. (2014). Health risk assessment of lead contamination in soil, drinking water and plants from Marrakech urban area, Morocco. *Journal of Materials and Environmental Science*, 5, 225–230.
- El Hamiani, O., El Khalil, H., Lounate, K., Sirguey, C., Hafidi, M., Bitton, G., Schwartz, C., & Boularbah, A. (2010). Toxicity assessment of garden soils in the vicinity of mining areas in Southern Morocco. *Journal of Hazardous Materials*, 177, 755–761.
- Falandysz, J. (1993). Some toxic and essential trace metals in cattle from the northern part of Poland. *Science of the Total Environment*, 135, 177–191.
- Fang, T., Liu, G., Zhou, G., & Lu, L. (2015). Lead in soil and agricultural products in the Huainan Coal Mining Area, Anhui, China: levels, distribution, and health implications. *Environmental Monitoring and Assessment, 187*, 152–162.

- FAO (2000). Infections and intoxications of farm livestock associated with feed and forage. www.fao.org/es/ESN/animal/ animapdf7annex-4.pdf
- Franz, E., Romkens, P., Raamsdonk, L. V., & Fels-Klerx, I. V. D. (2008). A chain modeling approach to estimate the impact of soil cadmium pollution on human dietary exposure. *Journal* of Food Protection, 71, 2504–2513.
- Gorell, J. M., Johnson, C. C., Rybicki, B. A., Peterson, E. L., Kortsha, G. X., & Brown, G. G. (1997). Occupational exposures to metals as risk factors for Parkinson's disease. *Neurology*, 48, 650–658.
- Gough, L. P., & Shacldette, H. T. (1976). Toxicity of selected elements to plants, animals and man—an outline. U. S. Dept. Interior, Geological Survey, Open-File Rep. No. 76-746.
- Güler, M. (2006). Levels of 24 minerals in local goat milk, its strained yoghurt and salted yoghurt (tuzlu yogurt). *In Small Ruminant Research*, 71, 130–137.
- Gutiérrez-Ginés, M. J., Pastor, J., & Hernand A. J. (2015). Heavy metals in native Mediterranean grassland species growing at abandoned mine sites: ecotoxicological assessment and phytoremediation of polluted soils. In Sherameti I, Varma A (Ed.) soil biology 44, *Heavy Metal Contamination of Soils Monitoring and Remediation* (pp. 159–178). New York: Springer.
- Houba, V. J. G., Novozamsky, I., Lexmond, T. M., & Van-Der-Lee, J. J. (1990). Applicability of 0.01 M CaCl₂ as a single extraction solution for the assessment of the nutrient status of soils and other diagnostic purposes. *Communications in Soil Science and Plant Analysis, 21*, 2281–2290.
- IARC (2006). International Agency for Research on Cancer, IARC monographs on the evaluation of carcinogenic risks to humans. Inorganic and organic lead compounds. http:// monographs.iarc.fr/ENG/Monographs/vol87/mono87.pdf. Accessed 6 Jan 2015.
- Ikem, A., Shanks, B., Caldwell, J., Garth, J., & Ahuja, S. (2015). Estimating the daily intake of essential and nonessential elements from lamb m. *longissimus thoracis* et *lumborum* consumed by the population in Missouri (United States). *Journal of Food Composition and Analysis*, 40, 126–135.
- INE (Instituto Nacional de Estatística) (2006). Balança Alimentar Portuguesa 1990–2003. Portugal: Lisboa.
- Islam, M. S., Ahmed, M. K., Al-Mamun, M. H., & Masunaga, S. (2015). Assessment of trace metals in foodstuffs grown around the vicinity of industries in Bangladesh. *Journal of Food Composition and Analysis*, 42, 8–15.
- Järup, L. (2003). Hazards of heavy metal contamination. British Medical Bulletin, 68, 167–182.
- JECFA (2010). Summary and conclusions of the seventy-third meeting of the Joint FAO/WHO Expert Committee on Food Additive. JECFA/73/SC, Geneva, Switzerland, 2010. http://who.int/foodsafety/publications/chem/summary73.pdf (accessed 01.06.15).
- JECFA: Joint FAO/WHO Expert Committee on Food Additives (1982). Evaluation of certain food additives and contaminants. Twenty-sixth report of the Joint FAO/WHO expert Committee on Food Additives. Technical Report Series 683, Geneva, Switzerland, 1982. http://whqlibdoc.who.int/ trs/WHO TRS 683.pdf (accessed 01.06.15).
- Kabata-Pendias, A., & Mukherjee, A. B. (2007). *Trace elements from soil to human.* Berlin: Springer.

- Madejón, P., Murillo, J. M., Maranón, T., & Cabrera, F. (2006). Bioaccumulation of trace elements in a wild grass three years after the Aznalcóllar mine spill (South Spain). *Environmental Monitoring and Assessment, 114*, 169–189.
- Mahaffey, K. R. (1977). Mineral concentrations in animal tissues: certain aspects of FDA's regulatory role. *Journal of Animal Science*, 44, 509–515.
- Nouri, M., & Haddioui, A. (2015). Assessment of metals contamination and ecological risk in Ait Ammar abandoned iron mine soil, Morocco. *Ekologia* (submitted: 10-11-15).
- Nouri, M., Gonçalves, F., Sousa, J. P., Römbke, J., Ksibi, M., Pereira, R., & Haddioui, A. (2013). Metal uptake by spontaneous vegetation in an abandoned iron mine from a semiarid area in center Morocco: implications for phytoextraction. *Environmental Research, Engineering and Management*, 64, 59–71.
- Nouri, M., Gonçalves, F., Sousa, J. P., Römbke, J., Ksibi, M., Pereira, R., & Haddioui, A. (2014). Metal concentrations and metal mobility in Ait Ammar Moroccan mining site. *Journal* of Materials and Environmental Science, 5, 271–280.
- ONHYM, The National Office of Hydrocarbons and Mines, http:// www.onhym.com/ (visited 06-05-2015).
- Oyaro, N., Juddy, O., Murago, E. N. M., & Gitonga, E. (2007). The contents of Pb, Cu, Zn and Cd in meat in Nairobi, Kenya. *Journal of Food, Agriculture and Environment*, 5, 119–121.
- Padmavathiamma, P. K., & Li, L. Y. (2007). Phytoremediation technology: hyperaccumulation metals in plants. *Water, Air,* and Soil Pollution, 184, 105–126.
- Puls, R. (1988). *Mineral levels in animal health: diagnostic data*. Clearbook, BC, Canada: Sherpa International.
- Reykdal, O., Rabieh, S., Steingrimsdottir, L., & Gunnlaugsdottir, H. (2011). Minerals and trace elements in Icelandic dairy products and meat. *Journal of Food Composition and Analysis*, 24, 980–986.
- Rodrigues, S. M., Pereira, M. E., Duarte, A. C., & Römkens, P. F. A. M. (2012). Soil-plant-animal transfer models to improve soil protection guidelines: a case study from Portugal. *Environment International*, 39, 27–37.
- Sedki, A., Lekouch, N., Gamon, S., & Pineau, A. (2003). Toxic and essential trace metals in muscle, liver and kidney of bovines from a polluted area of Morocco. *Science of the Total Environment*, 317, 201–205.
- Slob, W. (2005). Advies inzake de relatie tussen de herkomst van runderen en het gehalte cadmium in hun nieren. Wageningen, The Netherlands: RIVM-RIKILT Front Office.
- Smith, K. M., Abrahams, P. W., Dagleish, M. P., & Steigmajer, J. (2009). The intake of lead and associated metals by sheep grazing mining-contaminated floodplain pastures in mid-Wales, UK: I. Soil ingestion, soil-metal partitioning and potential availability to pasture herbage and livestock. *Science of the Total Environment, 407*, 3731–3739.
- Stanković, S., Jović, M., Stanković, A. R., & Katsikas, L. (2012). Heavy metals in seafood mussels, risks for human health. In E. Lichtfouse, J. Schwarzbauer, & D. Robert (Eds.), *Environmental Chemistry for a Sustainable World* (*Nanotechnology and Health Risk*, Part II, Chapter 9, Vol. 1, pp. 311–373). Netherlands: Springer.
- Underwood, E. J. (1977). *Trace elements in human and animal nutrition* (4th ed.). New York: Academic.
- USDA (United States Department of Agriculture) (2012). Composition of foods, raw, processed, prepared, USDA

National Nutrient Database for Standard Reference, Release 25. U.S. Department of Agriculture, Agricultural Research Service, Beltsville Human Nutrition Research Center, Nutrient Data Laboratory, Beltsville, MD, pp. 2070.

- WHO (World Health Organization) (1992). Cadmium environmental aspect. Environmental Health Criteria 135. Geneve.
- WHO (World Health Organization) (1995). Inorganic lead. Environmental Health Criteria 165. Geneve.

- Williams, P. G. (2007). Nutritional composition of red meat. *Nutrition and Dietetics*, 64, 113–115.
- Zhang, S., Li, T., Huang, H., Zou, T., Zhang, X., Yu, H., Zheng, Z., & Wang, Y. (2012). Cd accumulation and phytostabilization potential of dominant plants surrounding mining tailings. *Environmental Science and Pollution Research*, 19, 3879– 3888.