DOI: 10.2428/ecea.2012.19(10)118 ECOL CHEM ENG A. 2012;19(10):1239-1246

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SPATIAL DISTRIBUTION OF VARIOUS FORMS OF IRON IN HEAVY METAL POLLUTED SOILS

ROZKŁAD PRZESTRZENNY RÓŻNYCH FORM ŻELAZA W GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: The paper aimed to determine the content of total and soluble iron forms in the top soil horizon (0–10 cm) and present their spatial diversification in the area of zinc and lead ores presence in the vicinity of ZGH "Boleslaw" Mining and Metallurgical Plant in Bukowno near Olkusz.

In 139 soil samples total iron content was determined after sample digesting in concentrated mineral acids (HNO_3 + $HClO_4$) and soluble forms were extracted with 1 mol · dm^{-3} HCl and with 1 mol · dm^{-3} NH_4NO_3 solutions. Fe content in the obtained extracts was assessed by means of atomic absorption spectrometer with flame atomizer.

A considerable accumulation of iron, seriously exceeding the amounts most frequently noted in the soils of Poland was determined in the analyzed samples. Extractant solutions used for iron dissolving in the investigated soils were characterized by different abilities to release this element. Diluted hydrochloric acid dissolved on average 21.5 % and ammonium nitrate solution on average only below 0.1 % iron in soil. The highest contents of iron soluble in diluted hydrochloric acid were assessed in the areas with the highest total content of this metal to the north and north-west of ZGH "Boleslaw" and in the vicinity of post-flotation wastes settlement tanks. On the other hand, the greatest quantities of iron released with ammonium nitrate solution were found in the vicinity of Pomorzany Mine and on the most acidified soils of the analyzed area.

Keywords: iron, solubility, heavy metals, bioavailable forms

Iron chemistry in soils depends on many factors. It is most dependent on a number of soil physical and chemical properties which cause a reduction or increase in its solubility and bioavailability [1–3].

Amounts of this element contained in soil solution are usually very small and the bigger the lower the value of soil pH. Plants absorb iron as Fe^{2+} ions or in a chelate form. Their content in soil is the smallest at pH 6.5–8.0 [1, 4].

Two opposite phenomena: sorption and desorption [5, 6] affect iron solubility and bioavailability. Sorption occurs according to three basic processes:

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– arresting ions by mineral and organic elements of sorption complex,
– biological accumulation,
– precipitation of insoluble compounds.

These processes lead to limiting iron mobility and solubility. The opposite process – desorption increases this element bioavailability and mobility, among others by dissolving and mineralization of organic compounds. Intensity of these phenomena is conditioned by many physical and chemical properties of (not only soil) environment [4].

Limiting iron bioavailability to plants in result of its adsorption by mineral and organic soil colloids is a positive phenomenon. The result of this process is protection of subsequent links of food chain against the negative effect of excessive amounts of this element on plant healthiness [7].

The paper aimed to determine the total content of iron and its soluble forms in the top soil horizon (0–10 cm) and present their spatial diversification in the area of zinc and lead ores presence in the vicinity of ZGH "Boleslaw" Mining and Metallurgical Plant in Bukowno near Olkusz.

Material and methods

Analysis of iron mobility was conducted in soil samples collected in the Malopolska province near the town of Olkusz in the communes of Boleslaw and Bukowno, situated between two city agglomerations: Krakow and Silesia. Development of mining and zinc-lead ore processing in the region of Olkusz is connected with shallow deposits of metalliferous dolomites in this area in which beside zinc and lead also accompanying elements, such as Fe, Ag, Cd, Tl and As are present [8–11].

Iron is one of the elements accompanying ores extracted in the Olkusz vicinity. It belongs to the most mobile elements in soil, occurs in different forms, among others as concretion and hydroxides and colloidal forms which have a serious influence on soil forming processes but also on trace elements sorption and their solubility and bioavailability to plants [1].

Iron occurs in the soils of the investigated area in the amounts from 41 to 8.2 $g \cdot kg^{-1}$ [12], at an average content of this metal in the soils of Poland *ca* 20 $g \cdot kg^{-1}$ [13]. Therefore it may be expected that this element would enter the food chain with greater intensity.

The researched area covered 100 km^2 in the vicinity of ZGH "Boleslaw" Mining and Metallurgical Plant in Bukowno. Soil samples were collected from June to August 2008 from the top soil horizon (0–10 cm) in 139 points marked on the map (Fig. 1). Sampling places were determined according to previously assumed experimental design. One sample was collected from the area of 1 km^2, whereas in the areas situated in the immediate vicinity of ZGH "Boleslaw" Plant, density of sampling increased to 2 samples per 1 km^2.

Collected soil material was dried in the air and sifted through a plastic sieve with 2 mm mesh. Potentially bioavailable iron compounds were extracted from the collected soil samples by Rinkis method [14] using 1 $mol \cdot dm^{-3}$ HCl solution. Fe quantity actually bioavailable to plants was assessed by the method using 1 $mol \cdot dm^{-3}$ NH_4NO_3

Fig. 1. Places of soil sampling (based on [15])

solution as an extractant [14]. Total Fe content in soil was determined after its dissolving in a mixture of nitric(V) and perchloric(VII) acids (2:1. v/v) following previous mineralization of organic matter in a muffle furnace at 450 ^{o}C [16]. In the solutions prepared in this way iron content was assessed on *Solaar M6 atomic absorption spectrometer* with *flame atomizer*.

The soil basic physicochemical properties were also determined using methods generally applied in agro-chemical laboratories [16]:

– granulometric composition by aerometric Bouyoucose-Casagrande method in Proszynski's modification,

– soil reaction (pH) in 1 mol · dm^{-3} KCl suspension by potentiometric method,

– organic carbon content using Tiurin method.

The obtained results were analyzed by means of Microsoft Excel 2003 calculation sheet. The maps of spatial distribution of bioavailable iron contents in soil, extracted by 1 mol · dm^{-3} HCl and NH_4NO_3 were created using Surfer 8.0 packet. The maps prepared in this way were applied on the maps of the investigated area.

Results and discussion

While analyzing the data presented in Table 1 one may notice not only a considerable diversification of each analyzed forms of iron in the studied soils but also considerable differences between computed values of arithmetic mean, geometric mean and median which describe the assessed amounts of this element.

Table 1

Statistical characteristics of Fe content in the analysed soil samples

Parameter	Fe content [mg · kg^{-1} d.m.]		
	Total	Soluble	
		in HCl solution	in NH_4NO_3 solution
Minimum value	676.2	54.2	0.50
Maximum value	60282.8	6612.9	61.8
Arithmetic mean	6795.5	1392.6	7.2
Geometric mean	4485.0	996.5	3.9
Median	3908.7	1141.2	3.3
Relative standard deviation [%]	128.6	83.6	139.9

This evidences a considerable deviation of these values from normal distribution, caused by a natural and anthropogenic "enrichment" of the environment in the investigated area concerning iron content. At normal distribution of element contents the above-mentioned statistical features would be equal. On the other hand, at a considerable deviation of the normal distribution of data set, geometric mean is more approximate to the middle value of the set (median) than arithmetic mean, therefore in such cases, geometric mean better characterizes the analyzed data pool and is often used to describe the polluted environment [17].

Extractant solutions used for iron extraction from the soils collected around the ZGH "Boleslaw" Mining and Metallurgical Plant near Olkusz were characterized by different potential of this element desorption. Diluted hydrochloric acid dissolved on average 21.5 % of the iron amount assessed using concentrated mineral acids, whereas ammonium nitrate solution extracted on average only less than 0.1 % of this amount of iron. The content of potentially bioavailable iron in the analyzed samples assessed after extraction with 1 mol · dm^{-3} HCl solution ranged widely from 54.2 to 6612.9 mgFe · kg^{-1} d.m. On the other hand, amounts of iron directly available to plants, extracted with 1 mol · dm^{-3} NH_4NO_3 solution ranged from 0.5 to 61.8 mgFe · kg^{-1} d.m. (Table 1, Fig. 2). Relative standard deviation computed for this feature points to the greatest variability of the iron forms contents released by ammonium nitrate solution (Table 1). Relative standard deviation of iron extracted from the analyzed soils with diluted hydrochloric acid was visibly lower (83.6 %), despite the fact that the range of diversification of its contents released by both extractants was almost identical. Minimal iron content determined using HCl solution made up 0.82 % and when NH_4NO_3

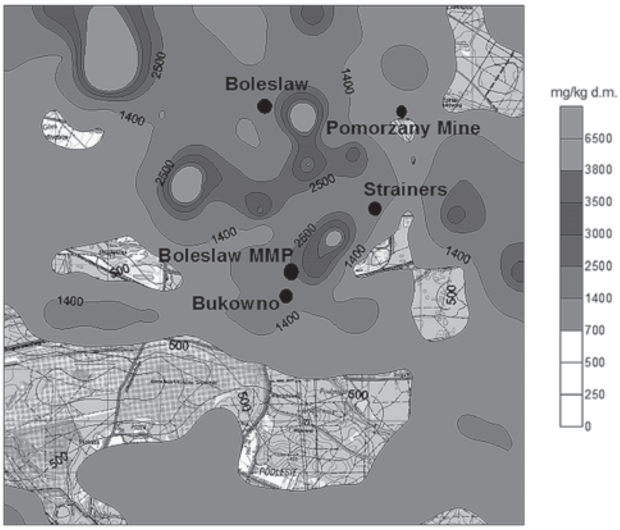

Fig. 2. Spatial distribution of iron content extracted with 1 mol · dm^{-3} HCl in soils around ZGH "Boleslaw" (based on [15])

solution was applied – 0.81 % of the maximum quantity of this element dissolved by both mentioned above extractants.

1 mol · dm^{-3} hydrochloric acid solution was identified in 1986 in Poland as a group extractant for an assessment of microelement contents, including iron, in mineral soils. Limit numbers for this method were published in "Fertilizer recommendations" issued by the Institute of Soil Science and Plant Cultivation [18].Three soil classes were indentified characterized by low, medium and high content of this element.

The investigated region reveals evidently elevated total iron content in soil resulting from both high natural content of this element in the parent rock and anthropogenic activity in this region. However, the assessment of determined contents of iron soluble in diluted hydrochloric acid reveals that only 5 % of samples were characterized by a high content of this metal, whereas as many as 63 % of samples were classified to soils with medium iron content (Table 2). Almost one third of samples contained small amounts of iron.

Table 2

Assessment of iron soluble by 1 mol · dm^{-3} HCl
(on the basis of Fertilizer recommendations [18])

Class of iron content	Estimation of content	Fe content [mg · kg^{-1} of soil]	Share of soils
III	Low	< 700	32
II	Medium	700–3800	63
I	High	> 3800	5

Spatial diversification of the amounts of iron extracted from the soils in ZGH "Boleslaw" Plant neighbourhood using both compared methods points to a dissimilarity and specific activity of applied extractant solutions (Fig. 2 and 3).

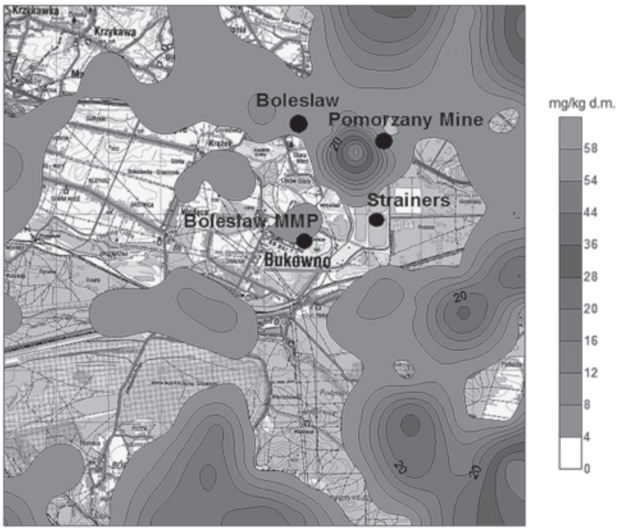

Fig. 3. Spatial distribution of iron content extracted with 1 mol · dm^{-3} NH_4NO_3 in soils around ZGH "Boleslaw" (based on [15])

The highest contents of iron soluble in diluted hydrochloric acid, exceeding 3800 mg · kg^{-1} of soil were assessed to the north and north-west of ZGH "Boleslaw" Plant but also in the vicinity of post-flotation wastes settlement tanks and in the vicinity of Boleslaw town. These regions usually overlie with the areas of the highest total content of this metal in the analyzed soils. Correlation coefficient describing the relationship between these forms of iron in the investigated soils is 0.64 and is significant at the significance level $\alpha \le 0.001$ (Table 3). Quantities of iron extracted from the researched soils using 1 mol · dm^{-3} HCl were also strictly, positively correlated with their contents of floatable particles and organic substance.

Table 3

Effect of selected soil properties on solubility of iron – linear correlation coefficients

Content of Fe soluble in	pH	Content			
		Fe_{tot}	Clay fractions	Colloidal clay	Organic carbon
1 mol · dm^{-3} HCl	0.33*	0.64*	0.54*	0.34*	0.54*
1 mol · dm^{-3} NH_4NO_3	–0.43*	0.00	0.01	–0.08	0.36*

* Significant at $\alpha \le 0.001$.

As has been mentioned earlier, ammonium nitrate solution extracted on average only *ca* 0.1 % of the total iron content in the studied soils. The greatest quantities of this form of iron were assessed in the most polluted area: north of ZGH "Boleslaw" close to Pomorzany Mine and in the north-eastern and south-eastern part of the area under investigations (Fig. 3), where most acidified soils occur [19]. In the other areas covered by the investigations, mainly light soils prevail with considerable proportion of various metals carbonates [8, 9], which suggests poor solubility and bioavailability of iron in the soil substratum. These findings confirm the opinions that this method is used to assess the amounts of elements approximate to assimilated by plants [20]. This conclusion is further corroborated by the values of correlation coefficients compiled in Table 3. Amounts of iron extracted by ammonium nitrate positively depended on the content of soil humus but negatively on changes of the analyzed soils pH.

These observations are best verified by the analysis of iron contents in plants in the area under investigations.

Conclusions

1. Statistical analysis of results of iron contents in soils around ZGH "Boleslaw" Plant in Bukowno points to a big accumulation of this element, considerably exceeding amount most frequently registered in the soils of Poland.

2. Solutions used for iron extraction in the analyzed soils were characterized by different abilities to release this element. Diluted hydrochloric acid extracted on average 21.5 % whereas ammonium nitrate solution on average less than 0.1 % of iron contained in soil.

3. Limit numbers suggested for the assessment of the amount of iron dissolved in 1 mol $\cdot$ dm^{-3} HCl reveal that 32 % of the analyzed soils had low and only 5 % high contents of this element.

4. The highest iron contents extracted by diluted hydrochloric acid were determined in the areas with the highest total content of this metal located to the north and north-west of ZGH "Boleslaw" and in the vicinity of post-flotation waste settlement tanks. On the other hand the greatest amounts of iron released by ammonium nitrate were registered in the neighbourhood of Pomorzany Mine and in the most acidified soils in this area.

Acknowledgements

The work has been co-financed by the European Union funds in the framework of the European Social Fund, Project "Doctus – the Malopolska PhD Scholarship Fund".

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ROZKŁAD PRZESTRZENNY RÓŻNYCH FORM ŻELAZA W GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

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Abstrakt: Celem pracy było określenie całkowitej zawartości i rozpuszczalnych form żelaza w wierzchniej warstwie gleby (0–10 cm) oraz przedstawienie ich przestrzennego zróżnicowania, na obszarze występowania rud cynku i ołowiu, w sąsiedztwie Zakładów Górniczo-Hutniczych „Bolesław" w Bukownie koło Olkusza.

W 139 próbkach gleby określono całkowitą zawartość żelaza po trawieniu próbki w stężonych kwasach mineralnych (HNO_3 + $HClO_4$), a rozpuszczalne formy ekstrahowano roztworem 1 mol · dm^{-3} HCl oraz roztworem 1 mol · dm^{-3} NH_4NO_3. Zawartość Fe w uzyskanych ekstraktach oznaczono spektrometrem absorpcji atomowej z atomizerem płomieniowym.

W przebadanych próbkach gleby stwierdzono duże naturalne i antropogenne nagromadzenie żelaza, znacznie przekraczające ilości najczęściej spotykane w glebach Polski. Roztwory ekstrakcyjne użyte do rozpuszczania żelaza w badanych glebach, charakteryzowały się odmiennymi możliwościami uwalniania tego pierwiastka. Rozcieńczony kwas solny rozpuszczał średnio 21,5%, a roztwór azotanu amonu przeciętnie tylko mniej niż 0,1% całkowitej ilości żelaza zawartego w glebie. Największe zawartości żelaza rozpuszczalnego rozcieńczonym kwasem solnym oznaczono w terenach z największą całkowitą zawartością tego metalu na północ i północny zachód od ZGH „Bolesław" oraz w pobliżu osadników odpadów poflotacyjnych. Natomiast największe ilości żelaza ekstrahowanego roztworem azotanu amonu stwierdzono w sąsiedztwie Kopalni Pomorzany i na najbardziej zakwaszonych glebach badanego obszaru.

Słowa kluczowe: żelazo, rozpuszczalność, metale ciężkie, formy przyswajalne