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# Compared Background and Reference Values in Sources of Cadmium-enriched Soils from Brazil

Fernando Machado de Mello<sup>1</sup>; Essaid Bilal<sup>2</sup>; Gustavo Neves<sup>3</sup>; Maria Eduarda Loureiro dos Reis Teodoro<sup>4</sup>; Thiago Peixoto de Araujo<sup>5</sup>

## RESUMO

A complexidade do processo de avaliação da variação dos níveis de contaminação do solo é, em parte, devido à imprecisão na caracterização de sua origem distinta, natural ou resultante de atividades antrópicas. O estabelecimento e a comparação de backgrounds e valores de referência do conteúdo destes contaminantes são importantes para nortear e contribuir na regulamentação e jurisprudência de cunho protetivo ambiental em geral. Algumas ações visando o controle de metais pesados, entre outros elementos químicos, apontam para um uso mais restritivo de fertilizantes fosfatados, ricos nestes elementos, em vários países. Reconhecer e caracterizar solos contaminados são uma séria preocupação com problemas que toda sociedade tem de lidar hoje em dia e é um dos maiores e mais negligenciados problemas no Brasil. Neste trabalho pretende-se fazer um balanço de fontes naturais de metais pesados e cargas adicionais destes contaminantes, em especial o Cádmiio, em solos brasileiros, principalmente através da aplicação de fertilizantes minerais, aplicados em grande volume e responsáveis pelo significativo incremento de sua concentração. Isto é uma ameaça à saúde pública em várias regiões, e é uma das prioridades na proteção e prevenção de suas fontes de concentração anômala no solo. A degradação da qualidade do solo concernente à contaminação e poluição por metais pesados é, hoje, reconhecido também como um sério risco ambiental e à saúde.

**Palavras Chave:** Solo, Cádmiio, Contaminação, Legislação, Valores de Referência.

## ABSTRACT

The complexity of the assessment process of variations in contamination levels of soils is in part due to distinct sources, natural or by some anthropic activities. Compare these different substances sources, backgrounds and guiding values is very important to introduce directions and contributions for regulations or environmental protection legislation in general, for heavy metals contents, among other chemical components, and are pointing to more restrictive use of phosphate fertilisers, rich in those pollutant elements, in many countries around the world. Recognize and characterize contaminated soils is a serious concern with issues that whole society have to deal with today and one of the largest and most neglected problems in Brazil. This works intends to obtain an insight in the natural sources and loads of heavy metals, especially cadmium to soils in Brazil, mainly with the application of huge volume of mineral fertilisers, directly linked with their dangerous concentrations. This is a threat to public health in many regions, and it is one of the priorities to protect it from all sources of anomalous concentration in the ground. Decreasing soil quality by means of contamination and pollution by heavy metals is now recognized also as a serious risk for environmental quality and to the health of people.

**Key words:** Soil, Cadmium, Contamination, Legislation, Reference Values.

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## 1. INTRODUCTION

Soils enriched in Heavy Metals Elements (HME) became a major worldwide environmental issue, not only by the well know toxicology risk linked with consumption of contaminated tobacco and food, but by the long-term effects related to its slow and continuous concentration in soils and water. This concentration is driven through their strong geochemical and physical affinity for some special soils and geologic terrains, specially a long residence time in surface.

The cadmium contamination is largely due to agricultural practices, mining and metallurgy. The current paper has the purpose to analyse and compare how this major issue is receiving attention in Brazil and in some developed countries, analyze the guiding values and behaviour of heavy metals in the soil, with emphasis in Cd from the fertilisers and mining industry; to compare protocols of sampling, methods of detection and regulations around the world; and to compare the minimum concentrations to establish levels of intervention and assess the risk. The distribution of most elements in soil shows a pattern related to geology and/or mineralisation. Past climates and the prevailing particular tropical conditions in Brazil caused strong argillic and ferrallitic weathering of some rocks, with a change in mineralogy, and a modification of vertical and lateral distribution patterns of most major elements, but the main source of the anomalous enrichment in arable soils remains the HME generated through time by agricultural activities on the environment, particularly in Latosols over volcano-sedimentary basins of Brazil. The current legal brazilian norm, established by the National Environmental Council (CONAMA, 2009) through resolution 420/2009 – proposed different values of reference for inorganic substances.

Quality control and risk assessment associated to the soil contamination requires the knowledge of the total content in those elements and the influence of source rock contents in HME in the various constituent compartments of the ground. In the present work, HME are considered as the sense of Alloway (1995), the metals/metalloids which behaves geochemically as Siderophiles (Co, Ni, Au, Mo, Pb, As), Calchophiles (Cu, Ag, Au, Zn, Cd, Hg, Pb, As, Sb, Se, Tl, Mo) and the Lithophiles (V, Cr, Mn, U, Ti).

In phosphate fertilisers some HME, like Cd contents, are expressed in mg Kg<sup>-1</sup> of P or P<sub>2</sub>O<sub>5</sub>. 1 kg of P is equivalent to 2.29 kg of P<sub>2</sub>O<sub>5</sub>. Comparing different types of units is sometimes difficult and may require conversions between P and P<sub>2</sub>O<sub>5</sub> or back calculating mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> based on an assumed fertiliser application rate. Phosphorus Pentoxide (P<sub>2</sub>O<sub>5</sub>) has 44% P. To obtain the value expressed in Cd Kg<sup>-1</sup> P one must divide it by 2.29 to express in the Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> form.

Soil contamination by HME became a problem in large agricultural areas, especially in extensive plantations, with the continuous use of phosphate based fertilisers. The option to protect this natural resource is by using the legislation to establish, in a clear manner the rules, regulations and norms. This is the base to support and increase the controls and monitoring of those elements. In the last years, biomedical research has shown a strong correlation caused by cadmium in diseases of humans. A recent line of research has concluded that cadmium is a major human toxicant; there is a need to limit exposure from as many sources as possible. The World Health Organization - WHO (2010) presented a list containing ten substances that threatens the public health and cadmium was the fifth one.

## 2. STANDARTS CADMIUM CONTENTS IN ROCKS, SOILS AND FERTILISERS

Cadmium has low crustal abundance, in the region of 0.1 mg kg<sup>-1</sup> (Alloway, 1995) and it is found rarely in its elemental form, in greenockite (CdS), octavite (CdSe) and monteponite (CdO) (Kabata-Pendias and Mukherjee, 2007). Cadmium is often found in association with zinc-bearing and zinc-bearing lead ores, which are the main source of cadmium production (Greenwood and Earnshaw, 1997). The high cadmium contents are also found in black shales and in phosphate rocks, varying considerably from one source to another, in general with two extremes, igneous rocks having the lowest contents compared to sedimentary (McLennan and Taylor, 1999; McLennan and Murray, 1999).

The phosphate rocks which are mined in Brazil, Russia, South Africa and Finland are igneous rocks and have very low cadmium contents (sometimes below 10 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>). In the other hand, those found in North and West Africa and in the Middle East are sedimentary rocks

formed in environments rich in organic matter, and generally have much higher cadmium levels. In Tunisia, Togo, Senegal, they reaching frequently values of 60 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> while in Morocco deposits, the most important supplier of Brazil and European Union (EU), deposits leads cadmium contents in fertilisers above 60 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>. Most natural soils contain less than 1 mg kg<sup>-1</sup> of cadmium resulted from the weathering of parent materials (Alloway, 1995). Generally lower levels are found in acid igneous rocks (mean granite 0.09 mg kg<sup>-1</sup>) than basic (mean basalt 0.13 mg kg<sup>-1</sup>). In sediments, sandstone and limestone shows lower levels, higher contents are found in black shales (0.3 to 219 mg kg<sup>-1</sup>), organic-rich sediments or marine manganese nodules and phosphorite (Fergusson, 1990). Elevated Cd values are generally linked with Pb and Zn of sulphide mineralisation from Sedex or VHMS mineralisation. The average Cd contents in soil surface is estimated to be 0.53 mg kg<sup>-1</sup>, with all higher values reflecting anthropogenic influences (Kabata Pendias 2001).

Although unevenly distributed by different regions of Brazil, the dominant soil type is the Latosol, with 56,30% in total area of the country, followed by the Argisol (20,68%) and Neosol (9,38%) (Coelho et al. 2002). That distribution is mostly due to the geologic ground and by extreme climatic differences in the country, inducing complexes and unique pedogenic processes. Proposed HME baseline values of natural concentrations in Brazilian soils by Amaral Sobrinho (1993) suggests that different values of HME could be found in the same class and level of soil or between different classes as a function of the variation of soil characteristics. Estimation of natural contents of HME in some soil types of Brazil was performed by Fadigas (2006), dividing the soils in seven groups (see **TABLE 1**), the first one (1) distinguished by high contents in Mn, Fe and clay is composed by Red Dystrophic Latosol, Brun Latosol and Red Argisol mainly formed in terrains of basaltic compositions, some of them over the huge Paraná Sedimentary Basin. This is the group that naturally concentrates the highest values of HME. The second group (2) includes those with high levels of silt, Mn and high CEC (Cation Exchange Capacity), including Chernozems, Luvisols, eutrophic soils, and some samples of Yellow Latosol, Red-Yellow Latosol and Red Argisol. The sixth and seventh groups (7 and 8) shows the lowest levels in HME and share the same composition but are differentiated by clay and Fe contents, includes Yellow Dystrophic Latosols and Argisols, and in minor quantity by soils derived by Tertiary and Quaternary sediments. Third, fourth and fifth (3, 4 e 5) groups share intermediate characteristics of those cited above and are mainly constituted by a great variety of Latosols and Argisols, and, with minor importance by Plinthosol, Cambisol, Nitosol with dystrophic character. Average values showed in **TABLE 1** are near the quality reference values (Casarini, 2000) for the State of Sao Paulo, Brazil, in which the concentrations, in mg kg<sup>-1</sup> are: Cd (0.5), Co (12.5), Cu (35.1), Cr (40.2), Ni (13.2), Pb (17), Zn (59.9).

**Table 1** - Normal considered values of Cd, Co, Cr, Cu, Ni, Pb and Zn in natural soils, proposed as a Reference Value (RV)<sup>1</sup>. Modified from Fadigas et al., 2006.

ELEMENT							
GROUP (G)	Cr	Co	Ni	Cu	Zn	Cd	Pb
Soil Concentration (mg kg <sup>-1</sup> )							
1	55	20	35	119	79	<b>1,0</b>	19
2	48	10	18	19	44	<b>0,8</b>	28
3	65	4	25	16	23	<b>1,6</b>	16
4	35	10	17	12	35	<b>0,9</b>	18
5	23	4	7	6	12	<b>0,4</b>	22
6	43	2	12	2	12	<b>0,4</b>	3
7	19	2	5	3	6	<b>0,3</b>	40
QSm <sup>2</sup>	41	8	17	25	30	<b>0,8</b>	20

<sup>1</sup> Concentration considered normal for the soils belonging to each group and corresponding to the value of the upper quartile (75%) of the frequency distribution of the sample data in each group.

<sup>2</sup> Mean upper quartile between groups

The adsorption/desorption of Cd and Zn presents a great sensibility to pH, compared with Cu and Pb. This chemical behaviour could contribute to explain the accumulation Zn and Cd in soil

surficial layers in locals with higher pH (Alloway, 1990), *i.e.* in topsoils, the upper, outermost layer of soil, usually the top 5 cm to 20 cm depth layer. It has the highest concentration of SOM (Soil Organic Matter) and microorganisms and is where most of the biological soil activity occurs, where plants nourishment by roots concentrates.

Phosphate fertilisers contain between 5 and 100 mg kg<sup>-1</sup> Cd and up to 300 mg kg<sup>-1</sup> Cd may be present in sewage sludge. Cd is a trace element in fertilisers, which have been applied extensively to arable and pasture land around the world. In United Kingdom (UK) the ECB (2007) reported that current fertilisers contain around 79 mg kg<sup>-1</sup> Cd of P. Based on the use of fertilisers in the 1980s and early 1990s, Alloway (1995) estimated that around 4.3 g of cadmium per hectare per year has been added to agricultural soils in the UK. Across the European Union, 231 tonnes of cadmium are added to agricultural soils each year from fertiliser use (EC, 2007). The average cadmium levels in fertiliser was estimated in 2000, showing that levels in cultivated soil have a trend, lower in the countries of northern Europe (about 2.5 mg Cd Kg<sup>-1</sup> P in fertiliser and 0.21 mg Cd Kg<sup>-1</sup> in soil) and much higher in other parts of Europe (about 138 mg Cd Kg<sup>-1</sup> P in fertiliser and 0.5 mg kg<sup>-1</sup> soil). It was concluded that this average cadmium content of European fertilisers, 138 mg Cd Kg<sup>-1</sup> P (or 60 mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>), would lead to a radical increase in the concentrations of cadmium in soil and crops, and in cadmium leaching.

Only 10% of the applied P as a fertiliser is taken by the plants, differing in this aspect by the higher taken of N and from K. This difference is also attributed by the higher P fixation in tropical soils, with high Fe-Al oxides (Raj, 2003). The Brazilian consumption of P<sub>2</sub>O<sub>5</sub> was in 2002 about 2.777.000 t (Lopes, 2003), 43% of monoammonium phosphate (MAP), 30% in the form of simple superphosphate (SSP), 15% triple superphosphate (TSP) and 12% of other sources of the market.

Langenbach and Sarpa (1985) compared the Cd concentration in eleven brazilian phosphates and observed that they Cd contents are lesser than 2.0 mg kg<sup>-1</sup> Cd. The brazilians phosphate rock from Catalão-GO presents 4 mg kg<sup>-1</sup> Cd, 19 mg kg<sup>-1</sup> Cr e 58 mg kg<sup>-1</sup> Pb, and the fine apatitic concentrate from Araxá-MG presents 7 mg kg<sup>-1</sup> Cd, 44 mg kg<sup>-1</sup> Cr e 127 mg kg<sup>-1</sup> Pb (Gabe and Rodella, 1999, in Alcarde & Rodella, 2003). Amaral Sobrinho et al. (1992) presented typical ranges of HME in phosphate fertilisers as 0.1–170 mg kg<sup>-1</sup> Cd, 7–225 mg kg<sup>-1</sup> Pb, 7–38 mg kg<sup>-1</sup> Ni, 1–300 mg kg<sup>-1</sup> Cu and 50–1450 mg kg<sup>-1</sup> Zn.

### 3. HEALTH PROBLEMS CAUSED BY CADMIUM

The ground contamination by heavy metals elements is a major environmental problem for two main reasons. Beside the well know ecotoxicology risk in food, this contamination can have very long-term effects because its continuous concentration and strong chemical and physical affinity for the solid matrix of distinctive geodiversity terrains and a long residence time in soils (Echevarria and More, 2006).

The kidney is the most sensitive organ to cadmium excess and the toxicity is driven by the diet, but the cadmium in food is only the second factor, smoking is the dangerous contribution to cadmium human body burden. Cadmium is also retained in liver and, once absorbed, is not easily excreted, its biological half life ranging between 10 to 30 years. Cd food intakes are in decreasing order of importance: cereals and cereal products; vegetables; meat products, offal (inner organs), fish and seafood. The highest inputs of phosphate fertilisers are in vegetables and wheat. Cd causes the augmentation of glucose excretion and amino acids, litiasis on kidney and urine calcium, decalcification of bones promoting fractures, enfisema of lungs and fibrosis peribronchial and perivascular (Johri et al., 2010)

The EU community promote long lived studies concerning cadmium exposure and have recently implemented fertiliser limits envisaging food safety standards that are more stringent than USA standards. EU concern about cadmium in food, since 1980, was triggered by a rising body burden in some segments of the population that approached the level of onset of adverse health effects. While the overall average cadmium intake from food alone does not pose a risk to most people, certain populations are considered at higher risk. As examples, vegetarians could consume more of the metal due to their diet, women may increase their absorption due to low levels of Fe, and tobacco consumers are exposed to an additional source of Cd.

#### 4. ANALYTICAL METHODS COMPARED

Comparison of three extraction procedures was performed by Campos et al. (2005) to assess HME in mineral fertilizers (Embrapa, 1999; USEPA 3051A and USEPA 3050B) for Cd, Cr, Cu, Ni, Pb, and Zn from Brazil and the main fertilizers commercialized there. The methods described do not fully solubilize the solid fraction of phosphates and are more indicated than total extractions for soil pollution studies, due to representation of maximum potential bioavailability of a certain pollutant (**FIGURE 1**).

The USEPA 3050B method, from the Environmental Protection Agency, EUA (Usepa, 1998a), takes 1 g of the material, while USEPA 3051A (Usepa, 1998b) less material, 0.5 g to 1.0 g. The Embrapa Method (Embrapa, 1999) uses approximately 0.5 g of the material added to 20 mL of HCl 2 mol L<sup>-1</sup>. The quantification of the trace elements content was performed (Campos et al., 2005) by air acetylene flame atomic absorption spectroscopy. Among the studied phosphates, the thermophosphate presented significantly greater concentrations of Cd, Cr, Cu, Ni, and Zn whereas Cu, Ni, Pb, and Zn were found in greater contents in the natural phosphate 2. The reactive phosphate 3 presented the greatest quantity of Cd ( $145 \pm 13$  mg kg<sup>-1</sup>) and the natural phosphate 2, the highest quantity of Pb ( $234 \pm 9$  mg kg<sup>-1</sup>).

The tested methods can be applied in studies concerning heavy metals in samples of brazilian natural phosphate fertilisers phosphates (FN1 e FN2) showed an average of 8.7 mg kg<sup>-1</sup> of Cd content, non-brazilian ones presented higher values, in average, 77 mg kg<sup>-1</sup> Cd (Campos et al., 2005). Phosphate rocks presented contents between  $5 \pm 0,6$  e  $145 \pm 13$  mg kg<sup>-1</sup> (Figure 1). Those values are in the range cited by Kabata-Pendias & Pendias (2001) phosphate fertilisers, 0,1–170 mg kg<sup>-1</sup> of Cd. Amaral Sobrinho et al. (1992) encountered lower contents for apatite rocks (2–7 mg kg<sup>-1</sup> Cd). As for Cu content, there was no difference between the extraction methods (**TABLE 3**). For Ni and Zn contents, there was no statistical difference between USEPA 3051A and USEPA 3050B, but they were superior than the Embrapa method (1999). The USEPA 3050B extracted more Cd than other methods, while for Cr contents, Embrapa method extracted the most.

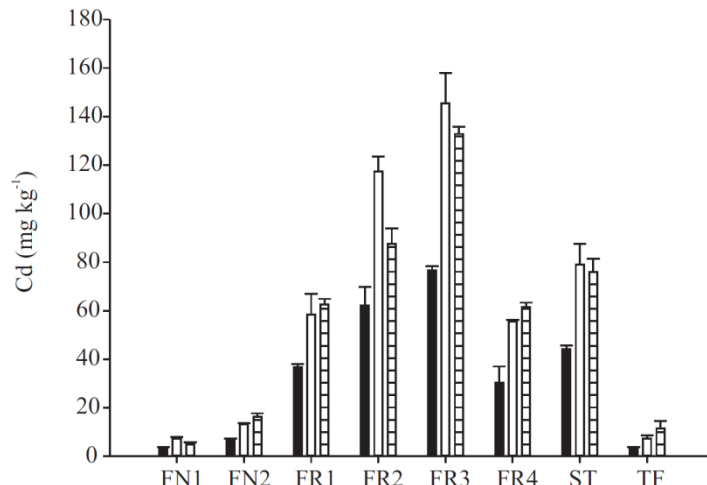


Figure 1 - Average contents of Cd in brazilian natural phosphates FN1 and FN2, brazilian triple superphosphate and reactive non-brazilian phosphates FR1, FR2, FR3 and FR4, determined by methods USEPA 3051A (in black bars), USEPA 3050B (white bars) and EMBRAPA (dashed bars). Higher traces are the standard deviation of average values. Modified from Campos et al., 2005.

#### 5. GUIDING VALUES IN BRAZIL AND EUROPE

The Brazilian Environmental Council (CONAMA), through Resolution n.420/ 2009, established that each state in the country must determine quality reference guiding values for heavy metal concentrations based on a set of soil samples that represent the local geomorphology, lithology and pedogenic processes. This was decided because the international values or those from other regions might result in erroneous interpretation regarding areas suspected of

contamination. The Brazilian resolution establishes three types of guiding values: Quality Reference Values (QRVs), which should be determined by each state, Prevention Values (PVs) and Investigation Values (IVs), that are established and is valid for the whole country. In São Paulo state the limits were determined by CETESB mainly in topsoil and are, in mg kg<sup>-1</sup> (As -15), (Cd - 1.3), (total Cr - 75), (Cu - 60), (Hg - 0.5), (Ni - 30), (Pb - 72) and (Zn - 1,900) to class it at risk.

Cadmium in fertilizer phosphate rock, animal manures and land applied municipal sewage sludge is increasingly regulated in different parts of the world. Initially, cadmium was regulated primarily because of concerns about the metal leaching from fertilized soil into ground and surface waters. However, as knowledge increased about cadmium as a major human toxicant in our food, the emphasis on allowable cadmium in fertilizer has shifted to the amount of uptake seen in agricultural commodities grown on soils that include added cadmium in fertilizer. The limits on cadmium in fertilizer have taken several forms, most commonly: (i) a limit on the amount of cadmium allowed per unit of phosphorous (mg Cd Kg<sup>-1</sup> P) and (ii) a limit on the amount of cadmium allowed per unit of phosphorous oxide (mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>). This limit is used because American Plant Food Control officials adopted P<sub>2</sub>O<sub>5</sub> as the standard for guaranteed analysis of phosphorous content based on an ancient measurement procedure. The method was replaced, but the form designation is in use today in fertiliser packs. This measure may be ambiguous because the actual phosphorous applied to soil is about 44 % of the P<sub>2</sub>O<sub>5</sub> weight percentage designated on pack.

In The Netherlands the Soil Quality Regulation (2006) and the Soil Remediation Circular (2009) focuses on the elaboration of the remediation criterion used to determine whether urgent remediation is necessary. To be compared worldwide, all values presented in **TABLE 2** are taken only from soils with 10% of organic matter and 25% of Clay. This restriction is due to strong correlation between HME, clay and SOM contents. Higher the SOM content, higher levels of HME. Sandy soils are poor in HME than argillic ones and the SOM. The highest allowed levels in EU community are 3 mg Cd kg<sup>-1</sup>, 150 mg Zn kg<sup>-1</sup>; 140 mg Cu kg<sup>-1</sup> and 50 mg Pb kg<sup>-1</sup> (Chaudri et al., 1993). In Poland, those limits are, for arable soil 3 mg Cd kg<sup>-1</sup>, 300 mg Zn kg<sup>-1</sup> and 200 mg Pb kg<sup>-1</sup> (Chlopecka et al., 1996).

**Table 2** - Background values, Intervention Values and Maximum Values in soil in function of its destination (Soil Remediation Circular 2009 e Soil Quality Regulation 2006). Modified from Ribeiro (2013)

Elements	Background values) <sup>a</sup> (mg/kg)	Sediment <sup>a</sup> (mg/kg)	Max Values		Intervention Value) <sup>a</sup> (mg/kg)	Intervention Value) <sup>b</sup> (mg/kg)
			Maximum values for residential soil quality class) <sup>a</sup> (mg/kg)	Maximum values for industrial soil quality class) <sup>a</sup> (mg/kg)		
As	20	29	27	76	76	76
Cd	<b>0.6</b>	<b>0.8</b>	<b>1.2</b>	<b>4.3</b>	<b>13</b>	<b>13</b>
Cr total	55	100	62	180	180	-
Cu	40	36	54	190	190	190
Hg Total	0.15	0.6	0.83	4.8	36	-
Pb	-	-	-	-	-	4
Ni	50	85	210	530	530	530
Zn	140	140	200	720	720	720

Legend: a) Soil Quality Regulation 2006; b) Soil Remediation 2009.

According to EU recommendations, soil treated with sewage sludge should not contain more than 3 mg kg<sup>-1</sup> Cd (86/278/EC/12-6-1986). Soil Guideline Values (SGVs) for cadmium in the Netherlands, are presented according to land use in **TABLE 2**. The SGVs apply only to cadmium and its inorganic compounds. For residential and allotment land uses, SGVs are based on estimates representative of lifetime exposure. Although young children are generally more likely to

have higher exposures to soil contaminants, the renal toxicity of cadmium are based on considerations of the kidney burden accumulated over 50 years or so (Environment Agency, 2009). It is therefore reasonable to consider exposure not only in childhood but averaged over a longer time period.

## 6. PROPOSED REDUCTION OF CADMIUM CONTENTS OF PHOSPHATE FERTILISERS IN EU

European Commission recently proposed a regulation (European Union Regulation - EC 2016) envisaging stringent limits of cadmium in phosphate fertilisers. Besides the proposals of no action and general actions for market incentives, they are synthetically: (i) an initial limit of 60 mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> will apply as soon as the regulation comes into force; (ii) more stringent limit of 40 mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> will phase in three years later; (iii) the lowest limit of 20 mg Cd Kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> will come into force nine years after the regulation initiation and (iv) a new Regulation setting a Community limit value for cadmium content in phosphate fertilisers at 60 mg cadmium/kg P<sub>2</sub>O<sub>5</sub> decreasing over time to 40 and eventually 20 mg cadmium/kg P<sub>2</sub>O<sub>5</sub> if decadmiation becomes available on industrial scale.

A new Regulation converges to a common proposal: establish an EU limit value of 60 mg cadmium/kg P<sub>2</sub>O<sub>5</sub> as a starting point. This limit would take effect after an appropriate transition period of e.g. 2 to 3 years. Flexibility should be given to allow Member States to set limit values at either 40 or 20 mg cadmium/kg P<sub>2</sub>O<sub>5</sub> in the light of specific conditions in their territories. Fertilisers would be labelled to provide an indication which limit value for cadmium they comply with.

## 7. DISCUSSION AND CONCLUSIONS

The metallic elements tracks (Cd, Cr, Cu, Hg, Ni, Pb, Zn) are rapidly increasing in soils mainly due to the indiscriminate use of fertilisers and, recently, urban sewage sludge. As some of them are potentially toxic and present no agronomic interest, their presences generate a major concern. The agricultural use of the residual mud allows the recycling of precious components such as the organic matter and many nourishing elements of the plant (Logan and Harrison, 1995). Residual muds can replace or reduce the use of this imported and expensive fertilisers. Economic and environmental issues are in the center of this debate, and this paper intends to expose the main advances in the knowledge.

Muds are products susceptible to supply in the cultures of the nourishing elements useful for their growth and for their development. Furthermore, certain sewage sludge (composted or limed) can play the role of amendment, by allowing maintaining or to improve the structure of the ground, its biological activity or still control its acidity. Nevertheless, from an agronomic point of view, and provided that the farmer respects the agronomic advice, the economy on the purchases of fertilisers can be considerable.

The calculated Cd increase with the application of 200 kg ha<sup>-1</sup> of the FR3 incorporated in 0.1m of soil depth by but and would reach 0.094 mg kg<sup>-1</sup>, by the way, it would 111 applications to attain the intervention level of 10 mg kg<sup>-1</sup> de Cd of CETESB (2001). In the other hand, they noticed that in five years, Cd contents could double, from one average soil of 0.5 mg kg<sup>-1</sup> Cd (Campos et al., 2005).

The possibility of overcome the maximum permissible concentration, not only for Cd, but also for other elements evaluated, increases with larger quantities of phosphates fertilizers associated with sewage sludge and other fertilizers containing trace elements. Ramalho et al. (1999) availed the use of polluted water and phosphate fertilisers combined, and observed that soils that received 25 years of phosphate fertilisers, showed a noticeable increase of Cd (0.66 mg kg<sup>-1</sup>) when compared with control area (0.5 mg kg<sup>-1</sup>), without however elevate it to critical levels. The conditions that determine the adsorption capacity, such as pH, organic matter content, content of clay and oxides of Fe and Al, affect the availability and mobility of heavy metals present in phosphates (Abdel-Haleem et al., 2001). It is also important to consider local conditions that could lead to losses by erosion of soil particles enriched with heavy metals, transported to other areas or water bodies.



Current limits of cadmium on fertilisers in Brazil are insufficient to meet health and environmental protection goals. The states that have previously established base levels need to review recent research on the health effects of cadmium, the increment of cadmium in soils, and the contribution of fertiliser to cadmium loading in surface waters. These states should lead the way toward health protection adopting more stringent limits that certainly will reduce exposures and prevent adverse health effects.

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