

Chromium, Nickel and Cobalt in Environmental Samples and Existing Legal Norms

D. Baralkiewicz, J. Siepak

Laboratory of Water and Soil Analysis, Adam Mickiewicz University,
60-613 Poznan, Drzymały 24, Poland

Received 12 February, 1999

Accepted 29 March, 1999

Abstract

This paper presents the occurrence, properties and origin of chromium, nickel and cobalt in environmental samples soil, water and the atmosphere. Methods of determining the above-mentioned elements and ways of preparing environmental samples for chemical analyses are presented. The content of chromium, nickel and cobalt in the atmosphere, naturally occurring waters, and soil is shown, along with the permissible concentrations of the above elements in the three divisions of the environment legally required in Poland and other countries.

Keywords: chromium, nickel, cobalt, occurrence, properties, origin, environmental samples.

Introduction

The choice of the above elements is not connected with their chemical or biogeochemical properties. These metals were chosen due to the level of environmental danger posed by their pollution of the natural ecosystem [1]. They belong to the group of rare metals and every change of the chemical balance in the natural environment causes not only disturbances in the growth and development of flora and fauna, but also (indirectly or directly) human health [2]. These metals are also of considerable interest to allergology and allergeny [3-7].

The main routes for the transport of metals throughout the environment are the atmosphere and flowing waters. Under normal conditions, the end results of migration are bottom sediments, soil and underground waters. Heavy metals in the environment originate from two anthropogenic sources, one connected with human activity and the other concerned with the natural circulation of the metals throughout nature. Thus, an index of environmental pollution may be found not only in the presence of the metals themselves, but when their natural concentrations (or the so-called geochemical background) have been exceeded.

This paper presents the origins of chromium, nickel and cobalt, methods of determining the given elements, and means of preparing samples for environmental analysis.

A rather large part of this paper concerns current legal regulations concerning permissible norms for concentrations in water, soil and the atmosphere, as enforced in Poland and other countries.

Occurrence, Properties and Origin

Chromium

Chromium is a metal that rarely occurs in nature. The main mineral containing this element is chromate FeCr_2O_4 , which contains up to 70% of pure Cr_2O_3 .

Its higher content in the environment is caused by human activity. The risk of global pollution of the natural environment by chromium does not yet exist, although its local emissions into the atmosphere, waters and soils may cause its excessive inclusion in biochemical circulation, thus posing a danger to man and animals. Chromium (in small quantities) is an element significant to the life of plants and animals. In large concentrations it is harmful. Chromium, with an oxidation number of six, is more dangerous to living organisms than trivalent chromium, due to its greater ability to diffuse through cell tissue.

The unique, chemical property of chromium is its differentiated oxidation level, which can change from as little

as -2 to as much as +6. Most often, in the natural environment, chromium occurs at an oxidation level of +2, +3 and +6. The cation Cr^{3+} is the most stable and forms stable compounds in the soil at a pH > 5.5. However, the cation Cr^{6+} is a form that is unstable in the natural environment and exists in the soil over a range of pH 5.5-7.5. It is the form of chromium (next to Cr^{2+}) that is most easily accessible, and at the same time, most harmful to plants [8-11].

Nickel

The occurrence of nickel is clearly connected with alkaline magma rock as well as silty sedimentary rock. Nickel most often accompanies rock-formative magnesium - iron silicates. Due to its sulfophilic tendency, it combines with arsenic and sulfur to form various minerals of its own. In the course of weathering processes, nickel easily undergoes activation, and in the cationic form of Ni^{2+} it can migrate together with its solutions over great distances. Often, however, it is quickly combined with iron and manganese hydroxides. A considerable part of nickel finds its way into the environment as a result of the burning of diesel oil containing nickel. In nature, it generally occurs at an oxidation level of +2, but its valence may change from -1 to +4. It easily forms quite stable chelate compounds as well as complex cations and anions. In both acid and alkaline environments, it primarily occurs as Ni^{2+} and NiHCO_3^{3+} ions. Among the inorganic ligands combining with nickel are the halides, sulfates, phosphates, carbonates and carbonyl compounds, and to the organic ones - oxygen, nitrogen and sulfur bondings. Humic acids form fairly strong complexes with nickel [9-13].

Cobalt

The occurrence of cobalt in the earth's surface varies greatly. This element does not exist in its native form and is encountered only in meteorites. Cobalt is most often found in the form of arsenides and sulphides. The most important cobalt minerals are cobaltite CoAsS , **linnaet** Co_3S_4 , **smaltyn** CoAs_2 and **karrolit** CuCo_2S_4 .

The source of cobalt pollution (apart from industrial waste) is the burning of cobalt. Cobalt may occur at oxidation levels of from -1 to +4, but in nature it occurs usually as a double-valenced cation Co^{2+} (cobalt compounds). In erosive environments it easily undergoes oxidation from Co^{2+} to Co^{3+} and creates the complex anion $\text{Co}(\text{OH})_3^{-3}$. It relatively easily becomes mobile in acidic oxidizing environments, but does not undergo extensive aqueous migration, since it combines with the hydroxides of iron and manganese as well as silty minerals [10, 13-14].

Methods of Analysis and Preparation of Samples

Developments in biochemistry and toxicology, expanded knowledge of metabolic processes, and resultant toxic effects caused by the presence of heavy metals in the organisms of plants and animals, leaves analytical chemistry with a difficult task. On the one hand are determinations of ever lower concentrations of metals (necessary to determine their changes in the organism) and their accumulation, or possible harmfulness. On the other hand is knowledge of these processes (particularly toxic effects), often causing a lowering of allowable metallic contents in the environment (atmosphere, water and soil) and, relative to this, the monitoring of ever lower levels of concentration. This

Table 1. Determinability of chromium, nickel and cobalt by various analytical methods [$\mu\text{g l}^{-1}$]

Element	FAA	GFAA	SV	ICP-AES	ICP-MS	NAA
Chromium	3	0.06	0.02	1.6	0.01	20
Nickel	6	0.3	0.001	2	0.04	15
Cobalt	9	0.15	0.005	1.5	0.01	0.03

Abbreviations explained:

FAA - *flame atomic absorption*

GFAA - *graphite furnace atomic absorption*

SV - *stripping voltamperometry*

ICP-AES - *inductively coupled plasma - atomic emission*

ICP-MS - *inductively coupled plasma - mass spectrometry*

NAA - *neutron activation analysis*

results in a tendency to develop analytical methods of ever lower determination thresholds, thus allowing analysis of samples with a differentiated matrix. There exist many methods for the analysis of trace amounts of metals, which extend from simple (i.e. spectrophotometric and potentiometric ones) to complicated (requiring extensive analytical equipment and even special laboratory facilities). The latter methods include flame atomic absorption (FAA) and graphite furnace atomic absorption (GFAA), polarography, neutron activation analysis, the inductively-coupled plasma method (ICP) and ionic chromatography. Table 1 shows comparisons of determinability in some of the methods discussed.

To determine chromium, nickel and cobalt in environmental samples, the most common method used is atomic absorption spectrometry using volatilization in flame as well as volatilization in a graphite cuvette, in accordance to the level of the tested metal contained [15-18]. In the course of the last thirty years, atomic absorption spectrometry has developed into the most important analytical method for determining inorganic traces in solutions. This also concerns, the analysis of solid substances and, partially, the analysis of gasses.

Below follows a discussion of ways for determining chromium, nickel and cobalt by the ASA method, both with and without flame. In abbreviated form, there is a presentation, for each element, of the advantages and problems of particular volatilization techniques and specific sources of radiation that are necessary. This paper is unable to accurately present the nature of matrix problems, since they are unique for each element and every matrix. An attempt, however, has been made to characterize the main problem.

Chromium

Source of radiation: Cr-HCl or Cr-EDL; spectral width of the gap between 0.1 and 0.5 nm have no influence.

Flame ASA (FAA). A flame of mainly $\text{C}_2\text{H}_2\text{-N}_2\text{O}$ is recommended. In the presence of a matrix, it is often more advantageous to use a hot flame (i.e. oxides of Cr-Fe-Ni are difficult to volatilize).

Graphite furnace atomic absorption (GFAA). Determinations are conducted in a tube of pyrolytic graphite or on a platform made of pyrolytic graphite. The characteristic sample mass is 1.5 μg ; the maximal temperature of incineration is 1100°C; recommended chemical modifier - pal-

ladium solution and ascorbic acid or magnesium nitrate; volatilization temperature 2700°C [19, 20].

Nickel

Sources of radiation: Ni-HCL or Ni-EDL; a spectral gap width of 0.2 nm is required.

Flame atomic absorption (FAA). Generally C₂H₂ - air flames are employed. In the presence of difficult-to-volatilize matrices, C₂H₂ - N₂O may also be used.

Graphite furnace atomic absorption (GFAA). Determinations are conducted in a tube of pyrolytic graphite or on a platform made of pyrolytic graphite. The characteristic sample mass is 4.5 pg; the maximal temperature of incineration is 900°C; recommended chemical modifier - palladium solution and ascorbic acid or magnesium nitrate; volatilization temperature 2400°C [19, 20, 21, 22, 23, 24, 25, 26].

Cobalt

Source of radiation: Co-HCL or Ni-EDL; spectral width of the gap between 0.1 to 0.2 nm is required.

Flame atomic absorption (FAA). Stoichiometric flames of C₂H₂-air. Flames of C₂H₂-N₂O may be employed in the event of difficult-to-volatilize matrices.

Graphite furnace atomic absorption (GFAA). Determinations are conducted in a tube of pyrolytic graphite or on a platform made of pyrolytic graphite. The characteristic sample mass is 4.2 pg; the maximal temperature of incineration is 900°C; recommended chemical modifier - palladium solution and ascorbic acid or magnesium nitrate; volatilization temperature 2300°C [21, 22, 23, 24, 25, 26].

An important element in trace analysis is sampling, storing and preparation of samples before their final determination [27, 28]. All utensils serving for sampling and storing of samples should be washed many times in a 5% solution of nitric acid and finally with distilled water with no significant traces of the metals to be determined. It is best to employ ultra pure distilled water obtained by the Millipore system. Reagents used in determining trace amounts of elements should also be ultra pure. If analysis cannot be performed immediately, samples should be immediately preserved in nitric acid. This will prevent the adsorption of trace amounts of metals on the utensil walls. All activities connected with the preparation of samples and its next determination should be performed in clean and previously prepared facilities. The proper drawing of conclusions connected with trace amounts of metals in environmental samples is required to obtain reliable results. Mistakes occurring during sampling, storing and preparation of the sample obviate the analytical effort and the costs of the analysis. The results of the analysis refers exclusively, then, to the immediate sample tested, and not the whole site, something which most often results in making the wrong decisions.

Preparation of Samples for Speciation Analysis

Every element is capable of forming several molecular bonds. Depending on the conditions, this may occur in the

environment in the form of one molecular bond or several bonds, the concentration of one being greater than that of others [21-32]. The overall concentration of an element may be employed to evaluate its influence on the environment only when it occurs in the form of one type of bond. This condition is very rarely ever fulfilled. The chemical reactivity of an element depends on the form in which it occurs, and since the dominant forms are not the most reactive ones, the behavior of an element in the environment (bioavailability, ecotoxicity, distribution of forms) cannot be described on the basis of its overall concentration.

The term "speciation" refers to the molecular forms of the atomic elements or groups of atoms of various molecules in a given elemental matrix. The concept of speciation forms of a given element refers to all the physical and chemical forms under which it occurs. A given element may occur in various concentration states. Within a given state, it may be concentrated in various physical forms (aerosol, mist, suspension, colloid, precipitate). Sequential extraction of precipitates (sediments) differentiates their various forms with relation to the metals: leachable metals, metals combined with carbonates, metals combined with hydrated oxides of iron and manganese, leachable metals, metals with organic bonds and metals connected with the remaining fraction.

The concept of chemical speciation encountered in literature refers to the occurrence of a given element at various oxidation levels. The definition of speciation introduced in 1992 by the Trace Analysis Commission of the International Union of Pure & Applied Chemistry (IUPAC) describes the identification of various forms and phases in which the element occurs within a given matrix. The form and phase of the occurrence may be defined for bottom sediments, soils and sewage sediments as follows:

functional - ion exchangeable forms, mobile and bioavailable,

operational - by means of analytical procedures, specific and selective reagents and extractants in order to isolate the form and quantitatively to describe it,

specific - in the form of a compound or level of oxidation.

The preparation of samples for speciation analysis is particularly difficult. Most of the analytical procedures performed at the level of sampling and sample preparation for analysis causes, at a differentiated level, a disruption of the original balance of the various forms of the analyte. The procedure of dissolving or mineralizing the sample causes a movement of analyte forms to one or two forms. This leads to a summative index which does not correlate with the form occurring in the environmental matrix. The results of speciation analysis in this case differ from those forms of interest to the analyst. The share of biologically available or ecologically toxic forms for the natural environment remains unknown. Speciation analysis today has presently become a necessity in ecological research and may be undertaken through:

- integration of analytical methods, where the approximate content of the sample is known,
- the use of combined techniques,
- employment of selective analytical procedures: dissolving, extraction, complex formation, precipitation and absorption.

Content of Chromium, Nickel and Cobalt in the Environment

Soil

Chromium

The occurrence of chromium in soils is generally dependent on its content in bedrock. The average range of chromium concentrations is 7-150 mg kg⁻¹, is generally as follows for the following types of soils: sandy, 30 ppm; clay, 40 ppm; limestone soil, 83 mg kg⁻¹. Polish soils contain chromium over a range of: sandy, 2-60 mg kg⁻¹; and clay, 14-80 mg kg⁻¹; and show an approximate level to the amount in the original scale. The greatest amounts of chromium (approaching 15%), occur in soils formed from ultra-alkaline rock as well as some metamorphic rock. In the Szklary region in Lower Silesia, soils formed on the detritus of nickel-bearing rock contain up to 0.25% Cr. Waste and industrial emissions are often the cause of polluting soils with chromium, which may accumulate gradually from sources of its relatively low content. After 80 years, the effect of communal sewage of low chromium content years on soils, raised its content from 43 to 113 mg kg⁻¹, whereas sewage and waste enriched in this metal cause its increase to even above 700 mg kg⁻¹. Soils endangered by the effect of industrial wastes coming from dump sites show a considerable concentration of chromium. Near the "Warszawa" smelter and the "Wierzbica" Asbestos-Cement Plants, up to approximately 1500 mg kg⁻¹, near the "Radoskor" Tannery up to 1000 mg kg⁻¹. It has been determined that in polluted soils, chromium is mainly concentrated at surface levels [1, 10, 32].

Nickel

The average extent of nickel content at the surface levels of various soils is from 4-50 mg kg⁻¹; lower concentrations occur on light sandy soil and are on average 15 mg kg⁻¹ greater concentrations (approximately 30 mg kg⁻¹) occur in clay soils. Some organic soils, as well as those created from alkaline magma or volcanic rock, contain an increased amount of this metal, particularly in soils formed from serpentinites, the concentration of nickel reaches a value of thousands of mg kg⁻¹. Soils usually contain more nickel in an organically combined form, to a considerable degree in the form of mobile chelates. Often, however (particularly in mineral soils) this metal is sorbed by hydroxides of iron and manganese, but also remains in easily soluble forms. The solubility of nickel in soils increases with its acidity, and its sorption by hydroxides of iron and manganese increases with its drop in acidity. The concentration of nickel in soil solutions is in a range of several to several-score µg l⁻¹, but in polluted acidic soils it can be in excess of these values by many times. The greatest pollution of soils by nickel was found in the region of highly developed nickel smelting in Canada, approximately 26,000 mg kg⁻¹, and in Great Britain, due to the use of communal waste for soil fertilization. An increased nickel content in Poland of 250 mg kg⁻¹ was determined in places polluted by galvanization plant sewage. The calcification of soils as well as increased amounts of phosphate fertilizers limit the phytoadaptability of nickel [1, 10, 32].

Cobalt

The occurrence of cobalt in soils is to a large extent determined by bedrock. Its content in the soil is within a fairly broad range, i.e. 0.1 to 100 mg kg⁻¹, the lowest average values occur in sandy podsol soils 5.5 mg kg⁻¹ and organic soils 4.4 mg kg⁻¹, and the highest for dark brown clay soils, fen soils and limestone soils 10-12 mg kg⁻¹. The average content of cobalt in the soils of the world amounts to 8 mg kg⁻¹. Its concentrations in the solutions of various soils oscillates from 0.3 to 87 µg l⁻¹ and is generally greater in the salted soils of a warm dry climate. An increased amount of cobalt occurs, as well, as a result of industrial pollution. The greatest concentrations have been found in regions with non-ferrous metal smelting industries in the USA (above 154 mg kg⁻¹) and Canada (above 120 mg kg⁻¹). The index of cobalt concentrations in the surface levels of Polish soils is relatively high and may indicate the influence of anthropogenic factors. Cobalt is easily sorbed by organic substances and creates organic chelates. These increase the mobility of cobalt and influence their mobility within the profile of the soils, and also increase its adaptability by plants, particularly in soils with an increased reactivity under oxidative conditions. Under reductive conditions, however, cobalt is also more readily soluble, as well as becoming more available for plants [1, 10, 32].

Natural Waters

Chromium

In water, chromium occurs in two oxidation states, +3 and +6. Under salt water conditions with a pH of approximately 8, cation Cr⁺⁴ may also be present. Oxidized chromium, Cr⁺⁶, under the form of anionic compounds is found in its unstable form mainly in the upper layers of the water. The anionic form of chromium is readily bioaccumulatable, but phyto- and zooplankton readily absorb chromium under every form. In an aqueous environment, chromium undergoes relatively rapid oxidation, thus, determination of various of its speciation forms causes many difficulties. In the natural aqueous environment, chromium is relatively unstable in the dissolved state and undergoes precipitation in the form of a suspension as well as undergoing bioaccumulation.

In many waters, chromium in suspension constitutes 34-65 % of the overall chromium. The content of chromium in naturally occurring waters is differentiated and dependent on its state. The chromium content in unpolluted lakes is approximately 1-2 µg l⁻¹, and in river waters 5-50 µg l⁻¹. Concentrations of chromium above 100 µg l⁻¹ are rarely encountered, mainly in industrial regions. Table 2 shows the content of chromium in naturally occurring waters both in Poland as well as abroad [1, 10, 32].

Nickel

In natural water environments, nickel concentration is generally small, because it mainly occurs in a colloidal form and is subject to rapid sorption by loamy minerals and hydroxides of iron and manganese in bottom sediments. Nickel is easily accumulated in the biological environment, particularly in the phytoplankton or other aquatic plants,

which are sensitive bioindicators of water pollution. The concentration of dissolved nickel in pure waters is from 1-3 $\mu\text{g l}^{-1}$, whereas in waters in industrialized areas it is 10-50 $\mu\text{g l}^{-1}$. Typical nickel concentrations in naturally occurring waters are presented in Table 3 [1, 10, 32].

Cobalt

Two oxidation levels occur in waters, but the more highly oxidized form, +3, is not very stable and undergoes rapid precipitation and bonding by the loamy and hydroxide fraction of bottom sediments, as well as the phytoplankton. Cobalt occurs in the surface waters in small concentrations, most often of from several to several-score $\mu\text{g l}^{-1}$. Typical concentrations of cobalt in pure surface waters is 0.05 $\mu\text{g l}^{-1}$. In naturally occurring waters, cobalt occurs in small amounts, its average natural content in river waters is approximately 0.2 $\mu\text{g l}^{-1}$. In ground waters, in reductive environments of temperate zones, cobalt concentrations were, on average, 0.4 $\mu\text{g l}^{-1}$, and in areas of salted over land, approximately 1.2 $\mu\text{g l}^{-1}$. The cobalt concentration in naturally occurring waters is presented in Table 4 [1, 10, 32].

Atmosphere

Chromium

The natural range of chromium in the atmosphere is from 0.01-1 ng m^{-3} . This element occurs in various concentrations of from 0.01 in unpolluted areas (e.g. the South Pole), to > 1000 ng m^{-3} in areas of industrial pollution. In Poland the most highly polluted area is Upper Silesia, where the annual precipitation of chromium in 1987 was from 30 to 235 g/ha [33].

Nickel

The concentration of atmospheric nickel fluctuates over a range from 1 to 150 ng m^{-3} . Much higher concentrations of nickel (approximately 2000 ng m^{-3}) are encountered in industrial regions and in the areas of large cities. The atmospheric precipitation of nickel in some cities of the Katowice voivodship is approximately 150 ng m^{-3} , whereas above the unpopulated areas of Great Britain, it is from 3-60 ng m^{-3} , and in the non-industrial areas of Germany and Sweden, it is somewhere around from 5-35 g/ha/year. The atmospheric pollution due to nickel is immediately connected with industrial metallurgical emissions and from the combustion of liquid fuels. Global emissions are estimated at < 100,000 t annually [33].

Cobalt

Cobalt concentrations in the atmosphere are the lowest among the three metals discussed and fluctuate from 0.0001 ng m^{-3} at the South Pole, to approximately 6 ng m^{-3} above the great cities of Japan and Germany. The natural range of cobalt in the air is accepted as 0.0005 - 0.005 ng m^{-3} . In 1986, the amount of cobalt above Spitsbergen was < 0.007 ng m^{-3} , and in 1972 - 81 above the inhabited areas of Great Britain 0.16-6.4 ng m^{-3} , where atmospheric precipitation was within a range of 1.5-6 g/ha/year [33].

Table 2. Chromium content in naturally occurring waters $\mu\text{g l}^{-1}$.

Water Type	Location	Concentration range
Rainwater	Germany – city	0 – 36
	Belgium	11 – 43
	Poland – area of the WNP*	0.5 – 2.5
River water	Germany	2.5 – 15.5
	Russia – Siberia	> 10
	Italy	0.1 – 1.2
	Poland	1 – 73
Lake water	Poland – lakes of the WNP*	0 – 3
	Poland – lakes of the Gołanieckie Stream	0 – 2
Underground water	Poland – Poznań	0.2 – 10
	Poland – Poznań voivodship	0.3 – 15
	Poland – Szczecin voivodship	0.4 – 8
Drinking water	USA	0.1 – 35
	Poland – Poznań	0.07 – 2

* Wielkopolska National Park

Table 3. Content of nickel in naturally occurring waters $\mu\text{g l}^{-1}$.

Water Type	Location	Concentration range
River water	Poland	2 – 75
	Germany – Rhine	8.9 – 24
	USA	0 – 71
Lake water	Poland – lakes of the WNP*	2 – 11
	Poland – Lakes of the Gołanieckie Stream	1 – 8
Underground water	Poland – Poznań	0.5 – 20
	Poland – Poznań voivodship	1 – 30
	Poland – Szczecin voivodship	1 – 15
Drinking water	USA	0.5 – 7
	Poland – Poznań	0 – 5

* Wielkopolska National Park

Table 4. Cobalt content in naturally occurring waters $\mu\text{g l}^{-1}$.

Water Type	Location	Concentration range
River water	Poland	0.04 – 8
	USA	1 – 36
	Germany – Rhine	4 – 12
Lake water	Poland – lakes of the WNP*	0 – 2.5
	Poland – lakes of the Gołanieckie Stream	0 – 1.5
Underground water	Poland – Poznań	0.02 – 1
	Poland – Poznań voivodship	0.01 – 3
Drinking water	Poland – Poznań	not determined

* Wielkopolska National Park

Permissible Concentrations of Chromium, Nickel and Cobalt in the Soil, Water and Atmosphere

Soil

In Poland there are no legal regulations on the basis of which the level of soil pollution by chromium, nickel and cobalt may be assessed. Accordingly, the State Inspectorate of Environmental Protection has presented permissible levels of soil pollution approximating those employed by the states associated with the European Union [34]. While setting the amount of permissible levels of soil pollution, the following elements were considered:

- the nature of the land use where pollution occurs (division into areas A, B, C);
- hydrogeological properties of the land, decisive in the rate of diffusion and proliferation of pollution (water permeability index);
- the depth to which pollution occurs, the danger to the natural environment.

Among others, area A includes the following:

- areas under legal protection (i.e. national parks, preserves)
- health spas with mineral waters (according to the Directive of the Minister of Health & Social Welfare)
- areas supplying resource reservoirs of underground waters as well as protected zones of sources and outlets of underground waters.

In area B the following, among others, have been included:

- areas of cropland included in the food chain (the cultivation of grain, grazing land, orchards, etc.);
- woodland areas;
- housing areas;
- recreational, rest, and public utilities.

In area C, among others, the following have been included:

- industrial plants;
- warehouses of liquid and solid fuels;
- communications routes;
- locomotive garages;
- waste storage sites;
- armed forces sites and facilities;
- airports; land for the cultivation of industrial crops;

Simplifying matters somewhat, it has been accepted that rock (having a filtration index of k in m/s with values above 1×10^{-7}) is representative of permeable rock, whereas rock with values below 1×10^{-7} is that which shows little permeability. This property of rock has been considered in setting permissible concentrations of substances polluting the soil.

A further element differentiating borderline concentrations of pollution in certain areas is the depth to which the pollution occurs. Three depth zones have been introduced in areas B and C. Area A includes no subdivision into classes of depth due to the nature of the land, which requires uniform purity over the whole perpendicular profile.

In area B the following zones have been assigned:

- zone 1 at a depth of 0.00 - 0.30 m, due to the depth where the root system of most of the cultivated plants reaches; through the roots, pollution enters the food chain, thus directly influencing man;
- zone 2 at a depth of 0.30 - 15.00 m, due to the indirect action on living organisms as well as the protection of underground waters against pollution;
- zone below a depth of 15.00 m.

Table 5 presents the permissible concentrations of chromium, nickel and cobalt in soils.

Table 6. The Netherlands List. Monitoring table to evaluate the concentrations of harmful substances in the soil [mg kg^{-1} dry mass].

No.	Element	Level		
		A	B	C
1	Chromium	x	250	800
2	Nickel	20	50	300
3	Cobalt	x	100	500

A - value of the reference level; B - value of the monitoring level to undertake more precise samples; C - value of the monitoring level to undertake purification measures.

To evaluate the level of concentration of harmful substances in the soil, there exist also two other documents: The Netherlands and the Berlin Lists, respectively. Tables 6 and 7 present the values of pollution levels by chromium, nickel and cobalt in the soil.

Table 5. Permissible concentrations of chromium, nickel and cobalt in soil in mg kg^{-1} d. m. on state inspectorate of environmental protection (PIOS) [34].

No	Element	Zone A	Zone B				Zone C				
			depth [m ppt]				Water permeability of soil [m ppt]				
			0-0.30	0.30-15	> 15		0-2	2-15	> 15		
				to below	to below		to below				
				1×10^{-7}	1×10^{-7}		1×10^{-7}				
1	Chromium	20	20	50	190	100	380	500	100	800	*
2	Nickel	35	35	50	100	70	210	300	70	500	*
3	Cobalt	20	20	30	60	50	120	200	50	300	*

* - in this zone (decisive in any eventual re-cultivation work) is the quality of underground waters, i.e. in the event they are polluted beyond a level of the parametric values for underground waters, described in the following Table for area C.

Waters

The highest permissible concentrations of chromium, nickel and cobalt in surface waters are described in the Decision of the Minister of Environmental Protection, Natural Resources and Forestry, from November 5, 1991 [35]. The values of the above elements are presented in Table 8, which also contains norms from the Czech Republic, the USA and the FIS for surface waters.

Table 7. Berlin List. Chromium, nickel and cobalt concentrations depending on the land category [mg kg^{-1} dry mass].

No.	Element	Category			
		Ia	Ib	II	III
1	Chromium (all)	150	100	400	800
2	Chromium VI	5	5	25	50
3	Nickel	200	50	250	300
4	Cobalt	100	100	200	300

Ia: lands containing waters under environmental protection measures, Ib: surfaces of sensitive utilization, II: lowlands, III: uplands.

The highest permissible concentration in drinking water was described in the Decision of the Minister of Health Social Welfare from May 4, 1990 [36]. Table 9 presents the values of the elements under consideration as described in Poland and other countries.

In the above ministerial decisions there is a lack of norms for cobalt. Its values are described by the State Inspectorate for Environmental Protection (PIOS). Table 10 presents permissible concentrations for cobalt and, for comparison, for chromium and nickel, contained in the methodological recommendation of PIOS and in the Netherlands & Berlin Lists.

Table 9. The highest permissible concentrations of chromium, nickel and cobalt in drinking water [$\mu\text{g l}^{-1}$]

No.	Element	Poland	EEC	WHO	USA	FIS
1.	Chromium VI	10				
2.	Chromium average		100	100	100	100
3.	Nickel	30	30	30	-	-
4.	Cobalt	-	-	-	-	-

Table 8. Values of permissible concentrations of chromium, nickel and cobalt in inland surface waters [$\mu\text{g l}^{-1}$].

No.	Element	Poland			USA	FIS*	Czech Rep.
		I class	II class	III class			
1.	Chromium VI	50	50	50	100 ¹	-	50
2.	Chromium III	50	100	100	-	-	100
3.	Chromium average	-	-	-	-	100	-
4.	Nickel	1000	1000	1000	0.5-10 ¹ ; 200 ²	100	50
5.	Cobalt	-	-	-	0.05 ²	1	-

- Federation of Independent States; ¹
- for irrigation; ² aquatic biocenoses

Table 10. Permissible concentrations of chromium, nickel and cobalt in underground waters [$\mu\text{g l}^{-1}$].

No.	Element	PIOŚ			Netherlands List			Berlin List			
		A	B	C	pos. A	pos. B	pos. C	Cat. Ia	Cat. Ib	Cat. II	Cat. III
1.	Chromium	5	50	200	x	50	200	150	100	400	800
2.	Chromium VI							5	5	25	50
3.	Nickel	15	40	200	x	50	200				
4.	Cobalt	20	90	200	20	50	200				

Table 11. Permissible concentrations of chromium and nickel in the atmosphere [$\mu\text{g m}^{-3}$].

No.	Element	Permissible concentration of pollution					
		Areas of the country			Areas under special protection		
		30 min	24 h	average annual	30 min	24 h	average annual
1.	Chromium	4.6	2.0	0.4	-	0.5	0.08
2.	Nickel	230.0	100.0	25.0	150.0	70.0	17.0

The Atmosphere

Permissible concentrations of substances polluting the air are described in the Decision of the Minister of Environmental Protection, Natural Resources and Forestry from April 28, 1998 [37]. These have been separately set for areas under special protection and for the remaining areas. The areas especially controlled include the areas of spas, spa protection, national parks, natural preserves and scenic parks. Table 11 presents the highest permissible concentrations of chrome and nickel polluting the atmosphere. The decision does not include the permissible concentrations of cobalt in the atmosphere.

EEC norms concerning atmospheric environmental protection consider permissible values only for suspended particles, sulfur dioxide, nitrogen oxides and lead.

Conclusion

Chromium, nickel and cobalt, due to their ever increasing technological significance, are joining those elements most responsible for toxicity in the environment. And although, on the one hand, they are among the elements essential to life, performing important functions in the metabolism of living organisms, on other hand, after exceeding certain defined limits, they become factors destructive of the ecosystem, pathogens to living organisms and, what's worse, mutagenic or carcinogenic factors for animals and people. In the final analysis, however, their action is dependent on many factors, whose discovery has become an immediate need. Of particular priority is a unification and standardization of permissible norms for compounds of chromium, nickel and cobalt in the environment.

References

- DOJLIDO J.R., BEST G.A. Chemistry of Water and Water Pollution, Ellis Horwood Limited; New York **1993**.
- SZTEKE B., KABATA-PENDIAS A. Problemy jakosci analizy sladowej w badaniach srodowiska przyrodniczego, Biblioteka Monitoringu Srodowiska, Warszawa **1996**.
- D. BARALKIEWICZ, Z. KARAS, J. SIEPAK, Application of the fast ETAAS Method for the determination of chromium, cobalt and nickel in samples of preserved food, Chem. Anal. **42**, 691, **1997**.
- DELESCULUSE J., DINET Y. Nickei allergy in Europe: the new European legislation., Dermatology, **189**, 56, **1994**.
- RUDZKI E. PRYSTUPA K. Contact Dermatitis, **30**, 254, **1994**.
- VEIEN N. K. HATTEL T. JUSTESEN C, NORHOLM A., ORAL A., Contact Dermatitis, **9**, 402, **1983**.
- Z. KARAS, D. BARALKIEWICZ, J. SIEPAK, Wplyw antropolopresji na poziom kumulacji i migracji niklu w srodowisku przyrodniczym czlowieka.; Ekologia i Technika, **2**, 26, **1997**.
- ANDERSON R. A. Essentiality of chromium in humans. The Science of the Total Environment, **86**, 75, **1989**.
- KABATA-PENDIAS A. Chrom, nikiel i glin - problemy ekologiczne i metodyczne., Z. Nauk. PAN, Czlowiek i Srodowisko, **5**, **1993**.
- DOJLIDO J. R. Chemia wód powierzchniowych, Wyd. Ekonomia i Srodowisko, Bialystok, **1995**.
- FIC M. Adsorptions - and Desorptions - Verhalten von Cadmium, Chromium und Zink an ausgewählten Boden und Sanden., Ph. D. Thesis, Christian - Albrechts - Universitat, 99 s, **1987**.
- NRIAGU J. O. Nickel in environment, New York, **1980**.
- Standard Methods for the Examination of Water and Wastewater. Washington DC, **1992**.
- TUREKIAN K. K. SCOTT M. Concentrations of Cr, Ag, Mo, Ni, Co and Mn in suspended material in streams. Environ. Sci. Technol. **1**, 940 **1994**.
- DITTRICH K. Absorpcyjna spektrometria atomowa., PWN, Warszawa, **1988**.
- WELZ B., SPERLING M. Atomic Absorption Spectrometry, Third, Completely Revised Edition, WILEY - VCH Verlag GmbH, **1999**.
- BEATY R. D. Podstawy, aparatura i metodyka atomowej spektrometrii absorpcyjnej Copyright **1988** by The Perkin - Elmer Corporation, t. dr Ewa Bulska.
- NIEDZIELSKI P. BARALKIEWICZ D., SIEPAK J. Absorpcyjna spektrometria atomowa jako metoda oznaczania sladowych ilosci metali w srodowisku, Ekologia i Technika **3**, 27, **1996**.
- SLAVIN W. MANNING D. C, CARNRICK G. R. At. Spectrosc. **2**, 5, **1981**.
- SLAVIN W., CARNICK G. R., MANNING D. C. Anal. Chem., **54**, 4, **1982**.
- BULSKA E., GODLEWSKA K., WROBEL K., HULANICKI A. CAN. J. Appl. Spectroscopy **36**, 4, **1991**.
- JAGANATHAN J., EWING L. E., PEITERTON L. E., O'BRIEN I. D., AGGARWAL I. D. Spectrochim. Acta, Part **B 46**, 5, **1991**.
- PEREZ-PARAJON J. M., SANZ-MENDEL A. Quim. Anal. (Barcelona), **12**, 1, **1993**.
- SAMPSON B., Anal. Proc. (London), **25**, 7, **1988**.
- SAMPSON B., J. Anal. At. Spectrom. **3**, 3, **1988**.
- SCHLEMMER G., GIT Fachz. Lab. **33**, **1989**.
- NAMIESNIK J., LUKASIAK J., JAMROGIEWICZ Z. Pobieranie probek srodowiskowych do analizy., PWN, Warszawa **1995**.
- HULANICKI A. Analiza specjacyjna probek biologicznych. Wiadomosci Chemiczne **51**, 3-40, 189, **1997**.
- HULANICKI A. Specjacja i analiza specjacyjna. Analityka Chemiczna w Badaniach Srodowiska Naturalnego, Wydawnictwo SGGW: Warszawa, pp 7-12, **1997**.
- NAKAYAMA E., SUZUKI Y., FUJIWARA K., KITANO Y. Chemical analyses of seawater for trace elements. Recent progress in Japan on clean sampling and chemical speciation of trace elements. Analytical Sciences **6**, 129, **1989**.
- TESSIER A., CAMPBELL P. G., BISSON M. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Anal. Chem., **51**, 844, **1979**.
- ZERBE J., SOBCZYNSKI T., SIEPAK J. Metale ciezkie w osadach dennych, ich specjacja na drodze ekstrakcji sekwencyjnej, Ekologia i Technika, **3**, 18, **1995**.
- KABATA-PENDIAS A., PENDIAS H. Biogeochemia pierwiastkow sladowych, Wyd. Naukowe PWN, Warszawa **1993**.
- Wskazowki metodyczne do oceny stopnia zanieczyszczenia gruntow i wód podziemnych produktami ropopochodnymi i innymi substancjami chemicznymi w procesach rekultywacji. PIOS, Warszawa **1994**.
- Zalacznik nr 1 do rozporzadzenia Ministra Ochrony Srodowiska, Zasobow Naturalnych i Lesnictwa, z dnia 5 listopada 1991 r. (poz. 503). Wartosci wskaźników zanieczyszczen srodosladowych wód powierzchniowych.
- Zalacznik nr 1 do rozporzadzenia Ministra Zdrowia i Opieki Spolecznej z dnia 4 maja 1990 r. (poz. 205). Warunki organoleptyczne i fizycznochemiczne jakim powinna odpowiadac woda do picia i na potrzeby gospodarze.
- Rozporzadzenie Ministra Ochrony Srodowiska, Zasobow Naturalnych i Lesnictwa, z dnia 28 kwietnia 1998 r., w sprawie dopuszczalnych wartosci stezery substancji zanieczyszczajacych w powietrzu.