

## Review article

# Methods for establishing baseline values for heavy metals in agricultural soils: Prospects for Colombia

## Metodologías para establecer valores de referencia de metales pesados en suelos agrícolas: Perspectivas para Colombia

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### Abstract

From an environmental perspective, the importance of heavy metals in soils is related to their toxicity either due to their accumulation or to any interaction between them and some of their specific properties. In each case, heavy metals can move through the soil profile and transfer into the trophic chain through water bodies or crops affecting human health. In developed countries, the establishment of baseline values has permitted improvements in the soil environmental management plans. Baseline values have become a control tool for environmental agencies to test the impact of heavy metals in a variety of agricultural activities. This article analyses different concepts related to heavy metals levels in agricultural soils and the effects of soil characteristics on their concentration, at the same time some methodologies to obtain specific baseline values from identification of the natural concentration are reviewed. It is included some prospects related to soil protection and remediation in Colombia. Currently, in Colombia there are no studies related to obtain baseline values of heavy metals in agricultural soils. For this reason it is necessary to get support from agencies such as the Ministry of Environment, Housing and Territorial Development and Ministry of Agriculture, in order to start and develop research in some primary agricultural sectors to guarantee the production and the environmental sustainability of soils.

**Key words:** Heavy metals, soil pollution, soil remediation.

### Resumen

Los impactos ambientales de los metales pesados en los suelos están relacionados con su carácter tóxico cuando se acumulan o cuando interactúan con algunas propiedades específicas, se movilizan a través del perfil a la cadena trófica mediante los cuerpos de agua o los cultivos y pueden llegar a afectar la salud humana. En países desarrollados, el establecimiento de valores de referencia de estos metales ha permitido el mejoramiento de la planeación y gestión ambiental del recurso suelo, convirtiéndose en un instrumento de control para las entidades ambientales que ha permitido evaluar el impacto en diferentes actividades agrícolas. En este artículo se analizan diferentes conceptos relacionados con los niveles de metales pesados en suelos agrícolas y la incidencia de las características edafológicas en su concentración, se revisan, igualmente, algunas metodologías para derivar valores de referencia específicos aplicables a suelos agrícolas colombianos y se plantean algunas perspectivas orientadas a la protección y recuperación de suelos en el país. En Colombia en la actualidad no se cuenta con criterios y estándares de calidad para metales pesados en suelos agrícolas, es por esto que se hace necesario gestionar el apoyo de entidades gubernamentales con el fin de iniciar y desarrollar investigaciones en diferentes sectores agrícolas primarios, contribuyendo de esta forma a garantizar la producción agrícola y la sostenibilidad ambiental del recurso suelo.

**Palabras clave:** Contaminación de suelos, metales pesados, recuperación de suelos.

## Introduction

Agricultural soil properties and characteristics, and environmental conditions affect the physicochemical properties of stored substances and determine their buffer capacity to the point where they can behave as toxic substances or contaminants, thus affecting ecosystem and biodiversity sustainability and preservation (Valladares *et al.*, 2009).

Due to the technological needs of modern agriculture and to changes in soil usage patterns, the different agricultural practices had been centered in yield improvement and plague and disease control by using phytosanitary products with positive results in crop yield but, due to their indiscriminate use, they have accelerated the incorporation of different substances containing heavy metals which may be toxic for crops, degrade soils, reduce biodiversity and contaminate water bodies (Micó, 2005; Díez, 2006; Díez *et al.*, 2009)

The environmental interest for heavy metals in agricultural soils is related to their accumulative character, their reduced biodegradability, their ability to accumulate in the soil profile until toxic concentrations in an unnoticed way, and their interaction with different soil properties which determine their accumulation, mobility and availability to other components of the ecosystem (Alloway 1995; Assadian *et al.*, 1998; García y Dorronsoro, 2005; Miller *et al.*, 2004; Dach y Starmans, 2005; Abreu *et al.*, 2005; Mapanda *et al.*, 2005; Lee *et al.*, 2006; Micó *et al.*, 2006; Hernández *et al.*, 2007; Yay *et al.*, 2008).

Soil contamination by heavy metals could persist hundreds or thousands of years, even after their incorporation had stopped. In metals such as Cd, Cu and Pb the mean life in soil could be from 15 to 1100, 310 to 150, and 740 to 5900 years, respectively, and their concentrations are influenced by soil type and relative mobility in function to the physicochemical properties, weather and topography (Alloway 1995; Mapanda *et al.*, 2005; Peris, 2006; Borges Júnior *et al.*, 2008; Krishna y Govil, 2008; Dantu, 2009).

In relation with toxicity, heavy metals could be absorbed by crop roots or lixiviated to the aquifers, causing subterranean waters

contamination, and in such way they become toxic for plants, animals and humans through the food chain. In the later years there has been a major awareness to the adverse effects of these metals, mainly to the child population, leading to the government of developed countries, mostly in highly populated regions where soils are intensively used, to renew their legislation in order to reduce heavy metals' concentration in the environment (Granero y Domingo, 2002; Hernández *et al.*, 2007; Udovic *et al.*, 2007; Borges Júnior *et al.*, 2008; Krishna y Govil, 2008; Dantu, 2009; Sun *et al.*, 2010).

In the European Union, e.g. in the last two decades, the heavy metals' contamination problem had led to the decision and planning makers on this resource to require more information on the soil quality for the different purposes (organic agriculture, agritourism, urbanism, subterranean waters protection area, remediation, among other uses). This has allowed an adequate planning and development on the soil as a resource in the different countries, by means of identifying the anthropogenic charge of heavy metals in the ecosystems, elaborating contamination risk maps to identify suitable areas for the diverse agricultural uses, and determining the maximum heavy metals' concentrations allowed in an established area. Nevertheless, before planning any solution to soil contamination by heavy metals, a distinction between those coming from natural sources and the ones derived from human activity has to be done (Micó, 2005; Romic *et al.*, 2007).

The quality criteria for soil heavy metals – reference values- have become the main requisite for the protection and preservation of agricultural soils, also they allow the acknowledgment of the background levels or natural levels associated to the parental matter which has low or minimum anthropogenic activity (Pérez *et al.*, 2000; Fadigas *et al.*, 2006; Micó *et al.*, 2007). For this reason, different countries have started investigations with the aim of proposing reference values that are adapted to the specific soil characteristics of a given geographical area, to their degradation level, to their degree of technological development, and the regulatory framework for preservation and conservation of edaphic systems (Pérez *et*

*al.*, 2000; Castillo Carrión *et al.*, 2002; Gil *et al.*, 2002; Sánchez, 2003; Fadigas *et al.*, 2006; Peris, 2006; Micó *et al.*, 2007; Borges Júnior *et al.*, 2008; Brus *et al.*, 2009; Díez *et al.*, 2009; Gallardo y González, 2009; Gjoka *et al.*, 2010).

In agreement with the previous considerations, and having into account that the agriculture in this century should respond to the sustainability of the food chain and guaranty that the production technologies do not degrade the environment and fulfill the environmental requirements (Dach y Star-mans, 2005), this review gives an analysis of soil contamination by heavy metals, considering the definition criteria for reference values and the adopted methodologies in different countries to establish such quality standards towards preserving and improving soil quality. Finally, it is hoped that this analysis serves as a conceptual basis to explain different perspectives in order to let the scientific development of a specific legislative framework for heavy metals in soils of different agricultural subsectors in Colombia.

### Heavy metals in agricultural soils

Heavy metals are elements with density > 5 g/cm<sup>3</sup>. Generally, they are found in small amounts and they become toxic over a determined concentration threshold. Among these we have more than 20 elements important to living beings because they are essential to complete their life cycle (Díez, 2006; Camilotti *et al.*, 2007). These metals are classified into two groups: the first one considers living being (plants, animals and human) essential

micro-nutrients e.g. Co, Cr, Cu, Fe, Mn, Ni and Zn, but they can be toxic when exceeding determined levels; and the second one is composed by those that do not represent a known biological function and after determined levels cause serious dysfunctions in organisms, including human beings, such as Cd, Pb, As and Hg (Moolenaar *et al.*, 1997; García y Dorronsoro, 2005; Granero y Domingo, 2002; Peris, 2006; Recatalá *et al.*, 2010). Table 1 shows the main characteristics of some heavy metals of interest for agriculture and the environment.

Generally, heavy metals in agricultural soils are in low concentrations and are highly variable depending on the composition of the parental material and the formation and evolutionary processes in the soil. Such concentrations can be modified or enhanced by diverse agricultural practices, i.e. mineral fertilizers and agrochemicals applications, organic fertilizers from animals or plants, organic amendments, residual water from water treatment plants, and domestic residual waters, which are the main sources of these metals (Alloway 1995; Granero y Domingo, 2002; Nicholson *et al.*, 2003; Sánchez, 2003; Alonso-Rojo *et al.*, 2004; García y Dorronsoro, 2005; Abreu *et al.*, 2005; Peris, 2006; Battaglia *et al.*, 2007; Battaglia *et al.*, 2007; Camilotti *et al.*, 2007; Rodríguez *et al.*, 2008; Yay *et al.*, 2008; Díez *et al.*, 2009; Valladares *et al.*, 2009; Gjoka *et al.*, 2010). Table 2 presents an estimate of the amount of heavy metals incorporated to the soil by diverse sources.

The accumulation of heavy metals in agricultural soils is a risk for organism life and human health, their negative effects

**Table 1.** Main characteristics of some heavy metals.

Heavy metal	Density (g/cm)	Atomic number	Normal level in soils (mg/kg)	Essential for living organisms	Toxic
Pb	11.3	82	20	—	A, P, H
Cd	8.7	48	0.35	—	A, P, H
Cu	8.9	29	30	A, P, H	P
Zn	7.1	30	90	A, P, H	P
Cr	7.2	24	40	A, H	P, H
Ni	8.9	28	20	A, P, H	A, P, H

A: Animals; P: Plants; H: Humans.

Source: Micó (2005).

depends on the metal concentration and the physical properties of soil (Gjoka *et al.*, 2010). To evaluate the environmental impact of these contaminant substances, in the latest years different researches have studied this problem and its correlation with the normal levels found in natural conditions (Moolenaar *et al.*, 1997; Granero y Domingo, 2002; Sánchez, 2003; Liu *et al.*, 2005; Mapanda *et al.*, 2005; Fadigas *et al.*, 2006; Micó *et al.*, 2006; Peris, 2006; Hernández *et al.*, 2007; Krishna y Govil, 2008; Dantu, 2009; Sun *et al.*, 2010), this has led to the identification of contaminated soils based on the definition of contamination threshold criteria, which, in turn, allowed the differentiation between the concentration of such elements in a natural soil and in one subjected to anthropogenic activity, their risk level, who is being affected, tolerance level and recuperation priorities (Castillo Carrión *et al.*, 2002; Fadigas *et al.*, 2006).

In this sense, when the buffer capacity is surpassed by a continue charge of contaminant substances or pH changes in the soil, heavy metals could be liberated and migrate to subterranean waters or stay bioavailable in the soil solution to be absorbed by plants through the roots (Micó, 2005). Additionally, the risk of heavy metals' movement to other ecosystem components (water and food) is related to the specific characteristics of each soil, such as content and type of clay, organic matter, cationic interchange capacity and other properties (Mapanda *et al.*, 2005). It is important to consider, in soil heavy metals' studies, that the total levels are a measurement of potential dangerousness of a soil in the future; however if the aim is to measure

the real dangerousness at the determination moment, the metals in the available or assimilable soil phase have to be measured (Tack *et al.*, 1997; Sánchez, 2003).

### Heavy metals background levels and reference values

As heavy metals are present naturally in the earth's crust, their soil distribution is conditioned by the natural concentration of the parental matter and by anthropological contributions; therefore, the establishment of heavy metals standard levels or reference values to evaluate soil contamination is the main requisite for the quality and protection of agricultural and ecological functions, and the main decision tool for future planning of soils. The definition of these levels will be related with the heavy metals dynamics in the soil and its characteristics that could modify toxicity thresholds (Pérez *et al.*, 2000; Sánchez, 2003; Brus *et al.*, 2009).

The geochemical background has been defined as the defects absence of an element or component in the soil, but it does not necessarily mean low concentration of such element or component. The natural background is the natural concentration of an element with low or minimum anthropogenic intervention which is associated with the soil parental matter (Diez, 2006). On the other hand, since it is almost impossible to find soils without human intervention, various studies have proposed the use of terms as *background* or *reference levels* to determine an element concentration with a significant degree of confidence; those levels establish

**Table 2.** Estimated contributions of heavy metals added to agricultural soils by different sources (mg/kg).

Heavy metal <sup>1</sup>	Phosphate fertilizers	Nitrogen fertilizers	Pesticides	Manure	Residual waters
Pb	7 - 225	2 - 27	60	6.6 - 15	50 - 3000
Cd	0.1 - 170	0.05 - 8.5	1.38 - 1.94	0.3 - 0.8	2 - 1500
Cu	1 - 300	1 - 15	12 - 50	2 - 60	50 - 3300
Zn	50 - 1450	1 - 42	1.3 - 25	15 - 250	700 - 49000
Cr	66 - 245	3.2 - 19	13	5.2 - 55	20 - 40600
Ni	7 - 38	7 - 34	0.8 - 14	7.8 - 30	16 - 5300

<sup>1</sup> Sources of these metals: Fertilizers, Water treatments plant residues, agrochemicals, composting, irrigation water.

**Source:** Sánchez, 2003; Micó, 2005; Peris, 2006; Delgado, 2008.

the total concentration of an element for a region and a time period, including general or area activities such as atmospheric depositions or fertilization (Horckmans *et al.*, 2005; Peris, 2006; Micó *et al.*, 2007). Reference levels are the maximum acceptable concentration without having adverse effects on soil organisms, those levels take into account aspects like metals availability, their physicochemical properties and land use (Micó *et al.*, 2007; Alloway 1995; Sánchez, 2003; Horckmans *et al.*, 2005; Díez, 2006; Fadigas *et al.*, 2006; Peris, 2006; Gjoka *et al.*, 2010).

Before a soil is declared contaminated it is required to establish its quality by determining its heavy metals background levels, which allows the adoption of adequate criteria in cleaning work and remediation of contaminated soils (Alonso-Rojo *et al.*, 2004; Díez, 2006; Micó *et al.*, 2007). Most of the reference values proposed in different regions of the world, based on background levels, have been established with the measurement of total metal concentration, without considering that metal toxicity depends on its mobility and bioavailability in the soil (Díez, 2006; Micó *et al.*, 2007).

To analyze the degree of advance in the research done on soil heavy metals' reference values is essential to present the evolution of the legislative framework on heavy metals contamination in soil which started in the 70's. It was in Europe where the environmental awareness emerged due to the increasing agriculture development, it grew from 200.000 hectares in organic crops in 1980 to 3.8 million hectares in 2000, which implied an increase in the vulnerability to heavy metals contamination (Dach and Starman, 2005).

The basic guidelines for soils in Europe are based on the Soil Chart, promoted by the European Council in 1972 and reaffirmed internationally in the Earth Summit in Rio in 1992, in which the participant countries sign a series of declarations on soil protection. In April 2002, the European Community Commission on Environment promulgated the document *Towards a strategy for soil protection* in the European Union, which included, as priority goal, the evaluation of soil contaminants based in their

concentration analysis, their environmental behavior and the exposition mechanisms. However, in September 2006 the commission established that there are 3.5 million places that are potentially contaminated and, therefore, it is important to keep protecting and using sustainably the soils adopting restraints on the source and restoring degraded soils (Castillo Carrión *et al.*, 2002; COM, 2002; COM, 2006; Micó *et al.*, 2007).

The country with more experience and development in soil protection against contamination is The Netherlands, which by means of the Ministry of Housing, Spatial Planning and Environment (NMHSPE) elaborated quality standards for soil and water in 1991, and reference and intervention values for soil quality in 1994. The reference values proposed for soils (Table A-B-C or "Dutch list" from the Dutch Ministry of Public Health, published in 1987 and review in 1991 and 1994) correspond to the 95 percentile value of the concentration found in different natural reservoirs of that country; in such scale, a reference value of "A" represents the lowest level of risk below which any land use is possible; values between "A" and "C" define the quality of soils that need to be considered for remediation; above the "C" level or intervention value, remediation actions are required to start (Pérez *et al.*, 2000; Castillo Carrión *et al.*, 2002; Sánchez, 2003; Brus *et al.*, 2009).

For Spain, the Spanish Royal Law 9/2005 established the criteria to declare a soil as contaminated, it includes the generic reference levels for ecosystems and human health protection in terms of land use, and also the criteria for its estimation, the development of toxicity test and risk analysis. According to this law, the reference values for metals will be adopted from the sum of the average concentration plus the double of the typical deviation on the existing concentrations in neighbor no-contaminated soils with similar geological substrates (BOE, 2005; Micó *et al.*, 2007; Recatalá *et al.*, 2010).

The official criteria for heavy metals contamination used to evaluate soil quality in Poland were developed by the Soil Science Institute in Pulawy. They included six heavy metals (Cd, Cu, Cr, Ni, Pb and Zn) and it established contamination categories: 1) light,

2) moderate, 3) considerable, 4) highly contaminated and 5) extremely contaminated. The first two categories are considered safe for the human health and the environment (Sánchez, 2003; Dach y Starmans, 2005). In the USA, the USEPA developed in 1996 the document “Soil Screening Guidance” in order to accelerate and facilitate the evaluation and cleaning of soils. In this document was included the methodology to determine the risk and exploration levels for contaminants in soils that allows the identification of environmental interest areas. These regulations are based on the policies for determining the risk assessment and, determine the background levels and the study of toxicity on humans and the environment (Sánchez, 2003).

Table 3 presents the different reference values for heavy metals that have been proposed for the recuperation and protection of agricultural soils in different world regions. The values are associated with the natural conditions for each soil type, thus the importance of their determination at a local level, avoiding copying to use in other regions in order to avoid misinterpretations of heavy metals contents on agricultural soils. Hence, the establishment of contamination cannot be done in a generic way for all types of soil, but

it must be beard in mind their type, composition and actual or potential use. The above interpretations allows the affirmation that the heavy metal contents in soils is highly variable, as such it is inadequate to establish a general criteria because the background levels could be higher or lower (Tack *et al.*, 1997; Sánchez, 2003; Horckmans *et al.*, 2005; Fadigas *et al.*, 2006).

### Methodologies to obtain reference values of heavy metals on agricultural soils

#### Criteria to establish background levels

Background levels of heavy metals in a geographical area could be determined by using concentration values intervals where the majority of sample data will be placed representing the values associated, mainly, to the soil parental matter or soils with low anthropogenic intervention. For that reason, different anthropogenic activities or intensive agricultural practices can elevate the total content of heavy metals, leading to conflicting values associated to specific contamination which generally requires a careful analysis for a correct background levels determination (Brus *et al.*, 2002; Peris, 2006).

Before the derivation of heavy metals

**Table 3.** Reference values of heavy metals in different regions (mg/kg).

City	Pb	Cd	Cu	Zn	Cr	Ni	Reference
The Netherlands	85	0.80	36	140	100	35	Lista Holandesa de Valores, 1994 (25% clay , 10% organic matter ) cited by (Brus <i>et al.</i> , 2009)
Málaga - Spain	69	0.50	65	132	132	58	(Castillo Carrión <i>et al.</i> , 2002)
Granada - Spain	36	-	26	76	66	20	(Díez <i>et al.</i> , 2009)
Brasil	17	0.5	35.1	59.9	40.2	13.2	(Fadigas <i>et al.</i> , 2006)
Almería - Spain			25	394			(Gil <i>et al.</i> , 2002)
Alicante - Spain	28	0.7	28	83	36	31	(Micó <i>et al.</i> , 2007)
Madrid - Spain	88	0.84	34	109	-	-	(Pérez <i>et al.</i> , 2000)
Medina del Campo Valladolid - Spain	13.78	0.44	9.41	33.44	16.14	9.81	(Sánchez, 2003)
Tirana - Albania	85.5	0.7	36.3	151	113.7	41.9	(Gjoka <i>et al.</i> , 2010)
China	37.5	0.43	31.7	117.7	58.9	27.5	(Wei y Yang, 2010)
South Hyderabad - India	20	-	35	71	35	20	(Dantu, 2009)
Worldwide average in soils	10 - 84	0.06 - 1.1	6 - 80	17 - 125	7 - 221	4 - 55	(McBride, 1994)

background levels on a region it is needed to assure the development of an accurate soil sampling phase and sample analysis. In the development of the process is necessary to ensure both the quality of the samples taken as aspects of the sampling procedure, hypothesis of contamination distribution and optimal simple size. These aspects are of vital importance to get confident data in the analysis phase which is normally done by atomic absorption spectrophotometry (AAS) and inductively coupled plasma (ICP) (USEPA, 1996, USEPA, 1997; De Miguel *et al.*, 2002).

The results coming from the analysis phase in the laboratory are the supplies for heavy metals background levels determination in soils, and different statistical methods are used for their derivation, e.g. mean, standard deviation, minimum and maximum. In some studies to determine heavy metal concentration the arithmetic mean has been used if they follow a normal distribution, for a log-normal distribution they have used the geometrical mean, and the median if it is a not-normal distribution. Other authors use percentiles to analyze a not-normal distribution (Esser, 1996; Díez, 2006; Peris, 2006). In the same way, in order to declare a soil as not contaminated by heavy metals, regression equations have been used to establish a correlation between some soil properties such as, clay percentage, organic matter content and maximum heavy metal concentrations (Díez, 2006). In The Netherlands the background level determination was done taking into account the soil nature and the analysis was made in function of clay percentage (H) and organic

matter (L). Table 4 includes the equations used to determine background levels ( $\text{mg kg}^{-1}$ ) in agreement with the Dutch criteria (Sánchez, 2003).

**Criteria to derivate the reference values**

Reference values are coming from the heavy metals background level determination in no-contaminated soils, the background levels increase on a statistical value that reflect the variability in the normal concentration found on soils. Different regions of the world have proposed diverse methodologies (Table 5) to determine the reference values which, in turn, have allowed the development of legislative frameworks for soil heavy metal contamination prevention and protection (De Miguel *et al.*, 2002; Peris, 2006; Gallardo and González, 2009).

**Descriptive statistical methods**

In the establishment of reference values for heavy metals in soils simple statistical descriptive parameters such as the mean, median and maximum value of concentration in a region, are used. From these data the reference values are derived. In general, generic reference data have been proposed that could be applied to any area of study, independently from the soil characteristics and specific reference values, these values are determined in function of the edaphic characteristics (Peris, 2006).

The statistical method widely used to obtain reference values is from the equation “X+nDE” where X is the mean value of the

**Table 4.** Calculation equations for background levels determination of heavy metals in soils in The Netherlands

Element	Calculation equations in soils	Element	Calculation equation in soils
Antimony	3.0	Mercury	$0.2 + 0.0017 (2H + L)$
Arsenic	$15 + 0.4 (L+H)$	Molybdenum	0.5
Barium	$30 + 5H$	Nickel	$50 + L+H$
Beryllium	$0.3 + 0.0333H$	Selenium	0.7
Cadmium	$0.4 + 0.007 (H + 3L)$	Thallium	-
Chrome	$50 + 2H$	Tin	$4 + 0.6H$
Cobalt	$2 + 0.28H$	Vanadium	$12 + 1.2H$
Copper	$15 + 0.6 (L + H)$	Zinc	$50 + 1.5(2H + L)$
Lead	$50 + L+H$		

Source: Sánchez. 2003.

background levels and DE is the normal standard deviation of the heavy metal concentration. When the data follows a normal distribution, 95% of the data would be included in the interval  $X \pm 2DE$  which is the value adopted in Spain with the Royal Law 9/2005 for the generic reference value determination, while 99.7% would be around  $X \pm 3DE$ . In general, the arithmetic mean has been used for the  $X$  value when the data follows a normal distribution, if it is not the case, quartiles or percentiles 90, 95 and 99 are used in order to proposed the reference values (Pérez *et al.*, 2000; Facchinelli *et al.*, 2001; Castillo Carrión *et al.*, 2002; De Miguel *et al.*, 2002; Vázquez *et al.*, 2002; BOE, 2005; Micó, 2005; Fadigas *et al.*, 2006; Peris, 2006).

In the community of Madrid, the quartile formula ( $VR = [(3I - 1I) * 1.5]$ ) was used to

calculate the reference values in no-normal populations, where  $I$  is the corresponding quartile (De Miguel *et al.*, 2002; Micó, 2005). In Brazil the reference values for heavy metals were proposed with the determination of the data superior quartile (75% of accumulated frequency distribution) (Fadigas *et al.*, 2006).

### Probabilistic graphics

Probabilistic relationships permit the identification of conflicting values in soil heavy metals in order to separate normal or not contaminated populations from the contaminated ones, however, this methodology requires large sampling numbers. The procedure consists on a graphical representation of the element in function to the percentage of accumulated

**Table 5.** Summary of the methodologies used to determine reference values.

Methodology	Analysis type	Background levels expression or reference values	Main requisites
Statistical descriptive methods	Analysis of total content of heavy metals to determine background population.  Correlation with heavy metals background levels.	Use of statistical descriptive parameters (n, mean, standard deviation, minimum, maximum). Use of statistical value $X + nDE$ in function of the distribution type of the background population where "n" equals 2 or 3. Use of $X$ as arithmetical mean, geometrical mean or median for normal, log-normal or non-normal distribution, respectively. Use of percentiles (p90, p95, p99). Use of quartiles in non-normal populations.	Identification of conflicting values by means of box diagrams. Use of descriptive statistics in function of the data distribution type.  Identification of data distribution type (normal, log-normal, and non-normal) for each heavy metal.
Probabilistic graphics	Identification of background and contaminated populations	Graphic representation of heavy metal concentrations in function of accumulated frequencies %. Calculation of mean and standard deviation for both populations. The reference value will be given by the upper limit given in the $X + nDE$ equation.	Use of all data (including conflicting values). Graphic identification of the inflexion point. Identification of data distribution type. If the inflexion point is not found only one population comprises the background population. It requires larger sampling size.
Bootstrap method	Intervals of confidence for the reference values are obtained.	Use of statistical parameters of arithmetic mean ( $X$ ) and standard deviation ( $DE$ ). Repetitive calculations to get statistical data associated to one sample (resampling). Distribution of $X + nDE$ values on a histogram and calculation of confidence intervals. The mean value is taken as reference value.	Use of all data (including conflicting data). Generally, the obtained values are higher because conflicting data is used as well.
Lineal equations	Equations derived specific reference values in function of pedological characteristics.	Use of descriptive parameters from the background population (arithmetic mean, geometric mean or median for normal, log-normal and non-normal distribution, respectively). Lineal equation definition by means of the background population, the characteristics affecting metal concentrations and the lineal regression analysis.	Pedological parameters identification that are highly correlated with the studied metals (organic matter, clay, carbonates, anion interchange capacity, etc).

**Source:** Adapted from Sánchez (2003); Micó (2005); Diez (2006); Fadigas *et al.* (2006) and Peris (2006)



frequencies by means of a statistical program (Fleischhauer y Korte, 1990; Tobías et al., 1997). To determine the reference values using probabilistic graphics, it is represented a graphic on arithmetic or logarithmic scale with the metal concentration in the soil in function of the analyzed population distribution versus the values of accumulated frequency. The inflexion point on the graphic representation differences the background population (population 1) from data of possible areas with punctual contamination (population 2) by heavy metals – Figure 1 (Peris, 2006).

Getting values by using probabilistic graphics needs to take into account the following criteria: (1) the threshold value corresponds to the value or metal concentration which makes the closest to zero asymmetry, and as such, the heavy metals values under that inflexion point belong to the normal or not contaminated population; (2) data over the inflexion point represent abnormal values or coming from anthropic activities; (3) when the two populations are identified the arithmetic mean and standard deviation are calculated for each population, the upper limit for the reference value is established with a value of  $X \pm nDE$  for populations with normal distribution and  $\text{antilog } X \pm nDE$  for population with log-normal distribution; (4) when the data

asymmetry is close to zero the population belongs only to background population. In this case it is better to use descriptive statistics to get the reference value (Micó, 2005; Peris, 2006).

### Bootstrap method

This method is based on repetitive calculations in order to get statistical values (e.g. mean, median, maximum value) associated with a soil sample; establish the relationship between the results obtained from the sample and the population from which the sample was extracted, assuming that there is a similarity between the sample distribution of the data and the sample distribution found by the iterative process. The method uses a number of repetitive calculations to estimate the sampling distribution of the statistical value, for that reason, this methodology is not compelling to eliminate conflicting data to get a determined distribution in the populations. In that case it is adequate to extract conclusions related to the population characteristics from all the data obtained in the area of study (Efron y Tibshirani, 1998; Yu et al., 1998).

In Alicante, Spain, this method was used to calculate the confidence intervals of the reference value. In each resampling an arithmetic mean ( $X$ ) and standard deviation ( $DE$ ) were obtained, and the reference value

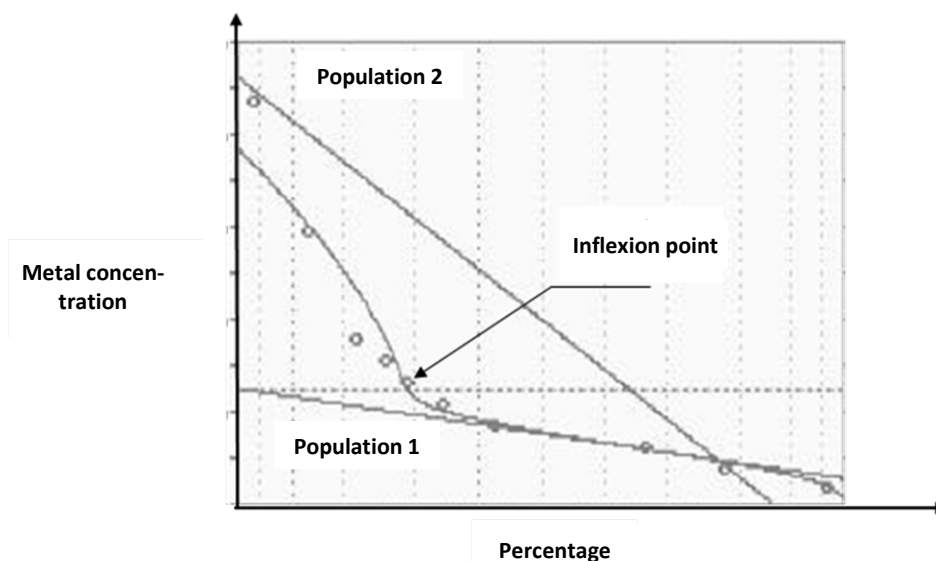


Figure 1. Probabilistics to determine reference values.

was calculated by the formula  $X+n*DE$ . In this study 999 resampling were determined and with the data a distribution histogram of the  $X+n*DE$  values was build; the upper and lower limits were calculated for a confidence level of 95%, and the reference value was the mean value of each metal. Generally, the reference values obtained with the bootstrap are slightly higher than the ones calculated by descriptive statistical methods because the conflicting values are considered (Micó, 2005).

### Lineal equations

In soil heavy metal studies lineal equations have been used to define the specific reference value of a study area, by relating the heavy metal concentration and the edaphic characteristics associated with metal retention-mobility; it is considered that the reference values coming from this methodology are similar to the ones coming from other methodologies (Vegter, 1995; Peris, 2006). Lineal equations consent the derivation of reference values for a specific case because they propose a correlation analysis between the heavy metal concentration and the content of some typical characteristics and pedological properties, such as organic matter, clay, carbonates and other parameters that could influence the heavy metal level on the soil profile. Table 6 summarizes the pedological characteristics used in different studies to propose the heavy metals reference values using lineal equations to correlate variables.

In order to calculate the generic reference values for heavy metals by using regression equations it has been proposed the equation  $VR= VP+ a A+ b B+...+zZ$  where VR is the

reference value, VP is the mean value of the trace element content in the studied soils and the arithmetic mean for heavy metals with normal distribution, the geometric mean for metals with log normal distribution or the median for metals with non-normal distribution; A, B, ..., Z are the mean value of the pedological parameters considered and; a, b, ..., z are the coefficients derived from the simple regression line slope (IHOBE, 1998; Vázquez *et al.*, 2002; Micó, 2005; Peris, 2006).

In agreement with the different analyzed methodologies and having into account the tendencies proposed mainly in European Union countries, in Colombian soils with no reference value is recommended to use the BOE annex VII (2005) which establishes the criteria and standards to declare contaminated soils. However, before using any of the described methodologies the conflicting data that could be associated to any punctual contamination should be identified, and the distribution type (normal, log-normal and non-normal) of the heavy metal data should be identified.

### Perspectives to implement reference values in Colombia

Modern societies require guaranties on soil environmental and agricultural sustainability, because its damage and degradation have been enhanced due to a higher demand on the resources and inadequate agricultural practices. In this sense, the study of soil contamination by heavy metals associated to intensive agricultural production systems has become an area of research with major advances in the last decades, because of the significant contributions of such substances

**Table 6.** Pedological characteristics used as standard soil in different studies to propose reference values using lineal equations

Main soil pedological characteristics		Country/ Region	Reference
Organic matter %	Other characteristics		
10	25% Clay	The Netherlands	Vegter (1995)
5	30% Clay	Basque country	IHOBE (1998)
2	30% Clay; 50% carbonates	Alicante Province	Micó (2005)
4.2	26% clay; 18.3 cmolc(+)/kg <sup>-1</sup> (CIC)	Castellon Province	Peris (2006)
1.25	7.9% carbonates, 13.4% Al oxides; 5.8% Fe oxides; 0.15% Mn oxides; 37% smectite.	Malaga Province	Castillo Carrión <i>et al.</i> (2002)

to the soil through diverse organic and chemical sources used in the different crop agricultural practices.

Since the 70's, Colombia has issued some general regulations to prevent and control soil contamination in areas of environmental concern; however, still, there are not specific regulations and laws in order to control soil protection as a result of anthropogenic contamination by heavy metals. Table 7 summarizes the main Colombian regulations which include actions to prevent and control soil contamination.

As tools for environmental planning and management, the Ministry of Environment, Housing and Territorial Development has developed environmental guides for the main agriculture subsectors in the country (cotton,

general rules to protect ecosystems but do not establish criteria to evaluate, prevent and reduce the impacts of heavy metals accumulation or mobilization due to fertilizers and pesticides, and their effects in the future.

In the framework of environmental responsibility and the prevention and protection of natural resources in Colombia, the universities and the environmental public bodies are the responsible to start studies oriented to determine reference values for heavy metals in soils; and the Ministry of Agriculture and the Ministry of Environment, Housing and Territorial Development are the government entities that have led the environmental regulations for soil protection in the different agricultural productive sectors of the country.

**Table 7.** Environmental legislation on soil resources in Colombia.

Year	Legislation	Scope
1974	Law 2811 of 1974 Natural resources code; articles 8, 178, 179, 180 y 182	It defines damaging factors on the environment such as degradation, erosion and soil slump, as well as the inadequate accumulation and disposition of residues, garbage and waste, and the inadequate use of dangerous substances. The obligation to apply management techniques rules to avoid loss or degradation, achieve recuperation and secure its conservation.  It defines that the agricultural, livestock, forestry and infrastructure activities which affect or can affect soils, are obliged to carry on the conservation and recuperation practices defined according to the regional characteristics. In the same way it sets out that soils subjected to physicochemical or biologic limitations that affect productivity should be recovered.
1991	Politic Constitution of Colombia, articles 360 and 361	It defines the conditions for non-renewable natural resources exploitation, the territorial entities rights on those. Also, it establishes the need to create a fund for mining promotion, environment preservation and investment projects.
1993	Law 99 of 1993 dispositions	It creates the Ministry of Environment, Colombian entity in charge of environmental and renewable natural resources management and conservation. It also organizes the Environmental National System (SINA) and defines the functions of the Ministry in relation to soil protection and conservation.
2001	Law 685 of 15 August, 2001, Mine code and other dispositions, article 194	It defines sustainability of renewable natural resources in the mining activity, with the duty to adopt and apply rules, restrains and decisions to regulate such activity.
2002	Law 1713 of 2002	It regulates the Integral Management of Solid Waste in Colombia and specifically the procedures and methods to prevent risks in the final disposition of the resources water, air and soil.

rice, banana, sugar cane, coffee, potato, fruits and vegetables). However, these guides define

Having into account that the actual situation of accumulated substances in

Colombian soils is unknown, which is a risk for human health, water resources and agriculture, the studies should be oriented to define a management plan for prevention of soil contamination by heavy metals and the sanitation and recuperation of contaminated soils. This plan should be led by environmental bodies in Colombia, and should include specific programs to identify and to make an inventory of the contaminated areas associated to the different anthropic activities and should use the required resources to finance and fulfill those objectives. The contaminated areas inventory will establish the physical, chemical and mineralogical characteristics of the agricultural soils and their influence in the heavy metals background levels.

To derive reference values for heavy metals it is suggested to make an initial comparative analysis of the different methodologies, in order to establish data behavior and quality standards for heavy metals in soils adjusted to the pedological characteristics of Colombian soils.

### Final considerations

- In the world, the establishment of reference values for heavy metals has become a tool for soil quality management and it is the main requisite of crop soils quality and protection since it allows discrimination between natural contributions of contaminants from parental matter (background level) and the ones derived from anthropic sources.
- There are different statistical criteria to derive heavy metal reference values in soil. The use of one or another methodology depends on the pedological characteristics of a given geographical area and the data type of distribution of contaminant concentrations.
- There is a need to develop studies in Colombia to establish specific reference values of heavy metals to use them as prevention, protection and recuperation tools for agricultural soils, mainly in agricultural subsectors that have had major technological and economic developments in the past century such as,

coffee, sugar cane, cotton, rice, banana, potato, fruits and vegetables.

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