



Dioxins, furans, biphenyls, arsenic, thorium and uranium in natural and anthropogenic sources of phosphorus and calcium used in agriculture



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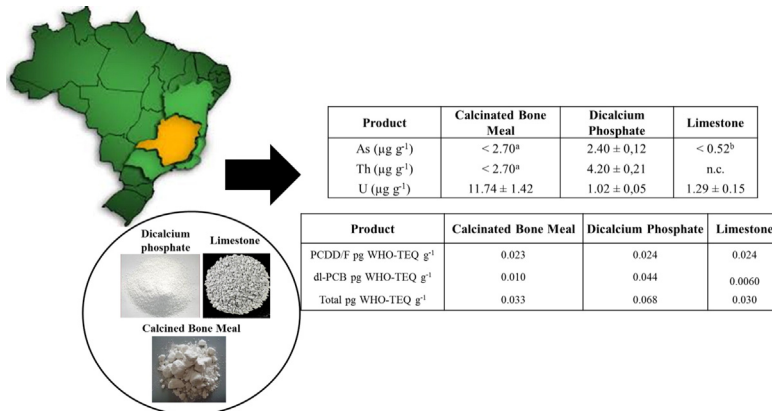
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HIGHLIGHTS

- PCDD/Fs dl- PCBs is not a matter since levels below the LOD in phosphate materials subject of study.
- Significant accumulation of As and U in Limestone. Th was originally found in dicalcium phosphate.
- High concentration of U in dicalcium phosphate suggests that a special attention should be paid.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to assess the presence of dioxins, furans and biphenyls, and the inorganic contaminants such as arsenic (As), thorium (Th) and uranium (U) in three main products used in Agriculture in Brazil: feed grade dicalcium phosphate, calcined bovine bone meal and calcitic limestone. The first two are anthropogenic sources of phosphorus and calcium, while calcitic limestone is a natural unprocessed mineral. Regarding to dioxin-like substances, all samples analyzed exhibited dioxins (PCDD) and furans (PCDF) and dioxin-like polychlorinated biphenyls (dl-PCBs) concentrations below limit of detection (LOD). In general, achieved is in accordance with regulation in Brazil where is established a maximum limit in limestone used in the citric pulp production (0.50 pg WHO-TEQ g⁻¹). In addition, reported data revealed very low levels for limestone in comparison with similar materials reported by European legislation. As result for toxic metals, achieved data were obtained using Instrumental Neutron Activation Analysis (INAA). On one hand, limestone sample exhibits the largest arsenic concentration. On another hand, dicalcium phosphate exhibited the largest uranium concentration, which represents a standard in animal nutrition. Therefore, it is phosphorus source in the animal feed industry can be a goal of concern in the feed field.

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1. Introduction

Phosphates mineral is found in natural rocks as phosphate rock deposits in the strata from earth. It is used worldwide for manufacturing phosphoric acid and various brands of chemical fertilizers and detergents as well as chemicals (Mazzilli and Saueia, 2013). Phosphate sites are widely distributed throughout the world, both geographically and geologically, but currently there are only a few sources of phosphate capable of meeting future demand. For instance, sedimentary deposits have provided about 80–90% of the worldwide phosphate production, while 17% is derived from igneous rocks and their derivatives and the remaining comes from residual sedimentary and guano-type deposits (FAO/IAEA, 2004a). However, in Brazil the main phosphate rock reserve correspond to igneous deposits, which represent 80% of the national reserves of phosphate rocks and are concentrated in the states of Minas Gerais, Goiás and São Paulo (DNPM, 2010). In addition, Brazil has remarkable limestone caves, but the largest production is located in the state of Minas Gerais with five mines and an annual capacity of 2000 thousand metric tons (Gurmendi, 2012; Antonioli et al., 2015).

It is known that the phosphate rock contains radionuclides of the U and Th natural decay series. In addition, phosphates present elements such Ca and P, accessory-gangue minerals and other toxic elements including As, Ba, Cd and F (Tokarnia et al., 2000). At present, adverse health effects in humans such as hypertrophy, hyperplasia, and liver fibrosis of the liver, lung metaplasia, adrenal gland atrophy, inflammation and atrophy of the pancreas, kidney nephropathy, cardiomyopathy, adrenal gland hypertrophy and atrophy of the thymus and spleen episodes are reported in the literature (Zeng et al., 2008; Misson et al., 2009; Gilman et al., 1998; Sardinha Oliviera, 2008). Thus, the ability to absorb hazardous substances makes phosphates in goal to research in order to achieve a better understanding and occurrence of these toxicants.

In Brazil the phosphate rock is used as raw material in the Brazilian phosphate industry, in which the presence of radionuclides of U and Th series is reported at levels ranging from 10 to 1200 Bq kg⁻¹ (FAO/IAEA, 2004a; Avelar et al., 2011). Also, studies in the 1970's from Germany reported an increase of uranium present in rivers and groundwater in regions with an intensive use of phosphate fertilizers in agriculture (Mangini et al., 1979). In this case, uranium from phosphate fertilizers is likely adsorbed on the upper layers of soil and its content on the water is correlated to the content of HCO₃⁻ present in the rivers (Mangini et al., 1979).

On the other hand, there are other contaminants as dioxins which can be naturally present in phosphates. These contaminants are also of concern since they are responsible for dramatic health effects. In general, dioxins (PCDDs), furans (PCDFs) and polychlorinated biphenyls (PCBs) are compounds produced unintentionally through several industrial processes that involve thermal processes, waste incineration to low temperatures, metal smelting and refining and production of pesticides (Yang et al., 2002). Properties such as high stability, low volatility, high resistance to degradation becomes to dioxins in highly persistent organic pollutants that experiment bioaccumulation and biomagnification phenomena, so they present health risk (WHO, 2000; Liem, 1999; Focant et al., 2002). In addition, they are extremely toxic substances. In fact, dioxins and related compound have been recognized to be carcinogenic for humans (IARC, 1997 and 2015; Kogevinas, 2001). Similarly, polychlorinated biphenyls are a group of compounds that have alike properties to dioxins and they have been intensively used worldwide until the 70's, when production was ceased and their use was banned in many countries. PCBs were commercially produced for electric industry as a dielectric insulating fluid for transformers and capacitors, also were used as electrical insulators, multiple applications for paints, plastics, plastics manufacturing and synthesis and production of others organic chemicals (Kimbrough and Jensen, 1989). These products were released into the environment through the use and disposal of products containing PCBs, as by-products during the manufacture of certain organic chemicals and during combustion of

waste materials (USEPA, 2000). Recently, several PCDD/Fs and PCBs congeners in phosphates used in Agriculture have been detected and published (EU, 2000; Institute of Medicine of the National Academies, 2003; Committee on EPA's Exposure and Human Health Reassessment of TCDD and Related Compounds, 2006; Chambers et al., 2012). In addition, a global regulatory framework and strict regulations were established for these pollutants in food, feed and raw material used as fertilizer. However, to date there are available relatively few data related to research and results in PCDD/PCDFs and PCBs in mineral products used as ingredients in feedstuffs (Parera et al., 2008). A study developed by the EU Directive in 2000, reported data related to PCDD/Fs content in phosphate (0.01–0.38 WHO-TEQ ng kg⁻¹) and meat bone meal (0.10–0.40 WHO-TEQ ng kg⁻¹) (EU, 2000).

Therefore, it is important to explore this kind of materials in order to determinate the toxic elements content and organic pollutants levels, which may produce adverse effects in humans and animals. In addition, achieve data provide basic information on the contamination levels suitable to be spread on environmental (ATSDR, 1999; Committee on EPA's Exposure and Human Health Reassessment of TCDD and Related Compounds, 2006; Institute of Medicine of the National Academies, 2003; Zeng et al., 2008, Wan Mahmood and Rahim Mohamed, 2010).

At present, studies related to content of toxic elements and persistent organic pollutants in extracted materials (limestone or phosphate rocks) is scarce, hence any data is always interesting and novelty. The objective of this study was to determine the content of hazardous substances and elements such as arsenic, thorium, uranium, PCDDs, PCDFs and PCBs in two sources of phosphorus and one source of calcium, which are widely used as feedstuff in agriculture and livestock.

2. Material and methods

For this study, the feed grade products dicalcium phosphate (Chemical Abstracts Service CAS 7789-77-7), calcined bovine bone meal also known as ash bone (CAS not applicable) and limestone (CAS 471-34-1) were selected and purchased in a local supermarket in city Uberaba, Minas Gerais State-Brazil. As mention before, Minas Gerais region has an important reserve of igneous deposits in Brazil. Moreover, according to the Brazilian market is not mandatory to present the exact origin of package product.

2.1. Organic assessments: HRGC-HRMS analyses for determination of PCDD/Fs and PCBs

In general terms, the analytical method has been extensively reported elsewhere. Analytical workflow includes an extraction process to remove the target compounds followed by a purification process and final determination by mass spectrometry using the isotopic dilution as quantification method (Parera et al., 2008).

Instrumental analysis for PCDD/Fs and dl-PCBs was based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) (Parera et al., 2008). Analyses were performed on a Agilent gas chromatograph fitted with a 40 m × 0.18 mm i.d. × 0.18 μm film thickness DB-5 ms fused silica column (J&W Scientific, USA) for PCDD/F coupled to a heated transfer line kept at 280 °C to a high resolution mass spectrometer (Micromass Ultima NT) with EBE geometry. Dioxins and PCBs extracts were carried out by a PAL System under data control system. The injector port temperature was 280 °C, and a helium carrier gas flow was maintained by an electronic pressure program. The GC capillary temperature program was started at 140 °C (hold for 1 min), then at 20 °C/min to 200 °C and kept isothermally to 1 min and at 5 °C/min to 310 °C (hold for 6 min). The HRGC-HRMS was used with a positive electron ionization (EI+) source operating in the MID mode at 10.000 resolution (10% valley definition).

Quantification was based upon relative response factors (or optionally average responses) in accordance to the isotopic dilution method. Relative response factors were measured for each individual compound

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