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DEGRADATION, REHABILITATION,  
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## Use of Regulatory Documents for Assessing the Contamination of Soils with Heavy Metals

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**Abstract**—The chronological review and analysis of the existing regulatory documents relevant to the assessment of soil contamination with heavy metals have been presented. Attention has been given to the incorrect use of the term “total heavy metal content” and the method of its determination in a 5 M nitric acid solution recommended by some regulatory documents. The maximum permissible concentrations (MPCs) and tentatively permissible concentrations (TPCTPCs) for the total heavy metal contents are based on the above method; therefore, the conventional methods of determining the true total contents of heavy metals overestimate the degree of contamination. To avoid confusion, it has been proposed to call the content of a heavy metal in a 5 M nitric acid solution the “pseudototal” content and to compare the experimental results with the MPC or TPCTPC values only if the methods recommended by the regulatory documents were used.

**Keywords:** heavy metals, maximum permissible concentrations, tentatively permissible concentrations, soil contamination, hygienic norms, total content, clarke, background content, extraction procedure, mobile heavy metal forms

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### INTRODUCTION

Numerous instruments for the rapid and accurate determination of pollutants in soils have been proposed. Much high-performance analytical equipment has been on the market in the last years. A researcher is exposed to the temptation to use rapid instrumental methods for acquiring a large body of data on the environmental status of soils. However, the assessment of the degree of soil contamination faces the problem of selecting the comparison criteria. The values of the maximum permissible concentrations (MPCs) and tentatively permissible concentrations (TPCTPCs) are most frequently used as criteria for assessing the degree of soil contamination. However, the current regulatory documents containing these parameters [4, 6, 10, 12] do not always allow correct conclusions about the contamination of soils with heavy metals to be drawn. This is related to the difference between the procedures used by the researchers for the extraction of the metals from soils and the methods recommended by the designers of MPCs and TPCTPCs [4, 6]. This problem was also noticed by Frid [31], who proposed to distinguish the terms of total content and total extractable content. The author defined the total content as the content of an element obtained at the full dissolution of the soil sample into solution or determined by physical methods, while the total extractable content is determined by the

treatment of the soil sample with a mixture of concentrated acids (hydrochloric and nitric) or another reagent. Some foreign authors also prefer to extract heavy metals from the soil with a mixture of acids with or without subsequent microwave degradation of the sample [33–35]. This diversity of the applied procedures creates some confusion at the comparative analysis of their results if the authors use the MPC and TPCTPC values as comparison criteria [1, 26, 32], but the procedures used differ from those recommended by the designers of the MPCs and TPCTPCs; therefore, the degree of soil contamination with heavy metals is frequently overestimated.

The main problem is that the MPCs and TPCTPCs for the total metal contents specified in the regulatory documents were determined using the extraction of metals from soils with a 5 M nitric acid [2, 3, 5], while the total content of an element is conventionally considered equal to the sum of all its forms [17]. It is possible that the designers of the regulatory documents imply the total content of the pollutant heavy metals that got into the soil because of anthropogenic activities. Then, the background content of each element should be taken into consideration, as is done for the lead, manganese, and vanadium MPCs; however, this is not the case for the list of TPCTPCs. Therefore, we

propose the total content of the pollutants specified in the regulatory documents to be termed as pseudototal.

### METHODS OF EXTRACTING HEAVY METALS AND THEIR HISTORY

The chronology of using the procedures for the extraction of heavy metals from soils reveals the inexactness that led to the confusion in the interpretation of the results based on the regulatory documents. For example, the instruction on the extraction of heavy metals proposed by Verigina [9] recommends extracting the total zinc, cobalt, and copper with a mixture of sulfuric and hydrofluoric acids, which allows comparing the obtained results with the clarkes. The instruction also includes a detailed procedure for the extraction of mobile heavy metals with a 1.0 N HCl solution.

In the late 1980s, the assessment of the effect of pollutants on the environment and the health of the population became an urgent problem. The criteria for estimating the contamination of soils were developed by organizations of the USSR Ministry of Public Health. Therefore, the sanitary norms for the MPCs of chemical compounds in soils were developed predominantly by hygienists [24], and the table of MPCs in these norms subdivided the pollutants depending on their forms of occurrence into the total, mobile, and water-soluble ones. The MPC for the total forms was developed only for lead, which is recommended to be extracted with concentrated nitric acid, but this obviously does not allow determining the *true* total content of this element. This procedure is proposed by Surkova and Zusman from the Irkutsk Medical Institute [24]. It recommends extracting the mobile element forms with an ammonium acetate buffer solution at pH 4.8 rather than with a 1.0 N HCl solution proposed earlier by Verigina [9].

Later on, the table of MPCs for pollutants in the soil, where their mobile and water-soluble forms were indicated, was included in the list of MPCs and TPCTPCs for chemical substances in the soil no. 6229-91 approved on November 19, 1991 [19]. However, the list of elements containing lead has no name, although the references include sanitary norms San-PiN 42-128-4433-87, which recommend the extraction of lead with concentrated nitric acid, as is described above.

The methodological guidelines [10] approved by the Russian Federation Ministry of Agriculture in 1992 indicate the methods for the determination of the total and mobile forms of heavy metals in the soils. The authors of this document noticed the conventional use of the total metal contents for the control of the technogenic contamination of soils and propose extracting the metals with 50% nitric acid. This is an inappropriate approach to the extraction of the total metals, because nitric acid is incapable of fully degrading the mineral matrix of soil. Several extraction methods are proposed for the determination of the

mobile heavy metal forms. The mobile acid-soluble forms of metals (copper, zinc, nickel, cobalt, cadmium, lead) are determined in solutions of 1 M nitric or hydrochloric acid, and it is indicated that 90 to 95% of the total heavy metals pass into the extract. This is also a questionable statement, because most of the heavy metals occur in low weatherable minerals (zircon, anatase, etc.), which cannot be destroyed with 1 M acid to extract 90–95% of the heavy metals [31]. An ammonium acetate buffer solution with pH 4.8 is used for the extraction of other mobile forms of elements from the soil; this solvent is used for assessing the supply of soils with these elements in the agrochemical service. However, of highest interest are the appendices to this document containing the MPCs for pollutants in soils. For example, in Appendix 6 of this document based on the Instructive Letter, it is indicated in the section on the total contents of copper, nickel, and zinc that the total content is a “tentative” total content [8]. The introduction and use of this new term raise questions, because the values given in this appendix do not coincide with the MPC and TPCTPC values from the other regulating documents [2–6]. This is rather strange, because the document is still in force. For example, some authors [32] refer to this procedure at the determination of the total heavy metal contents in the soils, although section 4.5.1 of this procedure, where the digestion of soil samples is described, does not mention fusion with sodium carbonate. As is noted above, the procedure also includes a table with MPC values; however, the authors interpret their results using the MPCs proposed by Motuzova [14] and Obukhov [15], which indicates again some problems in the understanding of the regulatory documents concerning the interpretation of data on soil contamination with heavy metals.

The next document concerning the norms for heavy metal contents in soils and methods of their extraction was issued in 1994; these are hygienic norms GN 2.1.7.020-94 [3], in which the list of MPCs and TPCTPCs no. 6229-91 is supplemented with TPCTPCs for heavy metals and arsenic in soils. The table legend indicates that “the procedures for the determination of the total nickel, copper, zinc, arsenic, cadmium, and lead in soils are described in RD 52.18.191-89.” At the same time, it is indicated in this RD (paragraph 5.5.2 in section 5 “Analytical Procedure”) that 5 M nitric acid is used as an extractant. Thus, the title of the document refers to the total heavy metals, but the procedure for their extraction from the soil involves the use of 5 M nitric acid at a soil : solution ratio of 1 : 5 [21]. In the document, the heavy metals extractable by 5 M nitric acid are simultaneously termed as total and acid-soluble ones. The use of the term “total” in its traditional sense in this document is also improper, because it does not refer to the overall content of metals.

Later on, the State Committee on Sanitary and Epidemiology Surveillance of the Russian Federation (Goskomsanepidnadzor) approved a new document

Methods of extracting heavy metals from soils and the parameters recommended for comparison

Terms used for heavy metal forms	Recommended terms for heavy metal forms	Method of extracting a heavy metal from the soil	Analytical procedure	Parameters recommended for comparison
Total (true)	Total	X-ray fluorescence method	OST 10 259-2000 [18]	Clark, background
		Fusion	TPI 1. 155.AAS.2010 NSAM 155-Khs [30]	Clark, background
		Treatment with a mixture of concentrated mineral acids	PND F.16.1;2.2;3.36-02 [20], TPI 1.341.AAS.2010 NSAM 341-Khs [28], TPI 1. 155.AAS.2010 NSAM 155-Khs [30], TPI 1.450.AAS.2006 NSAM 450-S [29]	Clark, background
Total or acid-soluble	Pseudototal	5 M nitric acid	RD 52.18.191-89 [21]	MPC (total content) from GN 2.1.7.2041-06 [5]
		50% nitric acid	Methodological guidelines concerning the determination of heavy metals in agricultural lands and crops [10]	TPC (total content) from GN 2.1.7.2511-09 [6], background
Mobile acid-soluble or acid-soluble	Acid-soluble	1 N nitric acid	Methodological guidelines concerning the determination of heavy metals in agricultural lands and crops [10]	Background
Mobile	Mobile	Ammonium acetate buffer solution with pH 4.8	Theory and practice of the chemical analysis of soils, 2006 [27], MG 52.18.289-90 [23], Methodological guidelines concerning the determination of heavy metals in agricultural lands and crops [10], GOST R 50683-94 [7]	MPC (mobile form) from GN 2.1.7.2041-06, background
Water-soluble	Water-soluble	Bidistilled water	Theory and practice of the chemical analysis of soils, 2006 [27], MG 52.18.286-91 [22]	Background

on October 31, 1996 [25], which includes a general table of the MPCs for the total contents of vanadium, vanadium + manganese, lead, and lead + mercury and the TPCTPCs for other elements. However, the document refers to specific methods of extracting heavy metals from the soil only for their mobile forms.

*The Hygienic Requirements for Soil Quality in Residential Areas* approved in 1999 [13] are a more consistent and more elaborated document, because they not only describe the procedures for the determination of the pollutants in the soils but also provide tools for the soil quality assessment. This document imposes sanitary and hygienic requirements on the soil quality (and control rules) and forms a normative and methodological basis for the preventing and current survey of the sanitary status of soils in residential areas, agricultural lands, resort zones, and separate institutions. The document includes a recommendation for the determination of chemical substances in the soil by the methods used for the substantiation of MPCs and TPCTPCs, as well as other metrologically certified methods. In the table of MPCs, the heavy metals are traditionally subdivided into the total and mobile forms. It is recommended to use 5 M nitric acid for the determination of the total metal forms [21], as in the earlier regulatory documents [2, 3]. A peculiar feature of this document is that it includes instructions on the interpretation of the results using the MPCs, background values, concentration coefficients, total contamination index, and additional supporting tables. Nonetheless, the term of the total content is not consistent with the reality, because the extraction with 5 M nitric acid is involved again.

*The Methodological Guidelines on the Integrated Monitoring of Agricultural Land Fertility* developed by researchers from the All-Russian Research Institute of Agrochemistry, the Soil Science Institute, and the centers (stations) of the agrochemical service and approved on September 24, 2003 [11] can be considered as the most detailed regulatory document accumulating all the known methods for the extraction of heavy metals from soils. In paragraph 13.5 of this document, it is recommended to determine the contents of the mobile and total heavy metals for assessing the contamination of soils. The degree of contamination is recommended to be revealed by comparing with the background content, MPC, or TPC for the corresponding element in the soil. In Appendix 6 of this document, all the methods recommended for the extraction of each of the studied elements are described. Their total forms are determined by the X-ray fluorescence method [18], the acid-soluble forms are determined after extraction with 5 M nitric acid [21], the mobile forms are extracted with an ammonium acetate buffer solution [7, 23], and the water-soluble forms are extracted with water [22]. However, the methodological guidelines [11] recommend using the MPCs and TPCs for the characterization of soil contamination, although the total metals

are determined after the extraction with 5 M nitric acid at their substantiation.

*The Methodological Guidelines on the Assessment of Urban Soils for the Development of Architectural and Town-Planning Documents* published in 2003 and applicable by now [12] can also be considered as a well-advised and organized regulatory document concerning the assessment of soil quality. In paragraph 3.4.3 "Content of Toxicants and Heavy Metals" of this document, the degree of soil contamination is determined by comparing the found values with the MPCs (TPCs) for chemical substances in the soil, and the TPCs for the total heavy metals and arsenic are borrowed from GN 2.1.7.020-94, where the total heavy metals are also determined after extraction with 5 M nitric acid [21].

The existing MPCs and TPCs were approved in 2006 and 2009 [4, 6]. In both documents, the total forms are determined after the extraction of the elements from the soils with 5 M nitric acid [21] according to the more complete preceding versions of the documents [3, 19].

Thus, in almost all the approved regulatory documents, 5 M nitric acid is used for the determination of the total metal forms, while this results in the obtaining of acid-soluble forms. This disturbs the meaning of the term "total forms" in the documents developed and approved by the State Sanitary and Epidemiological Service.

The handbooks used by soil scientists also do not clarify the situation. In the last edition of the textbook edited by Vorob'eva [27], an entire chapter is devoted to the fractionation of heavy metals. The following fractions of heavy metals are separated: the acid-soluble (extractable by 1 N nitric acid), mobile (extractable by an ammonium acetate buffer solution with pH 4.8), and water-soluble forms. The total forms are not considered at all. Hence, this term should be used in its traditional sense; that is, the determination of the total metal forms requires the full degradation of the silicate and aluminosilicate matrixes, which is not the case at the treatment of soils with 5 N nitric acid.

## CONCLUSIONS

The assessment of the degree of contamination of the soils and soil cover faces the problem of comparing the total contents of heavy metals obtained by direct methods (e.g., according to the branch standard GOST 10 259-2000) with the MPC and TPC values specified in the regulatory documents of the State Sanitary and Epidemiological Service, which recommend using extraction with 5 M nitric acid. This results in the incorrect assessment of the degree of contamination and significant overestimation of the results or the "pseudocontamination" of the studied areas.

The analysis of the methodological literature on the contamination of soils with heavy metals allowed the acquisition of information about the occurrence

forms of heavy metals in soils, the methods of their extraction, and data for comparing the obtained results (table).

To avoid confusion in the interpretation of the data on the contents of heavy metals in soils, one should be governed by the following guidelines.

(1) The interpretation of data on the contents of heavy metals in soils completely depends on the method of their extraction.

(2) There are only three occurrence forms of heavy metals in soils: the total, mobile, and water-soluble ones.

(3) The MPCs and TPCs of the total heavy metals can be used for comparing only when the elements are extracted by the procedure recommended in RD 52.18.191-89.

(4) The MPCs of mobile heavy metal forms can be used for comparing only when the elements are extracted by the procedure recommended in RD 52.18.289-90.

(5) For all other forms of heavy metals extracted using different procedures, the background contents of these elements in the soil should be taken for comparing.

(6) Because the external contamination of soils is considered, the term "total forms" of elements in the soil, which is used in the existing regulatory documents, should be replaced by the term "pseudototal (conventional total) forms," which implies the total content of the pollutant element arriving into the soil minus its background content.

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