

DATA ARTICLE

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# Inorganic contaminants and composition analysis of commercial feed grade mineral compounds available in Costa Rica

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## Abstract

**Background:** Heavy metals such as arsenic (As), mercury (Hg), lead (Pb) and cadmium (Cd), are potential toxic substances that may incorporate in productive systems in multiple ways including contaminated feedstuff. In this regard, we hypothesize that the main input of heavy metal contamination include mineral feed ingredients which, in turn, are included in compound feed to meet animals' nutritional requirements. Hence, we offer a comprehensive heavy metal determination on imported feed grade mineral supplement samples ( $n = 435$ ), comprised of 27 different sources including calcium/phosphorus, iron, cobalt, copper, cobalt, manganese, iodide, sulfur, potassium, sodium, selenium and magnesium were collected from eight different local feedingstuff manufactures, mineral and heavy metal as cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) analyses were performed using atomic absorption spectroscopy and microwave assisted digestion. Based on this premise, the main goals of the study were to determine mineral and trace mineral content and contrast these values with those advertised by the manufacturers and to determine heavy metal concentrations and compare these levels with the current regulation in commercially available mineral sources which are used in premixes and downstream formulation of compound feeds; a matter which remains undocumented.

**Results:** Our results show that occasionally mineral values for these supplements were lower than those declared. Additionally, several samples contravene, in at least one heavy metal, current regulations; samples in this condition correspond to 0.5 ( $n = 2$ ), 13.8 ( $n = 60$ ), 4.1 ( $n = 18$ ) and 2.5 % ( $n = 11$ ) for As, Hg, Pb and Cd, respectively with mercury as the most frequent mineral to surpass, in the majority of cases, current thresholds. Overall, 21.1 % ( $n = 92$ ) of the samples exhibited concentrations of heavy metals above those stipulated by European guidelines. Meanwhile potassium chloride, ( $n = 17$ ), exhibited the lower overall concentrations of heavy metals.

**Conclusion:** Samples of mineral origin may surpass, in some cases with elevated concentrations, permitted levels of undesirable substances, therefore, a monitoring programme for mineral ingredients in our country is recommended.

**Keywords:** Heavy metals; Mineral ingredients; Animal feed; Guaranteed analysis

## Background

Animal feed ingredients that constitute complete feed products are derived from a multitude of raw materials of plant and animal origin, as well as pharmaceutical and industrial sources. Many metallic compounds including calcium, copper, manganese, magnesium, and zinc compounds, as well as metal amino acid complexes (AAFCO

2014) are administered in animal feeds to satisfy nutritional needs of food-producing and companionship animals. Some minerals and/or premixes that may be by-products or co-products of industrial metal production might become contaminated with various heavy metals, (US FDA 2003) this is of particular concern from a public health perspective (Mamtani et al. 2011). In this regard, heavy metal contamination is especially important if one consider that a possible contamination in animal diets could consequently lead to transference to animal tissues and food products (Leeman et al. 2007).

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Arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) are widely dispersed in the environment. These elements have no known beneficial effects in humans or animals nor homeostasis mechanism for them (Poirier and Littlefield 1996). Furthermore, these metals are of special interest due to their inherent ability to bioaccumulate or biomagnify (Demirezen and Uruç 2006), transfer into and between food chains (Makridis et al. 2012) and their lack of biological functions (Singh et al. 2011). Although toxicity and the resulting threat to animal or human health of any contaminant are, of course, a function of concentration and inclusion rates in diet, it is well-known that sublethal chronic exposure to As, Cd, Hg, and Pb at relatively low levels can cause detrimental effects on physiological and/or biochemical processes (Sharma and Agrawal 2005).

AAFCO enlists different minerals used as feed ingredients and registers representative levels of toxic contaminants such as cadmium, arsenic, lead, and mercury in mineral feed ingredients, at the same time suggests guidelines for contaminants (based on toxicological capabilities) in complete feed and in mineral feed ingredients (AAFCO 2014).

Despite feedingstuff and its individual components (even those considered as minor ingredients) are the most probable and important way of acquiring these metals by husbandry animals, heavy metals may also enter productions systems in a variety of ways; these include atmospheric deposition, land application of inorganic fertilizers, biosolids, agrochemicals, and animal manure (Nicholson et al. 2003). However, the magnitude of these direct inputs will be determined by many indirect factors, such as farm location and type of production system (i.e. extensive or intensive) (López-Alonso et al. 2002; Blanco-Penedo et al. 2009).

It has been established that the most important source of heavy metal in concentrates and compound feeds are mineral supplements and premixes (Li et al. 2005) that are blended as additives during their formulation to supply the animal their dietary minimal intake of essential nutrients. However, it is still difficult to assess concentrations of toxic metal content in animal feed materials because of limited information, as most of the available data correspond to compound feed and few individual constituents whereas data on the particular mineral constituents to our knowledge is not existent. Hence, we found pertinent a comprehensive analysis of heavy metals in these mineral ingredients.

It is widely recognized that industrial and/or agricultural development is largely responsible for environmental pollution with toxic metals, though natural geochemical contamination has not been unheard of (Järup 2003). Most of these mineral sources are attained by industrial mining –mostly from metamorphic, igneous, volcanic, quarry or sedimentary rock (Elzea et al. 2006)– these types of raw materials often contain impurities, mainly fluorine

(in the case of feed phosphates) and heavy metal compounds (e.g. Pb, Cd, As, Hg). Additionally, these products must be subjected to physicochemical treatments in order to meet the zootechnical requirements or transformed to soluble species with improved digestibility and assimilability (van Paemel et al. 2010).

As a country with non-mining, mineral processing or industrial capabilities Costa Rica imports these minerals from world mayor producers which include Netherlands, Peru, Chile, USA, China, Brazil, France among others (up to ca 1300 ton/550 thousand USD in 2014 alone) (PROCOMER 2014). Hence, the quality of feed produced in our country will depend on exporters to abide by current regulations. For example, the current all-European regulations in this field specify the permissible content of undesirable substances in animal feed (EC 2002; Official Journal of European Communities 2012).

Finally, due to a worldwide concern during feed production is the availability of supplies of raw ingredients (Van der Weijden et al. 2013) animal specialists must seek highly productive animals while assuring feed, feed supplies and food products (as well as the rest of the food chain) safety (EC 2000) but at the same time, using cost effective feedstock (e.g. technological processes by-products). Therefore, a decrease in exposure to undesirable contaminants through correct monitoring of these raw materials is paramount.

The aim of this study was to determine mineral, trace minerals and heavy metal contents in commercially available mineral sources which are used in premixes and downstream formulation of concentrates. The importance of these results are threefold as 1. They may play an important role as a standpoint to evaluate regionally the quality of raw materials as mineral supplements imported to the country 2. could help establish the regional and local guidelines for heavy metals maximum limits and 3. may serve as a guideline to manufacturers to make decisions with regard of the quality and safety of materials they use to prepare feeds.

## Methods

### Sampling

A total of 435 imported feed grade mineral supplement samples were selected for analysis. Samples were collected from eight plants that use these minerals in the country during 2012 and 2014 by a rolling census sampling method, taking into consideration the most common used ingredients for feed elaboration. A portion of the material was collected according to a defined sampling procedure that included only those containers which, when arriving to the manufacturing plant, were already in use. Trial units were obtained directly from container bags found in-plant and represented several batches. Samples were transported to the laboratory, a 100 g subsample of each mineral was homogenized, sieved

and milled (up to a mm of particle size if deemed necessary) and kept in polyethylene sealed bottles at 24 °C until analyzed.

#### Mineral content

From 0.2 to 0.4 g sample was analyzed for total minerals resorting to wet mineralization carried out in an FOSS Tecator™ Digester Auto (FOSS, Hillerod, Denmark) using a mixture of perchloric acid, nitric acid (Merck suprapur; E. Merck, Darmstadt, Germany) and water. Mineral species in the form of carbonates were digested *in situ* using a 6 mol/L solution of hydrochloric acid (Merck suprapur; E. Merck, Darmstadt, Germany) with mild heating in a hot plate at 300 °C, and analyzed using the flame atomic absorption spectrophotometry (FAAS) technique (Perkin-Elmer AAnalyst 800 atomic absorption spectrometer, Perkin-Elmer Corp., Norwalk, CT, USA). The radiation source, a Hollow Cathod Lamp for each metal, was used at wavelengths and spectral slit widths recommended by the manufacturer.

In the case of phosphorus, UV-vis spectrophotometry using molybdovanadate method was employed for measuring this mineral based on AOAC official method 935.13. Formation of the complex was obtained using 3 mL molybdovanadate solution instead of 2 mL as described in the original method.

#### Heavy metal analysis

Methods AOAC 986.15 and 999.10 were used during this survey. Briefly, 100 g subsample of each mineral was milled and from 0.2 to 0.4 g was analyzed for total heavy metals (Pb, Cd, As and Hg) by 90:10 nitric acid:hydrogen peroxide (both Merck suprapur; E. Merck, Darmstadt, Germany) microwave digestion using a Berghof Speed-wave four (Harretstrasse, Eningen, Germany): Analyses were carried out either by flow injection metal hydride atomic absorption spectrophotometry (FI-MH-AAS, for Se and Hg) or graphite furnace atomic absorption spectrophotometry (GFAAS) technique (Perkin-Elmer AAnalyst 800 atomic absorption spectrometer, Perkin-Elmer Corp., Norwalk, CT, USA) in the case of As, Cd and Pb. Hydride generation was performed using a 30 g/L NaBH<sub>4</sub> in 10 g/L NaOH. The radiation source used was an Electrodeless Discharge Lamp for each metal used at wavelengths and a spectral slit widths recommended by the manufacturer.

#### Calibration curves

For metals analyzed with AAS or colorimetry, calibration curves were measure each time a metal was analyzed. Standards were prepared using commercially available NIST reference standard materials 10 mg/g (prepared from metal oxides and nitrates in HNO<sub>3</sub>). All solutions were prepared with ultrapure water with a final conductivity of 0.055 μS/cm obtained using a Millipore Elix 35/

Milli-Q Advantage A10 system (Millipore, Bedford, MA, USA) immediately before use. Magnesium nitrate and ammonium dihydrogen phosphate in a concentration of 10 g/L were used as matrix modifiers during Cd, As and Pb graphite furnace analyses.

#### Sulfur analysis

Sulfur was determined gravimetrically after a microwave digestion using a concentrated nitric acid and hydrochloric acid mixture (65:37). Hereafter, a 10 mL aliquot of a 10 g/100 mL barium chloride solution is added to the resulting digest. After 12 hours of idle time at 4 °C, the resulting crystalline solid is retained on a previously weighted 542 Whatman filter paper (GE Healthcare Bio-Sciences, Pittsburg, USA), both filter and solid are dried afterwards. The recovered barium sulfate precipitate is weighted and calculated as sulfur in the original sample.

#### Anion analysis

Fluorine analysis, using an ion selective electrode, was performed to dicalcium and monocalcium phosphates. This assay was performed according to AOAC OMA 975.08. Briefly, a well-mixed test portion containing ca. 400 mg F<sup>-</sup> was weighted into a, high-density polyethylene, 200 mL volumetric flask. A 20 mL aliquot 1 mol/L HCl was added and the mixture stirred during 20 min at high speed on magnetic stirrer. Solutions of sodium acetate and citrate are added to the mixture and the flask was made-up to volume with water. The mixture was transferred to a polyethylene sample cup. Total Fluorine concentration was determined by means of a calibration curve constructed with solutions of NaF (ACS grade, J.T. Baker, PA, USA) with concentrations between 0.3 to 10 mg/L Fluorine. Measurements were performed with a Fluorine sensitive electrode (Denver Instruments, Bohemia, NY, USA).

Chloride ion was determined by means of a potentiometric analysis according to AOAC OMA 969.10. Briefly, a test portion of ca. 0.25 grams was weighted in a 200 mL volumetric flask then 190 mL H<sub>2</sub>O and 1 mL TISAB II were added. The flask was made-up to volume with water. This mixture was titrated with a 0.1 mol/L AgNO<sub>3</sub> solution up to inflection point Measurements were performed with a chloride sensitive electrode (Denver Instruments, Bohemia, NY, USA).

Iodine analysis was performed by the indirect determination of iodide ion equivalents using an iodine ISE electrode (6.0502.160, Metrohm, Ionenstrasse, Switzerland) in the case of metal iodides and etilendiamine diiodide ca. 70 mg and 200 mg, respectively of each sample were dissolved to a total volume of 50 mL in a volumetric flask with ultrapure water. For iodate and microgran™ samples 100–200 mg of each sample were dissolved in concentrated HNO<sub>3</sub> and mixed with 10 mL of a 100 mmol/L

solution of hydrazine hydrate (ACROS Organics, Fair Lawn, NJ, USA), which oxidize  $\text{IO}_4^-$  ion to  $\text{I}_2$ , followed by a second reduction reaction from this species to  $\text{I}^-$  using a 100 mmol/L solution of sodium bisulfite to finally obtain a clear solution and finally adjusted pH of 7.0 before measurement. This procedure was adapted from an ISE-based method previously reported (Hasty 1973). Total iodide concentration was determined by a calibration curve constructed with solutions of KI (ACROS Organics, Fair Lawn, NJ, USA) with concentrations between  $5.0 \times 10^{-5}$  to  $5 \times 10^{-1}$  mol/L. Nitrate ion at 1 mol/L was added in all cases as an ionization buffer.

Carbonate ion was also analyzed potentiometrically according to AOAC OMA 955.01 using a glass pH electrode (Hanna Instruments, Carrollton, TX USA) and titrated using a 0.25 mol/L NaOH standard solution until sample solution attain pH 7. All anions were assayed using their respective electrodes coupled to a Denver Instruments 250 pH/ISE/potentiometric meter (Denver Instruments, Bohemia, NY, USA).

#### Quality control of results

An AAFCO Feed grade monocalcium phosphate sample (number 201298) was employed as a reference material throughout the heavy metal and Fluorine analyses. Beef cattle medicated feed sample (number 201228) was also used as a reference material for the rest of the minerals. Both samples were reprocessed and analyzed each time a given analyte was measured, in all cases  $z$  values  $< |3|$  we considered, for our purposes, to be satisfactory. The methods stated above (including those used for sample pretreatment) are traditionally the most common analytical methods for the determination of total heavy metal residues in feed, feedstuffs and animal tissues. And have demonstrated to be sensitive enough to monitor compliance of statutory limits and are supported by law enforcing organizations (EC 2007). Limits of detection (established as S/N of 3.3, based on blank samples and regression curves) for As, Hg, Pb and Cd calculated as follow: 1000, 20, 600, 10 ng/kg, respectively.

#### Statistical analysis

ANOVA using Tukey *post hoc* was used to statistically compare metal content between mineral samples of different origin. In some specific cases, Dunnett's test was performed to demonstrate, for a specific element, if values obtained were significantly lower than those guaranteed by the manufacturer label.  $p$  values  $< 0.05$  are considered to differ significantly.

#### Results and discussion

The typical concentrations of essential and contaminant heavy metals in common mineral ingredients used in

feed manufacturing is offered. Some information regarding heavy metals in compound feed is presented as well.

From all the mineral sources analyzed, without exception, sulfate ion-containing minerals exhibit a significantly ( $p < 0.001$ ) higher concentration of water (from 42.5 to 71.3 g/100 g dry matter) compared to other sources. This is an anticipated result as  $\text{SO}_4^{2-}$ , in accordance with Hofmeister series (dos Santos et al. 2010), is a small and multiply-charged ion, with high charge density, a poor disruptive of water's molecular binding (kosmotropic) (Wei et al. 2005) and thus exhibit stronger interactions with water (Plumridge et al. 2000). This said, is to be concluded that for all practical purposes in these type of salts, ions are to be treated as hydrated.

The case of calcium phosphates is singular. Degradation of orthophosphate into unavailable phosphate forms during manufacture (Hoffmann et al. 2011) is a possibility in those minerals which demonstrate lower values of phosphorus but calcium values within what is expected for these type of products. This occurs in exactly two ( $n = 2$ ) samples of dicalcium phosphate (Table 1).

Due to the diverse chemical composition of both feed phosphate sources analyzed, large differences do exist in their phosphorus availability for different animal species (Fernandes et al. 1999; Viljoen 2001; Petersen et al. 2011). Phosphates from the same source and produced by the same process, using raw substances of similar quality should offer consistent phosphorus concentrations. In this respect, we suggest that chemical data should always be accompanied by bioavailability assays.

In a similar fashion, we have found, for the colorimetric assay of phosphorus, standard amounts of molybdovanadate to be inadequate after wet acid digestion, probably due an incomplete complexation of phosphorus by this reagent (data not shown). Therefore, we suggest using a stoichiometric excess of color-forming agent or another quantitative technique such as GFAAS or ICP-MS for total phosphorus quantitation.

Another distinctive feature of feed phosphates is that fluorine can be used as a quality control for the inorganic synthesis and inputs used during its manufacture (e.g. wet acid route). In this case, only 4.5 % ( $n = 1/22$ ) of the samples, exceeded the 2 g/kg guideline for this anion (Table 1). So far, only dicalcium phosphate samples have exceeded regulatory guidelines for fluorine (Table 1). However, no significant differences ( $p < 0.05$ ) were found for this nutrient when both types of phosphate sources were compared. Synthesis-wise new technologies for the production of feed phosphates have been introduced with the sole purpose of reducing this contaminant to acceptable levels (Hoffmann et al. 2011).

On another hand, in the case of macronutrients, a worrisome situation was evidenced by the detection of some inconsistencies in labeling (either by the mineral

**Table 1** Mineral contents in typical mineral imported supplements employed in feedingstuff manufacture

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
<b>Calcium and phosphorus-containing mineral sources</b>						
<i>Dicalcium phosphate, n = 22</i>						
Dry matter, g/100 g	97.3	2.5	98.2	100.0	90.9	>88
Calcium, g/100 g <sup>[1; 4.5 %]</sup>	26.2	2.9	26.0	32.7	21.4	21.0 – 27.0
Phosphorus, g/100 g <sup>[1; 4.5 %]</sup>	19.5	1.7	19.8	22.0	15.5	18.0 – 21.0
<i>Monocalcium phosphate, n = 22</i>						
Dry matter, g/100 g	94.2	1.2	94.3	95.7	90.8	>88
Calcium, g/100 g <sup>[1; 4.5 %]</sup>	16.0	1.4	15.9	18.9	13.1	15.0 – 18.0
Phosphorus, g/100 g <sup>[1; 4.5 %]</sup>	21.0	1.2	20.9	23.6	18.0	21.0 – 23.0
<i>Calcium carbonate, n = 21</i>						
Dry matter, g/100 g	99.9	0.1	99.9	100.0	99.6	>88
Calcium, g/100 g <sup>[2; 9.5 %]</sup>	37.8	2.8	36.4	41.8	28.9	37.5 – 39.0
Carbonate (as CaCO <sub>3</sub> ), g/100 g	92.6	12.5	97.5	99.6	48.6	96.0 – 98.0
<b>Iodine-containing mineral sources</b>						
<i>Calcium iodate, n = 7</i>						
Dry matter, g/100 g	99.57	0.34	99.71	99.86	99.00	>88
Calcium, g/100 g	7.6	1.1	7.6	8.95	6.25	Not indicated
Iodide, g/100 g <sup>[1; 14.2 %]</sup>	61.4	4.7	62.6	64.7	50.3	63.5
<i>Microgran™ I 10 % BMP (calcium iodide), n = 10</i>						
Dry matter, g/100 g	99.45	0.24	99.51	99.76	98.90	>88.0
Calcium, g/100 g	16.9	5.1	18.4	20.8	4.8	-
Iodide, g/100 g <sup>[4; 40.0 %]</sup>	8.1	2.6	8.1	11.9	4.4	10.0
<i>Etilendiamine diiodide, n = 7</i>						
Dry matter, g/100 g	99.89	0.08	99.93	99.96	99.73	>88.0
Iodine, g/100 g <sup>[5; 83.3 %]</sup>	68.9	4.8	69.2	77.5	62.8	79.5
<i>Potassium iodide, n = 7</i>						
Dry matter, g/100 g	99.7	0.1	99.7	99.4	99.8	>88.0
Potassium, g/100 g	21.1	1.9	19.8	24.5	19.5	-
Iodine, g/100 g <sup>b</sup>	68.9	5.5	70.1	74.9	62.5	68.0
<b>Cobalt-containing mineral sources</b>						
<i>Cobalt carbonate, n = 13</i>						
Dry matter, g/100 g	94.68	3.36	96.47	99.00	88.40	>88.0
Cobalt, g/100 g <sup>[7; 53.8 %]</sup>	49.4	10.7	45.4	82.4	39.7	46.0
Carbonate (as CaCO <sub>3</sub> ), g/100 g	62.4	14.4	68.8	84.1	43.9	Not indicated
<i>Cobalt sulfate, n = 16</i>						
Dry matter, g/100 g	67.83	9.77	64.50	98.37	63.20	>88.0
Cobalt, g/100 g <sup>[2; 12.5 %]</sup>	23.2	3.4	25.8	27.7	21.0	19.5-21.0
<i>Microgran™ Co 5 % BMP (cobalt carbonate), n = 13</i>						
Dry matter, g/100 g	97.9	0.6	97.7	100.0	97.3	>88.0
Carbonate (as CaCO <sub>3</sub> ), g/100 g	7.9	1.8	7.2	13.5	6.1	Not indicated
Cobalt, g/100 g <sup>b</sup>	6.3	1.4	5.7	10.7	4.8	5.0
<b>Copper-containing mineral sources</b>						
<i>Copper oxide, n = 19</i>						
Dry matter, g/100 g	99.9	0.2	99.8	100.0	99.1	>88.0

**Table 1** Mineral contents in typical mineral imported supplements employed in feedingstuff manufacture (*Continued*)

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
Copper, g/100 g <sup>[3; 17.6 %]</sup>	71.7	5.9	71.3	85.0	59.6	75.0
<i>Copper sulfate, n = 18</i>						
Dry matter, g/100 g	73.4	6.5	71.9	99.7	68.8	>88.0
Copper, g/100 g <sup>[2; 12.5 %]</sup>	25.1	2.1	24.6	31.4	22.4	25.0
<b>Sodium containing mineral sources</b>						
<i>Sodium chloride, n = 23</i>						
Dry matter, g/100 g	96.2	6.1	98.8	99.9	71.7	>88.0
Sodium, g/100 g	36.6	4.0	36.4	46.7	26.7	38.5
Chloride (as NaCl), g/100 g <sup>[4; 19.0 %]</sup>	99.7	3.3	98.0	99.8	87.4	98.0
<b>Iron-containing mineral sources</b>						
<i>Ferrous carbonate, n = 21</i>						
Dry matter, g/100 g	99.0	0.54	98.9	100.0	98.15	>88.0
Iron, g/100 g <sup>[3; 15.8 %]</sup>	35.9	4.2	35.4	46.6	27.3	38.0
Carbonate (as CaCO <sub>3</sub> ), g/100 g	38.08	17.2	41.2	74.7	19.2	Not indicated
<i>Ferric oxide, n = 16</i>						
Dry matter, g/100 g	99.1	97.2	99.9	88.3	100.0	>88.0
Iron, g/100 g	37.6	13.0	37.3	65.0	16.2	Not indicated
<i>Ferrous sulfate, n = 17</i>						
Dry matter, g/100 g	75.4	17.3	62.6	99.1	62.0	>88.0
Iron, g/100 g <sup>[1; 6.3 %]</sup>	22.8	5.0	21.7	36.5	15.0	19.0
<b>Magnesium-containing mineral sources</b>						
<i>Magnesium oxide, n = 21</i>						
Dry matter, g/100 g	99.81	0.21	99.90	99.99	99.29	>88.0
Magnesium, g/100 g <sup>[6; 28.6 %]</sup>	42.1	15.1	40.5	85.4	22.4	50.0-54.0
<i>Magnesium sulfate, n = 18</i>						
Dry matter, g/100 g	63.1	9.2	60.8	99.8	57.5	>88.0
Magnesium, g/100 g <sup>b</sup>	8.8	1.1	8.6	11.7	6.8	6.8-11.6
<b>Manganese-containing mineral sources</b>						
<i>Manganous oxide, n = 21</i>						
Dry matter, g/100 g	99.6	0.24	99.7	99.9	98.9	>88.0
Manganese, g/100 g <sup>[7; 35.0 %]</sup>	58.6	6.6	56.2	77.8	50.4	60.0-62.0
<i>Manganese sulfate, n = 15</i>						
Dry matter, g/100 g	97.0	10.5	99.9	100.0	57.7	>88.0
Manganese, g/100 g <sup>[2; 13.3 %]</sup>	28.3	5.6	26.8	40.3	21.1	29.0-32.0
<b>Sulfur-containing mineral sources</b>						
<i>Elemental sulfur, n = 20</i>						
Dry matter, g/100 g	98.7	1.1	99.2	99.7	96.0	>88.0
Sulfur, g/100 g <sup>[4; 20.0 %]</sup>	98.4	1.7	99.0	99.6	93.7	99.5
<b>Zinc-containing mineral sources</b>						
<i>Zinc oxide, n = 22</i>						
Dry matter, g/100 g	99.5	1.7	99.9	100.0	91.5	>88.0
Zinc, g/100 g <sup>[1; 4.5 %]</sup>	76.0	12.3	72.4	108.4	58.3	72.0
<i>Zinc sulfate, n = 18</i>						
Dry matter, g/100 g	99.85	0.17	99.96	100.0	99.45	>88.0

**Table 1** Mineral contents in typical mineral imported supplements employed in feedingstuff manufacture (*Continued*)

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
Zinc, g/100 g <sup>[8; 44.4 %]</sup>	32.4	4.1	32.0	43.2	25.1	35.0
<b>Selenium-containing mineral sources</b>						
<i>Microgran™ Se 1 % BMP (sodium selenite), n = 13</i>						
Dry matter, g/100 g	99.7	0.19	99.7	99.9	99.2	>88.0
Selenium, g/100 g	1.7	1.1	1.2	4.2	0.8	1.0
Sodium, g/100 g	0.63	0.12	0.61	0.93	0.49	Not indicated
<i>Sodium selenite 1 %, n = 11</i>						
Dry matter, g/100 g	99.52	0.37	99.64	99.95	98.65	>88.0
Selenium, g/100 g	1.36	0.77	1.14	3.58	0.68	1.0
Sodium, g/100 g	1.03	1.42	0.62	5.50	0.21	Not indicated
<i>Sodium selenite, n = 8</i>						
Dry matter, g/100 g	99.76	0.19	99.82	99.99	99.48	>88.0
Selenium, g/100 g	44.3	2.6	44.2	47.7	40.0	45-46
Sodium, g/100 g	24.1	3.25	24.6	29.3	19.0	26-27
<b>Potassium-containing mineral sources</b>						
<i>Potassium Chloride, n = 17</i>						
Dry matter, g/100 g	94.2	22.9	99.92	99.99	2.42	>88.0
Potassium, g/100 g <sup>[9; 53.9 %]</sup>	49.9	13.7	46.9	97.6	34.5	62
Chloride (as NaCl), g/100 g	87.6	12.4	91.4	99.3	44.8	Not indicated

<sup>a</sup>Numbers in parenthesis represent the number (*n*) of samples with concentrations beneath the guaranteed analysis for a specific element. Concentrations considered were those which are not within the lower guaranteed range allowing for one SD (*σ*). <sup>b</sup>All samples for this mineral are within the guaranteed range

manufacturer or *in situ*), this issue seems to arise more frequently with selenium mineral sources. For example, samples branded as Microgran™ Se and sodium selenite were in some cases inverted i.e. the latter showed low sodium and selenium concentrations ( $\approx 5.0$ - $10.0$  g/100 g) and viceversa; a reagent grade NaSeO<sub>3</sub> with 99 % purity, when analyzed, should return values for sodium and selenium of at least 13.1 and 45.2 g/100 g, respectively (data not shown). A couple of the recollected samples, considered as manganese (IV) oxide, exhibited only concentrations ranging on the low side of the mg/kg of Mn whereas one might expect for a reagent grade MnO<sub>2</sub> at least 62.6 g/100 g of the metal (data not shown). Yet another example lies within samples labeled as zinc oxide (*n* = 2) in which Zn analysis verified concentrations > 90 g/100 g of this metal which is, chemically speaking, an impossibility in terms of formula, this suggest these samples were not metal oxides but other species entirely. The same occurs in a sample (*n* = 1) of CoCO<sub>3</sub> (82.4 g Co/100 g) and a sample (*n* = 1) of KCl (97.58 g K/100 g) (Table 1).

Some samples exhibit mean values significantly (*p* < 0.001) beneath the guaranteed analysis, important examples include KCl for potassium, MgO for magnesium, EDDI for iodine, ferrous and calcium carbonate for iron and carbonate, respectively (Table 1). Congruently, 16.8 % a total of the samples (*n* = 73) were found to be in this

condition. Incidence of some relevant samples was as follow: 83.6 (*n* = 5), 53.8 (*n* = 7), 52.9 (*n* = 9), 47.1 (*n* = 8), 35.0 (*n* = 7) and 28.6 % (*n* = 6) for EDDI, CoCO<sub>3</sub>, KCl, ZnSO<sub>4</sub>, MnO and MgO respectively (Table 1). Other minerals do not differ significantly or are between manufacturer assured ranges. Only for minerals Microgran™ Co (*n* = 14) and MgSO<sub>4</sub> (*n* = 17) all samples were within the expected concentration range (Table 1). In this regard, mineral deficiencies should be circumvented as these nutrients are relevant to health and their monitoring would consequently could prevent or manage mineral-associated deficiency diseases (Soetan et al. 2010). This is of foremost importance especially in countries when said minerals may be scarce or marginal due to geochemical characteristics of the region. Also, interrelationships and interferences among the mineral elements should be considered when mineral premixes are formulated (Soetan et al. 2010).

Regarding heavy metal concentrations, several mineral samples contravene current legislation in at least one metal. Number of samples in this condition correspond to 0.5 (*n* = 2), 13.8 (*n* = 60), 4.1 (*n* = 18) and 2.5 % (*n* = 11) for As, Hg, Pb and Cd, respectively (Table 2). Overall, 21.1 % (*n* = 92) of the samples exhibited concentrations of heavy metals and fluorine above those stipulated by European guidelines. Values for As, Hg, Pb and Cd ranged from 61.2 mg/kg (MnO) to 1.3 µg/kg (MgO),  $2.6 \times 10^3$  µg/kg

**Table 2** Contaminant concentrations in typical mineral imported supplements employed in feedingstuff manufacture

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
<b>Calcium and phosphorus-containing mineral sources</b>						
<i>Dicalcium phosphate, n = 22</i>						
<sup>b</sup> Arsenic, mg/kg <sup>[2; 9.1 %] (4; 18.2 %)</sup>	2.88	7.14	0.30	26.68	$9.8 \times 10^{-3}$	<10
<sup>b</sup> Mercury, µg/kg <sup>[8; 36.4 %]</sup>	96.18	80.69	71.00	392.50	6.89	<100
Lead, mg/kg	1.89	1.50	1.51	6.23	$4.8 \times 10^{-2}$	<15
Cadmium, mg/kg	1.94	2.46	0.29	6.73	$1.8 \times 10^{-3}$	<10
<sup>b</sup> Fluorine ( $\times 10^{-2}$ ), g/100 g <sup>[1; 4.5 %]</sup>	8.9	4.6	8.2	26.0	2.1	12.0 – 21.0 (<20.0)
<i>Monocalcium phosphate, n = 22</i>						
Arsenic, mg/kg <sup>(4; 18.2 %)</sup>	$3.9 \times 10^{-1}$	$5.8 \times 10^{-1}$	$1.1 \times 10^{-1}$	2	$4.9 \times 10^{-2}$	<10
<sup>b</sup> Mercury, µg/kg <sup>[12; 54.5 %]</sup>	118.85	72.04	110.73	364.00	21.10	<100
<sup>b</sup> Lead, mg/kg <sup>(2; 9.1 %) [2; 9.1 %]</sup>	38.16	153.47	0.48	706.00	$5.4 \times 10^{-2}$	<15
Cadmium, µg/kg	2.76	1.82	2.19	6.96	$1.6 \times 10^{-3}$	<10
Fluorine ( $\times 10^{-2}$ ), g/100 g	7.6	4.4	9.8	14.0	1.0	<0.21 (<0.20)
<i>Calcium carbonate, n = 21</i>						
Arsenic, µg/kg <sup>(7; 33.3 %)</sup>	383.4	199.4	362.7	818.5	50.9	$<1.5 \times 10^4$
Mercury, µg/kg <sup>(5; 23.8 %)</sup>	73.0	45.6	72.0	185.8	5.6	<300
<sup>b</sup> Lead, mg/kg <sup>(2; 9.5 %) [1; 4.8 %]</sup>	14.4	60.5	0.2	270.9	$1.4 \times 10^{-2}$	<20
Cadmium, µg/kg	647.7	559.3	382.9	$1.7 \times 10^3$	1.3	$<1.0 \times 10^4$
<b>Iodine-containing mineral sources</b>						
<i>Calcium iodate, n = 7</i>						
Arsenic, µg/kg <sup>(1; 14.3 %)</sup>	244.9	143.15	196.0	451.4	83.0	$<1.5 \times 10^4$
<sup>b</sup> Mercury, µg/kg <sup>(1; 14.3 %) [1; 14.3 %]</sup>	164.8	103.75	116.4	334.0	64.99	<300
<sup>b</sup> Lead, mg/kg <sup>(1; 14.3 %) [1; 14.3 %]</sup>	12.3	23.5	0.5	64.4	$3.5 \times 10^{-2}$	<20
Cadmium, µg/kg <sup>(2; 28.6 %)</sup>	47.4	34.0	41.9	110.5	10.3	$<2.0 \times 10^3$
<i>Microgran™ I 10 % BMP (calcium iodide), n = 10</i>						
Arsenic, mg/kg <sup>(3; 30.0 %)</sup>	0.69	1.32	0.18	3.92	$3.0 \times 10^{-2}$	<30
Mercury, µg/kg <sup>(1; 10.0 %)</sup>	98.5	40.6	115.8	143.68	17.5	<200
Lead, µg/kg <sup>(3; 30.0 %)</sup>	183.7	98.9	163.0	363.0	55	$<1.0 \times 10^5$
Cadmium, µg/kg	146.1	18.9	149.3	168.4	112.9	$<1.0 \times 10^4$
<i>Etilendiamine diiodide, n = 7</i>						
Arsenic, µg/kg <sup>(2; 28.7 %)</sup>	65.0	42.3	64.1	118	13.98	$<3.0 \times 10^4$
Mercury, µg/kg <sup>(1; 14.3 %)</sup>	104.3	31.0	116.1	131.3	45.7	<200
Lead, µg/kg <sup>(1; 14.3 %)</sup>	170.9	73.1	148.0	301.0	78.0	$<1.0 \times 10^5$
Cadmium, µg/kg <sup>(2; 28.7 %)</sup>	319.8	502.5	35.7	1190	17.5	$<1.0 \times 10^4$
<i>Potassium iodide, n = 7</i>						
Arsenic, µg/kg <sup>(2; 28.6 %)</sup>	237.9	171.0	156.5	509.6	57.0	$<3.0 \times 10^4$
Mercury, µg/kg	117.7	71.9	102.2	245.7	10.3	<200
<sup>b</sup> Lead, mg/kg <sup>(2; 28.6 %), [1; 14.3 %]</sup>	42.3	83.7	0.25	209.6	$5.7 \times 10^{-2}$	<100
Cadmium, µg/kg <sup>(1; 14.3 %)</sup>	150.8	163.8	35.0	382.4	34.9	$<1.0 \times 10^4$
<b>Cobalt-containing mineral sources</b>						
<i>Cobalt carbonate, n = 13</i>						
Arsenic, mg/kg <sup>(5; 38.5 %)</sup>	$7.4 \times 10^{-1}$	1.6	$9.5 \times 10^{-2}$	5.10	$1.3 \times 10^{-2}$	<30
<sup>b</sup> Mercury, µg/kg <sup>(1; 7.7 %)</sup>	97.3	69.5	97.5	302.0	23.9	<200
Lead, µg/kg <sup>(3; 23.1 %)</sup>	664.5	582.8	414.0	1920.0	2.3	$<1.0 \times 10^5$

**Table 2** Contaminant concentrations in typical mineral imported supplements employed in feedingstuff manufacture (*Continued*)

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
Cadmium, µg/kg <sup>(6; 46.1 %)</sup>	34.0	19.6	38.0	55.7	8.3	<5.0 × 10 <sup>3</sup>
<i>Cobalt sulfate, n = 11</i>						
Arsenic, µg/kg <sup>(3; 27.3 %)</sup>	65.2	61.4	32.8	151.2	18.0	<3.0 × 10 <sup>4</sup>
Mercury, µg/kg	81.7	29.6	80.0	133.7	28.2	<200
Lead, mg/kg <sup>(2; 18.2 %)</sup>	17.6	37.3	1.26	101.0	7.0 × 10 <sup>-3</sup>	<100
Cadmium, µg/kg	835.3	880.8	192.3	2.2 × 10 <sup>3</sup>	66.1	<5.0 × 10 <sup>3</sup>
<i>Microgran™ Co 5 % BMP (cobalt carbonate), n = 13</i>						
Arsenic, mg/kg <sup>(8; 61.5 %)</sup>	1.07	1.65	0.36	4.72	3.42 × 10 <sup>-2</sup>	30
<sup>b</sup> Mercury, µg/kg <sup>(1; 7.7 %), [2; 15.4 %]</sup>	95.0	58.0	83.1	220.7	37.0	<200
Lead, mg/kg <sup>(4; 30.8 %)</sup>	16.2	48.2	1.4 × 10 <sup>-1</sup>	160.7	1.8 × 10 <sup>-3</sup>	<100
Cadmium, µg/kg	84.3	78.2	34.1	239.2	0.95	<5.0 × 10 <sup>3</sup>
<b>Copper-containing mineral sources</b>						
<i>Copper oxide, n = 19</i>						
Arsenic, mg/kg <sup>(1; 5.3 %)</sup>	2.38	2.19	2.25	8.38	1.29 × 10 <sup>-1</sup>	100
<sup>b</sup> Mercury, µg/kg <sup>(1; 5.3 %), [3; 15.8 %]</sup>	128.4	88.8	99.1	384.5	48.3	<200
<sup>b</sup> Lead, mg/kg <sup>[12; 63.1 %]</sup>	96.0	113.2	60.9	455.0	3.80 × 10 <sup>-1</sup>	<30
<sup>b</sup> Cadmium, mg/kg <sup>(1), [3; 15.8 %]</sup>	3.09	2.31	1.85	7.41	1.09 × 10 <sup>-1</sup>	<5
<i>Copper sulfate, n = 18</i>						
Arsenic, µg/kg <sup>(1; 5.5 %)</sup>	500.6	537.4	366.3	2.29 × 10 <sup>3</sup>	18.4	5.0 × 10 <sup>4</sup>
Mercury, µg/kg	69.4	35.1	69.4	118.3	9.04	<200
Lead, mg/kg <sup>(2; 11.1 %)</sup>	9.9	10.2	8.8	39.8	4.4 × 10 <sup>-2</sup>	<100
Cadmium, µg/kg <sup>(4; 22.2 %)</sup>	544.0	1.2 × 10 <sup>3</sup>	150.8	4.1 × 10 <sup>3</sup>	4.41	<5.0 × 10 <sup>3</sup>
<b>Sodium containing mineral sources</b>						
<i>Sodium chloride, n = 23</i>						
Arsenic, mg/kg <sup>(16; 69.6 %)</sup>	101.1	61.1	97.5	231.0	15.7	30
Mercury, µg/kg <sup>(4; 17.4 %)</sup>	80.6	43.4	85.0	157.0	1.2	<200
<sup>b</sup> Lead, mg/kg <sup>[1; 4.5 %], [15; 65.2 %]</sup>	26.2	68.8	1.7 × 10 <sup>-1</sup>	208.4	4.6 × 10 <sup>-2</sup>	<100
Cadmium, mg/kg <sup>(5; 21.3 %)</sup>	1.21	3.12	3.4 × 10 <sup>-2</sup>	9.46	4.2 × 10 <sup>-3</sup>	<5
<b>Iron-containing mineral sources</b>						
<i>Ferrous carbonate, n = 21</i>						
Arsenic, mg/kg	6.50	5.07	5.55	19.4	1.15	30
<sup>b</sup> Mercury, µg/kg <sup>[3; 14.3 %]</sup>	149.0	142.9	110.2	594.0	8.3	<200
Lead, mg/kg	14.51	17.35	7.44	72.06	1.1 × 10 <sup>-2</sup>	<200
Cadmium, mg/kg <sup>(2; 9.5 %)</sup>	0.73	1.36	1.0 × 10 <sup>-1</sup>	4.45	7.7 × 10 <sup>-3</sup>	<5
<i>Ferric oxide, n = 16</i>						
Arsenic, mg/kg <sup>(1; 6.2 %)</sup>	6.38	5.28	4.89	18.49	1.7 × 10 <sup>-2</sup>	30
<sup>b</sup> Mercury, µg/kg <sup>[3; 18.7 %]</sup>	155.1	126.1	122.1	603.0	26.2	<200
Lead, mg/kg	8.94	13.57	2.67	49.18	1.14	<100
<sup>b</sup> Cadmium, mg/kg <sup>(4; 25.0 %), [1; 6.2 %]</sup>	0.82	1.95	7.0 × 10 <sup>-2</sup>	6.31	1.1 × 10 <sup>-2</sup>	<5.0 × 10 <sup>3</sup>
<i>Ferrous sulfate, n = 17</i>						
Arsenic, µg/kg <sup>(4; 23.5 %)</sup>	1323.7	3395.1	118.2	12750	3.02	3.0 × 10 <sup>4</sup>
Mercury, µg/kg	169.4	319.7	100.2	1439.0	23.8	<200
<sup>b</sup> Lead, mg/kg <sup>(2; 11.8 %), [1; 5.9 %]</sup>	34.8	96.1	8.8	393.00	3.1 × 10 <sup>-2</sup>	<100
Cadmium, µg/kg <sup>(6; 35.3 %)</sup>	45.8	30.7	45.1	107.1	6.1	<5.0 × 10 <sup>3</sup>

**Table 2** Contaminant concentrations in typical mineral imported supplements employed in feedingstuff manufacture (Continued)

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
<b>Magnesium-containing mineral sources</b>						
<i>Magnesium oxide, n = 21</i>						
Arsenic, µg/kg <sup>(8; 38.1 %)</sup>	944.4	1289.9	559.4	5200.0	1.3	2.0 × 10 <sup>4</sup>
<sup>b</sup> Mercury, µg/kg <sup>(1; 4.8 %, [2; 9.5 %])</sup>	81.1	72.1	68.1	287.0	6.6	<200
Lead, mg/kg <sup>(11; 52.4 %), [1; 4.8 %]</sup>	39.0	135.8	7.7 × 10 <sup>-1</sup>	628.1	6.0 × 10 <sup>-2</sup>	<100
Cadmium, µg/kg <sup>(4; 19.0 %)</sup>	54.4	79.6	28.0	262.1	7.7	<5.0 × 10 <sup>3</sup>
<i>Magnesium sulfate, n = 18</i>						
Arsenic, µg/kg <sup>(8; 44.4 %)</sup>	288.1	297.8	75.1	784.7	7.38	2.0 × 10 <sup>3</sup>
Mercury, µg/kg	86.0	34.9	79.1	164.1	5.02	<200
Lead, mg/kg <sup>(11; 61.1 %)</sup>	5.1	11.5	2.4 × 10 <sup>-1</sup>	33.2	2.2 × 10 <sup>-2</sup>	<100
Cadmium, µg/kg <sup>(10; 55.5 %)</sup>	18.5	13.7	10.4	40.6	3.6	<5.0 × 10 <sup>3</sup>
<b>Manganese-containing mineral sources</b>						
<i>Manganous oxide, n = 21</i>						
Arsenic, mg/kg	28.6	18.3	29.0	61.2	1.2	100
<sup>b</sup> Mercury, µg/kg <sup>[6; 28.6 %]</sup>	348.6	543.0	198.1	2.6 × 10 <sup>3</sup>	1.23	<200
Lead, mg/kg	28.5	19.6	26.1	79.8	2.7 × 10 <sup>-2</sup>	<200
<sup>b</sup> Cadmium, mg/kg <sup>(1; 4.8 %), [6; 28.6 %]</sup>	2.84	2.25	3.47	5.49	2.0 × 10 <sup>-3</sup>	<5
<i>Manganese sulfate, n = 15</i>						
Arsenic, µg/kg <sup>(4; 26.7 %)</sup>	418.8	470.2	271.9	1.6 × 10 <sup>3</sup>	18.8	2.0 × 10 <sup>4</sup>
Mercury, µg/kg	67.2	41.9	69.3	163.4	6.2	<200
Lead, µg/kg <sup>(8; 53.3 %)</sup>	1.3 × 10 <sup>3</sup>	2.1 × 10 <sup>3</sup>	265.2	5.0 × 10 <sup>3</sup>	6.3	<1.0 × 10 <sup>5</sup>
Cadmium, µg/kg <sup>(2; 13.3 %)</sup>	1.1 × 10 <sup>3</sup>	1.5 × 10 <sup>3</sup>	287.2	4.0 × 10 <sup>3</sup>	48.11	<5.0 × 10 <sup>3</sup>
<b>Sulfur-containing mineral sources</b>						
<i>Elemental sulfur, n = 20</i>						
Arsenic, µg/kg <sup>(15; 75.0 %)</sup>	76.1	38.0	71.2	145.8	39.4	2.0 × 10 <sup>4</sup>
<sup>b</sup> Mercury, µg/kg <sup>[6; 30.0 %]</sup>	21.4	52.1	1.7 × 10 <sup>-1</sup>	149.0	2.6	<200
Lead, mg/kg <sup>(13; 65.0 %)</sup>	1.6 × 10 <sup>-1</sup>	5.2 × 10 <sup>-2</sup>	1.6 × 10 <sup>-1</sup>	2.4 × 10 <sup>-1</sup>	6.9 × 10 <sup>-2</sup>	<100
Cadmium, µg/kg <sup>(7; 35.0 %)</sup>	30.6	15.4	30.3	52.4	4.5	<5.0 × 10 <sup>3</sup>
<b>Zinc-containing mineral sources</b>						
<i>Zinc oxide, n = 22</i>						
Arsenic, µg/kg <sup>(1; 4.5 %)</sup>	1.3 × 10 <sup>3</sup>	2.3 × 10 <sup>3</sup>	365.2	9.8 × 10 <sup>3</sup>	12.75	<1.0 × 10 <sup>5</sup>
<sup>b</sup> Mercury, µg/kg <sup>[2; 9.1 %]</sup>	133.1	181.0	78.9	882.0	16.1	<200
Lead, mg/kg	55.8	68.2	26.5	252.0	2.5 × 10 <sup>-2</sup>	<400
<sup>b</sup> Cadmium, µg/kg <sup>(1; 4.5 %), [1; 4.5 %]</sup>	2.5 × 10 <sup>3</sup>	1.7 × 10 <sup>3</sup>	2.8 × 10 <sup>3</sup>	5.0 × 10 <sup>3</sup>	5.03	<5.0 × 10 <sup>3</sup>
<i>Zinc sulfate, n = 18</i>						
Arsenic, µg/kg <sup>(11; 61.1 %)</sup>	347.4	667.2	83.9	2.0 × 10 <sup>3</sup>	15.79	2.0 × 10 <sup>4</sup>
Mercury, µg/kg <sup>(1; 5.5 %)</sup>	95.6	44.8	81.4	186.6	28.7	<200
Lead, mg/kg <sup>(8; 44.4 %)</sup>	2.9 × 10 <sup>-1</sup>	2.3 × 10 <sup>-1</sup>	2.1 × 10 <sup>-1</sup>	7.0 × 10 <sup>-1</sup>	5.9 × 10 <sup>-2</sup>	<100
<sup>b</sup> Cadmium, µg/kg <sup>[1; 5.5 %]</sup>	2.7 × 10 <sup>3</sup>	2.9 × 10 <sup>3</sup>	1.8 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>	1.75	<5.0 × 10 <sup>3</sup>
<b>Selenium-containing mineral sources</b>						
<i>Microgran™ Se 1 % BMP (sodium selenite), n = 13</i>						
Arsenic, µg/kg <sup>(5; 38.5 %)</sup>	544.7	721.8	310.8	2.4 × 10 <sup>3</sup>	10.2	<2.0 × 10 <sup>4</sup>
<sup>b</sup> Mercury, µg/kg <sup>[4; 30.8 %]</sup>	148.4	126.7	118.9	457.5	28.0	<200
Lead, µg/kg <sup>(9; 69.2 %)</sup>	6.1 × 10 <sup>-1</sup>	6.0 × 10 <sup>-1</sup>	4.0 × 10 <sup>-1</sup>	1.6	2.4 × 10 <sup>-2</sup>	<1.0 × 10 <sup>5</sup>

**Table 2** Contaminant concentrations in typical mineral imported supplements employed in feedingstuff manufacture (*Continued*)

Assay <sup>a</sup>	Mean	SD	Median	Max	Min	Guideline value or guaranteed analysis
Cadmium, µg/kg	133.5	82.8	162.2	230.8	17.1	<5.0 × 10 <sup>3</sup>
<i>Sodium selenite 1 %, n = 11</i>						
Arsenic, µg/kg <sup>(5; 45.5 %)</sup>	1.4 × 10 <sup>3</sup>	9.6 × 10 <sup>2</sup>	1.4 × 10 <sup>3</sup>	2.8 × 10 <sup>3</sup>	172.9	2.0 × 10 <sup>4</sup>
<sup>b</sup> Mercury, µg/kg <sup>[3; 27.3 %]</sup>	165.8	87.5	146.1	330.7	33.44	<200
Lead, µg/kg <sup>(1; 9.1 %)</sup>	32.5	50.6	7.2 × 10 <sup>2</sup>	1.1 × 10 <sup>3</sup>	13.3	1.0 × 10 <sup>5</sup>
Cadmium, µg/kg	625.2	344.9	725.7	1.1 × 10 <sup>3</sup>	13.3	<5.0 × 10 <sup>3</sup>
<i>Sodium selenite, n = 8</i>						
Arsenic, µg/kg <sup>(2; 25.0 %)</sup>	3.1 × 10 <sup>3</sup>	2.3 × 10 <sup>3</sup>	2.9 × 10 <sup>3</sup>	7.2 × 10 <sup>3</sup>	6.0 × 10 <sup>2</sup>	2.0 × 10 <sup>4</sup>
<sup>b</sup> Mercury, µg/kg <sup>[4; 50.0 %]</sup>	264.0	146.4	241.5	462.0	93.9	<200
Lead, mg/kg <sup>(4; 50.0 %)</sup>	3.79	3.36	3.45	8.16	1.5 × 10 <sup>-1</sup>	<100
Cadmium, µg/kg <sup>(5; 62.5 %)</sup>	34.8	10.1	34.8	44.9	24.7	<5.0 × 10 <sup>3</sup>
<b>Potassium-containing mineral sources</b>						
<i>Potassium Chloride, n = 17</i>						
Arsenic, µg/kg <sup>(10; 58.8 %)</sup>	188.1	210.9	124.3	672.2	9.6	2.0 × 10 <sup>4</sup>
Mercury, µg/kg <sup>(1; 5.9 %)</sup>	85.3	46.4	81.1	181.3	3.9	<200
Lead, µg/kg <sup>(6; 35.6 %)</sup>	69.3	110.1	4.5 × 10 <sup>-1</sup>	323.1	5.5 × 10 <sup>-2</sup>	1.0 × 10 <sup>5</sup>
Cadmium, µg/kg <sup>(8; 47.0 %)</sup>	120.9	187.1	50.1	492.7	3.4 × 10 <sup>-1</sup>	<5.0 × 10 <sup>3</sup>

<sup>a</sup>Numbers in parenthesis represent the number (n) of samples that are not detected using our current method of analysis. <sup>b</sup>Represent minerals for which at least one sample's concentration is above the European guidelines and square brackets represent the actual number of samples in this situation

(MnO) to 1.2 µg/kg (NaCl), 706.2 mg/kg [Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>] to 5.5 × 10<sup>-2</sup> mg/kg (KCl) and 9.46 mg/kg (NaCl) to 3.4 × 10<sup>-1</sup> µg/kg (KCl), respectively (Table 2). Other especially elevated Hg and Pb concentrations (over the 200 µg/kg and 100 mg/kg respective permitted levels) found during our survey are 1439 (FeSO<sub>4</sub>), 882 (ZnO) and 603 (Fe<sub>2</sub>O<sub>3</sub>) µg/kg and 628.1 (MgO) and 455 (CuO) mg/kg, respectively (Table 2).

In decreasing order of heavy metal overall concentrations the following minerals showed the less contamination: MnSO<sub>4</sub> < EDDI < KCl (Table 2). Microgran™ Se, Co and I samples also showed relatively lower concentrations of heavy metals. This may be expected as this ingredient's presentation mineral input is from 1 to 10 g/100 g, maximum. The fact that the one iodine source from organic synthesis has a lower concentration of heavy metals, sustains our hypothesis that higher contents come from inorganic synthesis raw materials. In the light of this findings other organic sources could be examined, especially since iodine organic salts have demonstrated potential as additives. Actually, iodine consumption through feed (pet and cattle mostly) is primarily as the compound EDDI (Lyday 2005).

Of the heavy metals assayed As showed, in general, the lowest values. These results are especially reassuring considering that all livestock species are susceptible to toxic effects of inorganic arsenic and some feeds may even contain organoarsenical species (e.g. roxarsone) as

growth promoters to improve feed efficiency (Chapman and Johnson 2002), occasionally in combination with ionophores. Strikingly, As has been suggested to possess some essential or beneficial functions at ultra-trace concentrations (Uthus 2003).

There is considerably less incidence of relatively elevated As concentrations, however As regulation is in some cases 100 fold more permissive with respect to Hg. In contrast, the higher number of incidents of irregular concentrations for Hg is evident. This is expected as Hg is the most abundant naturally-occurring heavy metal and is emitted primarily due industrial sources and mining ore deposits (Goyer 1996). As most information on mercury residues in feedstuffs, data presented here is given as total mercury concentrations. In this regard, although inorganic mercury toxicity profile due to accumulation include kidney damage, methylmercury (CH<sub>3</sub>-Hg) is the form considered of greatest toxicological concern which very well be non-existent, considering the nature of the samples tested.

Moreover, up to 30.0 % (Table 2) of samples of sulfur assayed (n = 20) showed residues of Hg > 200 µg/kg. This result may be explained by sulfur chemisorption capability of Hg (Feng et al. 2006). In turn, the same samples showed relatively low concentrations of the other heavy metals despite its tendency to associate with them.

Overall, calcium phosphates and metal oxides showed a significantly higher (p < 0.001) levels of arsenic and lead relative to other mineral sources (Table 2). This fact

could be explained due to the fact that minerals such as Zn, Mn and Fe oxides have such redox potentials that can oxidize As and will thus alter the extent of As retention. In fact,  $Mn^{3+}/Mn^{5+}$  oxides are strong oxidants that can oxidize and sequester many trace metals found in nature (García-Sánchez et al. 1999). The capacity of these two minerals in terms of As adsorption will be determined by their adsorption isotherms and the origin of the mineral (or its parent compounds during synthesis) and the predominant species of arsenic found. Ferrous carbonate and manganese sulfate seem to have the same ability. Other researchers already have established a stronger association between lead and metal oxides with respect to other ions and an adsorption of lead by the manganous oxides was up to 40 times greater than that by the iron oxides (McKenzie 1980). This result seems to be the case for our analysis as well; levels of As and Pb are significantly ( $p < 0.05$ ) lower for ZnO (mean values of  $1.3 \times 10^3$   $\mu\text{g}/\text{kg}$  and 55.8 mg/kg, respectively) and higher for FeO (mean values of  $6.38 \times 10^3$   $\mu\text{g}/\text{kg}$  and 155.1 mg/kg, respectively) (Table 2). The latter mineral is of special importance as is known, in some cases, to be used as a pigment (Potter 2000) hence its input in compound feed may be higher relative to other minerals. Heavy metals have been associated with a high sorption in metal oxides even in environmental samples such as sediments (Brown and Parks 2001).

Congruently, dicalcium- and monocalcium- phosphate samples showed the highest frequency in contaminated samples  $n = 10/22$  and  $n = 14/22$ , respectively (Table 2). In this specific case, the presence of arsenic could indicate a certain degree of substitution between arsenate and phosphate ions in the lattice of the calcium salt (Tawfik and Viola 2011) or co-precipitation of the arsenate oxyanion in the presence of calcium phosphate (Clara and Magalhães 2002; Sahai et al. 2007; Henke 2009). In this case, Pb and Cd concentrations in monocalcium phosphate are significantly higher ( $p < 0.001$  and  $p < 0.05$ , respectively) than in dicalcium phosphate. The converse is true for As ( $p < 0.001$ ). Hg concentrations showed no significant differences between both minerals ( $p < 0.05$ ).

On the other hand, despite the relatively lower concentrations of Cd found in the samples, this metal has

been reported (Chaney and Ryan 1994; Chaney et al. 1999; Li et al. 2005) to have the greatest potential for transmission through the food chain at levels that present risk to the final consumer.

One key aspect that follows from the regulatory and food safety standpoint, is the amount of heavy metals that is ingested as a result from the mixture of several of these mineral feeds and ingredients. For example, if a compound feed for swine is manufactured with dicalcium phosphate and sodium chloride as metal sources exhibiting the maximum concentration of, say, mercury detected in them and contains ca. 0.8 g/100 g Ca and 0.4 g/100 g salt (a common formulation for swine nutrition and are components with relatively high concentrations in feed) assuming this two as the only sources of Hg then this feed will have a total of the metal of 0.38  $\mu\text{g}/\text{kg}$ . If a pig of 22 weeks of age was fed with 4 000 g of such feed daily, then it would ingest 15  $\mu\text{g}$  mercury every 24 h.

Even though the amount may seem small, it must be taken into account that health effects from this substance exposure are chronic events, taking time and repeated exposure for the contaminants to bioaccumulate up to toxic levels. Hence, animals with longer life spans may exhibit higher concentrations of heavy metals in their tissues. As a result of this bioaccumulation, the consumption of meat from older animals could represent an increased risk for ingestion to a final consumer. This may suggest animals to be vectors in heavy metal transmission along the food chain (Pagán-Rodríguez et al. 2007).

However, considering that several of these minerals are added to a compound feed, in different proportions, not only the additive character of the concentrations of these heavy metals should be addressed, but also the possibility of dilution by other individual components with lower concentrations of said metals (e.g. maize mill) which results in a relatively low heavy metal containing feed (Table 3). We did not find any of the samples assayed ( $n = 50$ ) [bovine ( $n = 10$ ), fish ( $n = 10$ ), poultry ( $n = 10$ ), shrimp ( $n = 10$ ) and swine ( $n = 10$ ) feeds from the most important production facilities across the country] to surpass current legislation; in fact maximum levels of contaminants found were of 156.7  $\mu\text{g}/\text{kg}$  (Table 3).

**Table 3** Heavy metal concentrations found in Costarican animal feed samples

Metal/Feed type	Concentration range, $\mu\text{g}/\text{kg}$ <sup>a,b</sup>					Guideline
	Bovine	Fish	Poultry	Shrimp	Swine	
Arsenic	Not detected	19.3 – 25.4	48.5 – 90.4	37.8 – 53.5	7.7 – 30.5	2000
Mercury	60.2 – 186.8	50.0 – 55.9	35.9 – 38.6	39.3 – 41.8	38.5 – 71.4	100
Lead	Not detected	125.7 – 127.0	Not detected	Not detected	132.9 – 151.7	5000
Cadmium	113.1 – 156.7	39.9 – 40.3	35.3 – 107.9	19.3 – 35.0	59.5 – 61.2	1000/500

<sup>a</sup>Values obtained from  $n = 10$ . <sup>b</sup>For all cases SD < 5 %; three replicates per sample

These metals are of special importance as they are usually documented as substances with strong toxigenic and carcinogenic capacities (van Paemel et al. 2010). For example, both As<sup>3+</sup> and As<sup>5+</sup> are classified as group A human carcinogens (US EPA 1998; Sapkota 2007). This is of foremost importance in mineral feed since most vitamins and minerals are “generally recognized as safe” according with food additive regulation (US FDA 2014). However, some protection policies warnings to the feed industry have been issued against the use of mineral sources that are by-products or co-products of industrial metal production (US FDA 2003).

Considering the data provided herein, a programme that strictly monitor the quality on mineral ingredients and heavy metal concentrations should be implemented in order to maintain toxic metal residues within acceptable levels and avoid contaminated feed ingredients entering the food chain. This is especially relevant for cadmium and lead (considering their prevalence in the environment) and mercury contemplating the relatively elevated values found during our survey. Trends in concentration of contaminants in feed and feed ingredients should also be observed and from the animal and human health standpoint, interactions between heavy metals and essential nutrients (D’Souza et al. 2003) should be also considered.

Noteworthy, thanks to our work and the data compiled here, several Costa Rican feed manufacturers had taken steps on improving their manufacturing practices and had avoided all together the use of several raw materials with recurrent irregular mineral or heavy metal concentrations. Finally, we recommend further research include speciation as toxicity of the heavy metal involved is closely related to its oxidation state.

## Conclusions

Occasionally, mineral ingredient samples surpass, in some cases with elevated concentrations, permitted levels of undesirable substances in this case specifically, toxic metals. As the relative frequency is relatively high, a strict monitoring programme of both main composition and toxic metals must be sustained regularly in order to guarantee both the quality and safety of the ingredients used in animal feeds. Finally, mineral values of these raw materials on some instances were lower than declared possibly due to errors in manufacturing, local shipping, handling or in-plant repackaging.

## Abbreviations

AAFCO: Association of American Feed Control Officials; AAS: Atomic Absorption Spectrometry; ACS: American Chemical Society; AOAC: Association of Official Analytical Chemists; EC: European Community; EDDI: ethylenediamine dihydroiodide; EPA: Environmental Protection Agency; FAAS: Flame Atomic Absorption Spectrometry; FDA: Food and Drug Administration; FI: Flow Injection; GFAAS: Graphite Furnace Atomic Absorption Spectrometry; OMA: Official Methods of Analysis; MH: Metal Hydride; TISAB: Total Ionic Strength Adjustment Buffer; SD: Standard Deviation; USD: United States Dollars; UV: Ultraviolet.

## Competing interests

The authors declare that they have no competing interests.

## Author’s contributions

LM, SP and FG designed the experiment; LM recollected the samples and devised the sampling design; FG and SP designed the analysis approach and performed measurements; FG, SP and LM analyzed the data; FG wrote the draft of the manuscript. All authors read and approved the final manuscript.

## Acknowledgements

The authors would like to thank the plants and their respective representatives who were willing to participate in this research proposal. Marian Flores and Andrea Porras are acknowledged for their technical assistance. Vicerrectoría de Investigación supported this initiative by means of project B2059.

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Received: 12 February 2015 Accepted: 3 May 2015

Published online: 31 May 2015

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