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Health risk assessment and soil and plant heavy metal and bromine contents in field plots after ten years of organic and mineral fertilization

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ABSTRACT

Heavy metals and bromine (Br) derived from organic and industrialized fertilizers can be absorbed, transported and accumulated into parts of plants ingested by humans. This study aimed to evaluate in an experiment conducted under no-tillage for 10 years, totaling 14 applications of pig slurry manure (PS), pig deep-litter (PL), dairy slurry (DS) and mineral fertilizer (MF), the heavy metal and Br contents in soil and in whether the grains produced by corn (*Zea mays* L.) and wheat (*Triticum aestivum* L.) under these conditions could result in risk to human health. The total contents of As, Cd, Pb, Cr, Ni, Cu, Zn and Br were analyzed in samples of fertilizers, waste, soil, shoots and grains of corn and wheat. Afterwards, enrichment factor (EF), accumulation factor (AF), health risk index (HRI), target hazard quotient (THQ) and target cancer risk (TCR) were determined. Mineral fertilizer exhibited the highest As and Cr content, while the highest levels of Cu and Zn were found in animal waste. The contents of As, Cd, Cr, Cu, Ni, Pb and Zn in soil were below the limits established by environmental regulatory agencies. However, a significant enrichment factor was found for Cu in soil with a history of PL application. Furthermore, high Zn contents were found in shoots and grains of corn and wheat, especially when the plants were grown in soil with organic waste application. Applications of organic waste and mineral fertilizer provided high HRI and THQ for Br and Zn, posing risks to human health. The intake of corn and wheat fertilized with pig slurry manure, swine deep bed, liquid cattle manure and industrialized mineral fertilizer did not present TCR.

1. Introduction

The southern region of Brazil has the highest concentration of pigs and dairy cattle, which are mostly raised in confined or semi-confined systems, generating large amounts of waste. In this region, 134 million m^3 of pig slurry manure (Tavares et al., 2014) and 300 million kg of cattle manure are produced daily (Machado, 2010). Pig and cattle manure are applied to soil as single or supplementary sources of nutrients to plants, especially N, P, K, Ca and Mg (Couto et al., 2015, 2016). However, animal waste contains heavy metals such as Cu, Zn, Mn, As, Cd, Pb, Cr and Ni (Gunkel-Grillon et al., 2015; Couto et al., 2016) and halogens such as Br. Thus, soils submitted to successive applications of waste over several years may cause excess accumulation of these elements.

In most cases, animal waste is distributed on the surface without incorporation into the soil, due to the predominance of no-tillage

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system for both grain and fodder production. Part of the elements derived from animal waste can be adsorbed at the most avid binding sites, after which the rest is redistributed into fractions that are retained with lower binding energy and greater availability and mobility (Couto et al., 2016, 2017; Qiutong and Mingkui, 2017). The total contents of heavy metals and Br can be interpreted in accordance with the environmental legislation of the European Union (CEC, 1986), the US (EPA, 1995) and Brazil (CONAMA, 2009), among others. Legislation establishes the concentrations in soil that may cause environmental liabilities, such as phytotoxic effects to plants and animals, as well as contamination of water sources.

The cultivation of plants causes the transfer of part of the chemical elements from the soil into the plant, where it is redistributed to the shoots and grains of corn and wheat, for instance. Later, these grains are directly or indirectly consumed by humans, through the ingestion of a variety of industrialized food (Avkopashvili et al., 2017). In organs of plant shoots, levels below 20 mg Cu kg^{-1} and 10–100 mg Zn kg^{-1} of dry matter are commonly found (Lemtiri et al., 2016; Minkina et al., 2017). Contents lower than 3 mg kg^{-1} for As, Cd, Cr, Ni, Pb and Br and 2–50 mg Mn kg^{-1} are normally observed in dry matter (Kabata-Pendias, 2011; Shtangeeva et al., 2017). However, in dry matter of cereal grains grown in soils with excess heavy metals in Brazil and in the world, concentrations of 1, 0.6, 4, 22, 360, 70, 170 and 4 mg kg^{-1} have been found for As, Ni, Cd, Cu, Mn, Pb, Zn and Cr, respectively (Nogueira et al., 2007; Silva et al., 2007; Huang et al., 2008). Cu, Zn, Ni, and Cr are considered essential to humans and can be ingested in very small quantities (FAO/WHO, 1995; EPA, 1995; Tchounwou et al., 2012). On the other hand, Pb, Cd, As, and Br are not essential to living organisms from a biological point of view and are considered toxic even at low concentrations (Tchounwou et al., 2012). Thus, prolonged intake of food with high concentrations of these elements may promote accumulation in the human body and cause diseases (Mendoza et al., 2017).

Excess As, Cd and Cu in the human body can cause disturbances in the respiratory, gastrointestinal, cardiovascular and nervous system, genomic instability, endocrine disruption, neurotoxicity, immunological problems and also impair psychosocial behavior (Dyer, 2007; Mendoza et al., 2017). Pb is responsible for increasing blood pressure and tumor infection, improper synthesis of hemoglobin and of the reproductive system. High concentrations of Ni and Cr can cause cancer, fatigue, headache, rashes, dizziness, heart problems and respiratory diseases (Zambelli et al., 2016). Br is particularly harmful to the human nervous and endocrine systems (Winid, 2015). For this reason, safe levels of daily intake for heavy metals have already been established (FAO/WHO, 2006; EPA, 1993).

The reference dose (RfD) for As, Cd, Cr, Cu Ni, Pb, Zn and BrO_3 is 20, 300, 1500, 4, 20, 40, 300 and 3 μg kg^{-1} body weight day^{-1}, respectively (EPA, 1993). However, when ingested for long periods in a lifetime, even in safe doses, these elements can cause deleterious effects to humans (EPA, 1997). These levels are defined based on the degree to which the element may cause disorder, the body's ability to accumulate the element and the weight of the individual ingesting it (Abbasi et al., 2013). To evaluate the risk of intake of a given element during the course of an individual's life, it is necessary to consider the period of intake, in addition to the daily limits considered safe. In this sense, health risk index, target hazard quotient and target cancer risk were established to verify the risks elements tend to cause throughout the life of children and adults (EPA, 2010; Abbasi et al., 2013).

The study aimed to evaluate the levels of heavy metals and Br in soil and in plants grown under the application of organic waste and mineral fertilizer and whether corn and wheat grains produced under these conditions pose a risk to human health.

2. Material and methods

2.1. Characterization of the experimental area and the applied waste

The study was carried out in the experimental area of the Department of Soil Science of the Universidade Federal de Santa Maria (UFSM), located in the city of Santa Maria, state of Rio Grande do Sul, southern Brazil (29°42′50.92″S 53°42′25.55″W, altitude of 100 m). The climate of the region is humid subtropical (Cfa), with average annual temperature of 19.3 °C, average precipitation of 1561 mm and relative humidity of 82%. The soil was classified as Typic Hapludalf (Soil Survey Staff, 2006). In the setup of the experiment the soil had the following physical and chemical attributes: 180 g kg^{-1} of clay, 193 g kg^{-1} of silt and 627 g kg^{-1} of sand (Pipette method); 19 g kg^{-1} of organic matter (Walkley Black method); pH in water 4.9 (1:1 ratio); 20.3 mg P kg^{-1} and 60 mg K kg^{-1} (extracted by Mehlich-1); 0.03 $cmol_c$ dm^{-3} of exchangeable Al, 0.8 $cmol_c$ dm^{-3} of exchangeable Ca and 0.3 $cmol_c$ dm^{-3} of exchangeable Mg (extracted by KCl 1 mol L^{-1}); 3.7 $cmol_c$ kg^{-1} of H + Al; 1.3 $cmol_c$ kg^{-1} of $CEC_{effective}$; 5.0 $cmol_c$ kg^{-1} of $CEC_{pH\ 7.0}$; Al saturation of 2.0% and base saturation of 25.4%.

The experiment was installed in 2004 in an area that had been managed under no-tillage for 10 years. The experimental design was randomized block with four replicates and plots with dimensions of 5 × 5 m (25 m^2). The treatments were soil without nutrient application (control), and with the application of pig slurry manure (PS), pig deep-litter (PL), dairy slurry (DS) and mineral fertilizer (urea + triple superphosphate + potassium chloride = MF). The crop rotation implemented over the years consisted of black oat (*Avena strigosa* Schreb) and wheat (*Triticum aestivum* L.) in the winter and corn (Zea *mays* L.) and bean (*Phaseolus vulgaris* L.) in the summer. From 2004 to 2010, the treatments were applied only once a year, at the implantation of the summer crop. However, from the summer crop of 2010, the applications were carried out twice a year, one before the winter crop and another before the summer crop. During the period considered for this study, the following crops were grown: corn in the 2013/2014 crop season and wheat in the winter of 2014. This means that the treatments had already been applied 14 times.

Liquid waste (PS and DS) was composed of feces, urine, food debris and water from the washing of the premises, and stored in anaerobic reservoirs. PL was composed of processed waste of rice, feces, urine and food debris. Samples of the organic sources were collected at the site of origin for further analysis of their chemical composition, including total N content. Doses of organic and mineral sources were established based on the N requirement of the plants of each crop, according to the recommendation proposed by CQFS-RS/SC (2004) and considering the efficiency index of each organic source. As a result, the amounts of N applied were 30 kg of N ha^{-1} for black oat, 105 kg of N ha^{-1} for corn and 110 kg of N ha^{-1} for wheat.

2.2. Collects and analyzes soil, shoot and crop grains

Samples of DS, PS and PL were collected in May and December 2013 and May 2014, dried in an oven with forced air circulation at 45 °C until constant mass, weighed and stored. Mineral fertilizer (MF) was collected only in May 2014 and stored.

In August 2014, when wheat was at full flowering, soil samples were collected at 0–5 cm, dried and separated into two parts. The values of pH in water (1:1); exchangeable Al, Ca and Mg contents (extracted by KCl 1 mol L^{-1}) were determined in the first part (Tedesco et al., 1995). Ca and Mg content were determined by atomic absorption spectrometry (AAS, Varian SpectrAA-600, Australia). Al was determined by titration with 0.0125 mol L^{-1} NaOH. Potential acidity (H + Al) was also determined and cation exchange capacity at $pH_{7.0}$ ($CEC_{pH\ 7.0}$), aluminum saturation and base saturation were calculated. Total organic carbon (TOC) content was determined by digestion with chromic acid solution (Embrapa, 1997) and determined by titration. In order to obtain values