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# BACKGROUND AND REFERENCE VALUES FOR THE CADMIUM CONTENTS OF BRAZILIAN SOILS COMPARED

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**Abstract:** The difficulty on quality assessment of soils arises is in part due to distinguish pollutant sources, natural or anthropogenic. Compare this different sources backgrounds and guiding values is very important to instruction on regulations and legislation in general, for heavy metals contents, among other chemical components, and are pointing to more restrictive use of cadmium-rich phosphate fertilisers in many countries. 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 work 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.

**Keywords:** soil, Brazil, heavy metals, cadmium, contamination, legislation, reference values, fertilisers

## 1. INTRODUCTION

Soil contamination by Heavy Metal Elements (HME) is largely due to agricultural practices, mining and metallurgy. The current paper has the purpose to analyze and compare how this major issue is receiving attention in Brazil and in some developed countries, their guiding values and behavior of some heavy metals in the soil, with emphasis in cadmium from fertilisers and mining industry; to compare protocols of sampling, methods of detection and regulations around the world and also 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 mineralization. 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 remains the HME generated through time by agricultural activities on the environment, particularly in Latosols over volcano-sedimentary basins. In the actual brazilian norm, the CONAMA Resolution Nº 420/2009, each state (federation) must determine the guiding values of prevention. 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).

Soil contamination by HME became a problem in large agricultural areas, especially in extensive plantations, with the continuous use of phosphate based fertilisers, rich in HME, especially cadmium. 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.

## 2. CADMIUM CONTENTS IN ROCKS, SOILS, FERTILISERS AND SEWAGE SLUDGE

The phosphate rocks which are mined in Brazil, Finland, Russia, and South Africa are mainly igneous rocks and have very low cadmium contents (sometimes below 10 $mg•kg^{-1}$). 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 are reaching frequently values of 60 $mg•kg^{-1}$ while in Morocco deposits, the most important supplier of Brazil and European Union (EU), the cadmium contents in fertilisers are above 60 $mg•kg^{-1}$. Most natural soils contain less than 1 $mg•kg^{-1}$ of cadmium resulted from the weathering of parent materials (Alloway, 1995). Generally lower levels are found in acid igneous rocks (granite average 0.09 $mg•kg^{-1}$) than basic (basalt average 0.13 mg•kg$^{-1}$). In seds, sandstone and limestone show lower levels, higher contents are found in black shales (0.3 to 219 mg•kg$^{-1}$), organic-rich seds or marine manganese nodules and phosphorite (Fergusson, 1990).

The average Cd content in soil surface is estimated to be 0.53 mg•kg$^{-1}$, with all higher values reflecting anthropogenic influences (Kabata Pendias and Pendias, 2001). Although uneven 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. 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.

Studies assessing natural contents of HME in some soil types of Brazil by Fadigas (2006), divides 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 Distrophyc 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 Chernosols, Luvisols, Eutrophic soils, and some samples of Yellow Latosol, Red-Yellow Latosol and Red Argisol. The sixth and seventh groups (6 and 7) 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 São Paulo-Brazil, in which the concentrations, in mg•kg$^{-1}$ are: Cd (0.5), Co (12.5), Cu (35.1), Cr (40.2), Ni (13.2), Pb (17), Zn (59.9). 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. It has the highest concentration of SOM (Soil Organic Matter) and microorganisms and is where most of the biological soil activity occurs. Plants generally concentrate their roots there to obtain nutrients.

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

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

[1] 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.
[2] Mean upper quartile between groups

Phosphate fertilisers contain between 5 and 100 mg•kg$^{-1}$ Cd and up to 300 mg•kg$^{-1}$ Cd may be present in sewage sludge. Cadmium is a trace element in fertilisers, which have been applied extensively to arable and pasture land around the world. In United Kingdom (UK) the European Risk Assessment Report (ECB, 2007) related that current fertilisers contain around 79 mg•kg$^{-1}$ 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 tonns of cadmium are added to agricultural soils each year from fertiliser use European Union Regulation (EC, 2007). It was concluded that this average cadmium content of european fertilisers, 138 mg•kg$^{-1}$, would lead to a radical increase in the concentrations of cadmium in soil and crops, therefore 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 K. This difference is due to the higher P fixation in tropical soils, with high Fe-Al oxides (Raij, 2003). The Brazilian consumption of $P_2O_5$ 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 their Cd contents are lesser than 2.0 mg•kg$^{-1}$ Cd. The brazilian phosphate rock from Catalão-GO contains 4 mg•kg$^{-1}$ of Cd, 19 mg•kg$^{-1}$ Cr and 58 mg•kg$^{-1}$ Pb, and the fine apatitic concentrate from Araxá-MG shows contents of 7 mg•kg$^{-1}$ Cd, 44 mg•kg$^{-1}$ Cr and 127 mg•kg$^{-1}$ Pb (Gabe and Rodella,1999). Amaral Sobrinho et al. (1992) presented typical ranges of HME in phosphate fertilisers as 0.1–170 mg•kg$^{-1}$ Cd, 7–225 mg•kg$^{-1}$ Pb, 7–38 mg•kg$^{-1}$ Ni, 1–300 mg•kg$^{-1}$ Cu and 50–1450 mg•kg$^{-1}$ Zn.

## 3. HEAVY METALS EXTRACTION ANALYTICAL METHODS COMPARED

Comparison of three extraction procedures was carried out 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 the market in Brazil. 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 potentially bioavailable of a certain pollutant (Fig. 1).

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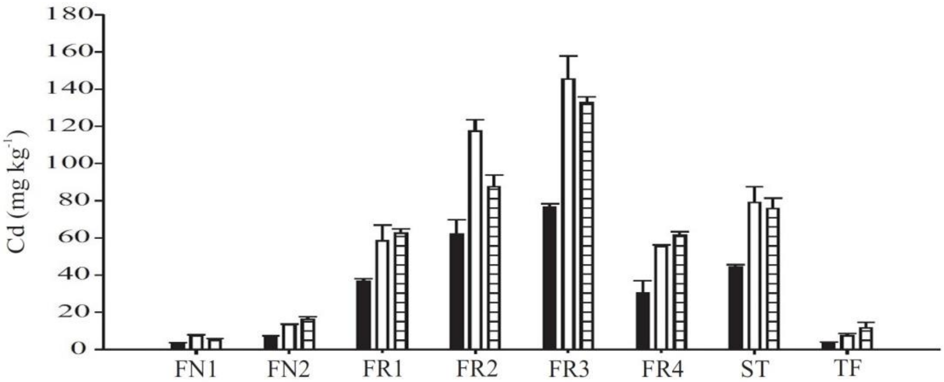


**Fig. 1**. Average contents of Cd in brazilian natural phosphates FN1 an FN2, brazilian triple superphosphate and reactive non-brazilian phosphates FR1, FR2, FR3 and FR4, determined by different methods: USEPA 3051A (in black bars), USEPA 3050B (white bars) and EMBRAPA (dashed bars). Higher traces are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

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 Brazilian method (EMBRAPA, 1999) uses approximately 0.5 g of the material added to 20 ml of HCl 2 mol•l$^{-1}$. The quantification of trace elements content was performed 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 FN2. The reactive phosphate FR3 presented the greatest quantity of Cd (145±13 mg•kg$^{-1}$) and the natural phosphate FN2, the highest quantity of Pb (234±9 mg•kg$^{-1}$).

The tested methods can be applied in studies concerning heavy metals in samples of brazilian natural phosphate fertilisers phosphates (FN1 e FN2) which showed an average of 8.7 mg•kg$^{-1}$ of Cd content, while non-brazilian ones presented higher values, in average, 77 mg•kg$^{-1}$ Cd (Campos et al., 2005). Phosphate rocks presented contents between 5±0,6 and 145±13 mg•kg$^{-1}$ (Figure 1). Those values are in the range cited by Kabata Pendias and Pendias (2001) for phosphate fertilisers, namely 0,1–170 mg•kg$^{-1}$ of Cd. Amaral Sobrinho et al. (1992) encountered lower contents for apatite rocks (2–7 mg•kg$^{-1}$ Cd).

For Cu content, there was no difference between the extraction methods. 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.

## 4. GUIDING VALUES IN BRAZIL AND EUROPE

The Brazilian Environmental Council (CONAMA, 2009), through the Resolution n.420/2009, established that each state in the country must determine its own guiding values for heavy metal concentrations based on a set of soil samples that represent the local geomorphology, pedology and lithology. This was decided because the international values, or those from other regions, might result in erroneous interpretation regarding areas suspected of being contaminated. 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), which are established and are valid for the whole country. In São Paulo state the risk limits were recent determined by CETESB (2016) mainly in topsoil and are, in mg•kg$^{-1}$, as follows: (As -15), (Cd -1.3), (total Cr - 75), (Cu - 60), (Hg - 0.5), (Ni - 30), (Pb - 72) and (Zn - 1,900).

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. 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 minerals. This restriction is due to strong correlation between HME, clay minerals 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•kg$^{-1}$ Cd, 150 mg•kg$^{-1}$ Zn;140 mg•kg$^{-1}$ Cu and 50 mg•kg$^{-1}$ Pb (Chaudri et al., 1993). In Poland, those limits are, for arable soil 3 mg Cd kg$^{-1}$, 300 mg•kg$^{-1}$ Zn and 200 mg•kg$^{-1}$ Pb (Chlopecka et al., 1996).

According to the EU recommendations, soil fertilised with sewage sludge should not contain more than 3 mg•kg$^{-1}$ 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.

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

| Elements | Background values) [a] (mg kg-1) | Sediment [a] (mg kg-1) | Max Values mg kg-1 | | Intervention Value) [a] (mg kg-1) | Intervention Value) [b] (mg kg-1) |
|---|---|---|---|---|---|---|
| | | | Residential [a] | Industrial [a] | | |
| As | 20 | 29 | 27 | 76 | 76 | 76 |
| **Cd** | **0.6** | **0.8** | **1.2** | **4.3** | **13** | **13** |
| 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 |

The SGVs apply only to cadmium and its inorganic compounds. For residential (10 mg Cd kg$^{-1}$) allotment (1.8 mg•kg-1 Cd) and commercial (230 mg•kg$^{-1}$ Cd) 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.

## 5. PROPOSED REDUCTION OF CADMIUM CONTENTS OF PHOSPHATE FERTILISERS IN EUROPEAN UNION

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, the limits are synthetically: (i) an initial limit of 60 mg•kg$^{-1}$ Cd will apply as soon as the regulation comes into force; (ii) more stringent limit of 40 mg•kg$^{-1}$ Cd will phase in three years later; (iii) the lowest limit of 20 mg•kg$^{-1}$ Cd 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•kg$^{-1}$ Cd decreasing over time to 40 and eventually 20 mg•kg$^{-1}$ Cd if decadmiation becomes available on industrial scale.

A new Regulation converges to a common proposal: establish an EU limit value of 60 mg•kg$^{-1}$ Cd 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•kg$^{-1}$ 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.

## 6. DISCUSSION AND CONCLUSIONS

The metallic elements tracks (Cd, Cr, Cu, Hg, Ni, Pb, Zn) are rapidly increasing in soils with the indiscriminate use of fertilizers, manures and 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 these 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.

The estimated Cd increase with the application of 200 kg ha$^{-1}$ of the FR3 incorporated in 0.1 m depth of soil would reach 0.094 mg•kg-1, and in that way needs 111 applications to attain the intervention level of 10 mg•kg$^{-1}$ Cd (CETESB 2016). In the other hand, they noticed that in five years, Cd contents could double, from one average soil of 0.5 mg•kg$^{-1}$ Cd (Campos et al., 2005).

The possibility to attain the maximum permissible concentration, not only for Cd, but also for other evaluated elements, 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$^{-1}$) when compared with the control area (0.5 mg•kg$^{-1}$), 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.

The ground contamination by heavy metals elements is a major environmental problem for two main reasons. Beside the 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 distinct geologic grounds and a long residence time in soils (Echevarria and Morel, 2006).

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.

## REFERENCES

Abdel-Haleem A.S., Scroon A., El-Bahi S.M., Zohny E. (2001) Heavy metals and rare earth elements in phosphate fertilizer components using instrumental neutron activation analysis. Applied Radiation and Isotopes, v. 55, p. 569-573.

Alloway B.J. (1995) Cadmium. In: Alloway B.J (ed.) Heavy Metals in Soils (2nd ed.). London: Blackie Academic & Professional. 368 p.

Amaral Sobrinho N.M.B., Costa L.M., Oliveira C., Velloso A.C.X. (1992) Metais pesados em alguns fertilizantes e corretivos. Revista Brasileira de Ciência do Solo, v. 16, p. 271- 276 .

Amaral Sobrinho N.M.B. (1993) Interação dos metais pesados de resíduos siderúrgicos com um podzólico Vermelho Amarelo [Interaction of Heavy Metals from siderurgy waste with Red-Yellow Podzolic sol]. Viçosa UFV. Dsc.Thesis, 163 p.

Campos M.L., Pierangeli M.A.P., Guilherme L.R.G., Marques J.j.. Curi N. (2003) Baseline concentration of heavy metals in Brazilian Latosols. Communications in Soil Science and Plant Analysis, v. 34, p. 547-558.

Casarini D. C. P. (2000) Proposta de valores de referência de qualidade e intervenção para solos e águas subterrâneas no estado de São Paulo. In: Sem. Internacional sobre Qualidade de Solos e Águas Subterrâneas, 2., SP. An. CETESB, 165p.

CETESB (Companhia de Tecnologia de Saneamento Ambiental) (2016) Relatório de estabelecimento de valores orientadores para solos e águas subterrâneas no Estado de São Paulo [Report of the establishment of guiding values for soils and underground water]. São Paulo: Secretaria de Estado do Meio Ambiente, 230p.

Chaudri A.M., McGrath S.P., Giller K.E., Rietz E., Sauerbeck D.R. (1993) Enumeration of indigenous Rhizobium leguminosarum biovar trifolii in soil previously treated with metal-contaminated sewage sludge. Soil Biol. Biochem., 25, p. 301-309.

Chlopecka A., Bacon J.R., Wilson M.J., Kay J. (1996) Forms of Cadmium, Lead, and Zinc in contaminated Soils from Southwest Poland. J. Environ. Qual., 25, p. 69-79.

Coelho M.R., Santos H.G., Silva E.F., Aglio M.L.D.O. (2002) Recurso natural solo [Natural resource soil]. Uso agrícola dos solos brasileiros. Rio de Janeiro, Embrapa Solos, p. 1-11.

CONAMA- Conselho Nacional de Meio Ambiente (2009) Resolução CONAMA n 420, de 28 de janeiro de 2009. Brasília, 16 p.

Echevarria G., Morel J.-L. (2006) Caractérisation de la biodisponibilité des éléments en traces dans les sols et validation de mesures fiables. Sols et environnement. Vandœuvre-lès-Nancy, 57 p.

ECB (2007) European Union Risk Assessment Report. Volume 72, Cadmium oxide and cadmium metal, Part 1 - Environment (EUR 22919 ENV). Luxembourg: Office for Official Publications of the European Communities, 2007.

Environment Agency (2009). Contaminants in soil: updated collation of toxicological data and intake values for humans. Cd Science Report SC050021/SR TOX7. Bristol: Environment Agency. 11p

EMBRAPA (1997) Manual de métodos de análise de solo. 2nd ed., Rio de Janeiro, 212 p.

Environment Agency (2009) Soil Guideline Values for cadmium in soil. Science Report SC050021 / Cadmium SGV. Bristol, UK: Environment Agency, 11 p.

European Union Regulation EC (2016) Limits for cadmium in phosphate fertilisers. Proposal for a Regulation of the European Parliament and of the Council amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009. 91 p.

Fadigas F. S., Amaral Sobrinho N.M.B., Mazur N., Anjos L.H.C., Freixo A.A. (2006) Proposição de valores de referência para a concentração natural de metais pesados em de solos brasileiros [Proposition of Reference Values to natural brazilian soils]. Revista Bras. de Eng. Agrícola e Ambiental v.10, n.3. p. 699-705.

Fergusson J.E. (1990) The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Oxford: Pergamon Press. p. 382–399.

Gabe U., Rodella A.A. (1999) Trace Elements in Brazilian Agricultural Limestones and Mineral Fertilizers. Communication Soil Science Plant Anal. 30(5/6), p. 605-620.

Greenwood N.N., Earnshaw A. (1997) Zinc, cadmium and mercury. Chemistry of the Elements, 29, p. 1201–1226.

Kabata-Pendias A., Pendias H. (2001) Trace Elements in Soils and Plants, Third Edition. Boca Raton: CRC Press LLC.

Langenbach T., Sarpa M. (1985) Teor de cádmio nos fertilizantes fosfatados brasileiros. Revista Brasileira de Ciência do Solo, v.9, p.179-181,

Logan T.J., Harrison B.J. (1995) Physical characteristics of alkaline stabilized sewage sludge (Nvitro soil) and their effects on soil properties. J. Environ. Quality, 24, p. 153-164.

Lope A.S. (2003) Reservas de fosfatados e produção de fertilizantes fosfatados no Brasil e no mundo [Phosphate reserves and phosphate fertiliser production in Brazil and the world]. In: Simpósio sobre fósforo na agricultura brasileira, 2003, Piracicaba. Anais. Piracicaba: Potafos/Anda,. 1 CD-ROM.

Raij B. van (2003) Fósforo no solo e interação com outros elementos. In: Simpósio sobre fósforo na agricultura brasileira. Piracicaba. Anais. Piracicaba: Potafos/Anda. 1 CD-ROM.

Ramalho J.F.G.P., Amaral Sobrinho N.M.B., Velloso A.C.X. (1999) Acúmulo de metais pesados em solos cultivados com cana-de-açúcar pelo uso contínuo de adubação fosfatada e água de irrigação. Revista Brasileira de Ciência do Solo, v.23, p. 971-979 .

Ribeiro M.A.C. (2013) Contaminação do solo por metais pesados [Soil contamination by heavy metals]. Lisbon. Universidade Lusófona de Humanidades e Tecnologias. Unpublished M.Sc Dissertation. 249 p.

Usepa (1998a) Method 3050B Available at: http:// www.epa.gov/SW-846/pdfs/3050b.pdf. Accessed in Feb. 2004.

Usepa (1998b) Method 3051A. Available at: http://www.epa.gov/SW-846/3051a.pdf. Accessed in March 2004.