CIVIL AND ENVIRONMENTAL ENGINEERING REPORTS

No. 7 2011

ACCUMULATION OF IRON IN THE SOIL-PLANT SYSTEM IN A METAL INDUSTRY AREA

Róża FRUZIŃSKA*
Institute of Environmental Engineering
University of Zielona Góra
Szafrana st 15, 65-516 Zielona Góra, Poland

The paper presents the results of research on the content of iron in a subtotal form in the soils of metal industry areas and the content of iron in the grass growing in the test area. Research on the content of iron in soils and grasses was carried out in 2009-2010. The results indicated that the content of iron in soils taken from the premises of the metals industry plant was greater than in soils from areas not covered by direct anthropopressure. The content of iron found in soils was from 1,06% dw to 8,13% dw with the content of 0,6% dw in the control areas. The plants studied showed the presence of iron at the level of 0,027-0,104% dw with a content of 0,009% dw in the control areas. The accumulation of iron in the soils of the area under research is the result of a long-term industrial activity (which started in 1876), based on the manufacture of rolling stock and steel elements.

Keywords: metal industry, soil contamination, bioaccumulation of iron

1. INTRODUCTION

Iron is a key element of the globe. According to various sources, it constitutes 30-40% of the composition of the Earth. In its base state it constitutes about 90% of the Earth's core [Polański and Smulikowski 1969, Polanski 1988]. The main source of iron in the soil are mineral compounds such as limonite, hematite, magnetite, pyrite, siderite, goethite and some iron-magnesium silicates: olivine, augit, hornblende, biotite [Gliński 1999, Lityński and Jurkowska 1982]. With organic matter it creates chelates. It is also available in pure form, as ferrite [Chmielnicka 2002]. Its circulation is associated with the circulation of oxygen, sulfur and carbon [Kabata-Pendias and Pendias 2001].

* E-mail: r.fruzinska@iis.uz.zgora.pl

It is chemically active, it is present in the form of oxides, hydroxides, sulfides, carbonates, silicates, sulfates, chlorides and cyanides. Metals in the form of pure elements do not have a negative impact on the environment because they are not soluble in water and weakly concentrated solutions of salts, acids and alkalis. Metal compounds are potentially toxic, because they can be dissolved and dissociated and can penetrate cell membranes of organisms [Bezak-Mazur 2001, Lityński and Jurkowska 1982].

The amount of iron is different in soils of various origins and used differently. Its natural, average content in soil is 0,6% [Kabata-Pendias and Pendias 1999, 2001] and may undergo significant changes due to the high vertical mobility of iron in soil profiles [Gliński 1999]. The least iron is found in limestone and dolomite [Kabata-Pendias and Pendias 1999]. Iron, like other heavy metals, has a long life in the natural environment.

Economic activity, including industrial activity, causes a continuous supply of metallic elements in the environment in the form of different compounds. Continuous emissions of metal bearing dust and fumes, as well as discharge of sewage and waste deposition cause increased concentration of heavy metals in the environment. The result is a continuous increase of their content in soils, surface waters and groundwater in highly industrialized regions. The main sources of iron in the environment are emissions from metal and metallurgical establishments and coal combustion.

Participation of iron in the overall pollution of the environment is not usually defined, because in most cases metals do not pose a threat to organisms [Kabata-Pendias and Pendias 1999]. Some authors emphasize, however, possible negative effects of high concentrations of Fe, both for land ecosystems, as well as water [Hüttl 1998, Lesley et al. 2008].

The purpose of this research is to determine the anthropopressure from the metal industry in soils and plants, calculated as an increase in the content of iron.

2. DESCRIPTION OF THE RESEARCH OBJECT

The research object is the metal industry area located in Zielona Gora, which occupies about 11.5 acres, located on Sulechowska Street and its immediate surroundings. Industrial activities in that area started in 1876 with the production of wooden wagons. Then the activities involved the production of agricultural machinery, steel structures of industrial halls, bridges and railway stations. In 1886, the construction of railway freight and passenger carriages, tanks, mail carriages, refrigerated carriages, etc. During the Second World War the factory produced vehicles and equipment for the army. It produced armored trains, cannon parts, military vehicles, submarine hulls, aircraft parts. After

1945 the factory was taken over by the State, created “Zaodrzańskie” Metal Industry Plant. “Zastal” was founded, which produced rolling stock, freight carriages and locomotives, but also the steel constructions [Borkowski et al. 1985, Eckert 1980]. Currently the site produces rolling stock and steel structures.

The present location of the area under research shows a number of planning and environmental drawbacks, because pollution generated during the technological processes of the industrial plant is likely to get into the air, soil, surface water and groundwater. As a result of the expansion of buildings the industrial plant has been surrounded with single-and multifamily houses. These adjacent areas, used in a completely different way should be separated from each other to improve the lives of the people living in them. A result of the presence of the industrial plant has also an impact on the flora and fauna, landscape and climate. Even compliance with the required quality of the soil in areas used for such a different purpose becomes problematic for the functioning of the city [the regulation issued by the Minister of the Environment on 9 September 2002 on soil quality standards], or compliance with the regulations on the restriction of negative effects of industrial activities to the area where an industrial plant is located [the Environmental Protection Law of 27 April 2001].

3. RESEARCH METHODS

Test samples were obtained in accordance with the provisions of the standard ISO 10381-1:2008, ISO 10381-2:2007 and ISO 10381-5:2009.

The test site was divided into 10 sub-areas, from which samples of a disturbed structure were taken. Soil samples were taken twice: in June 2009 and June 2010. The research areas comprised open-air areas near the hangars, cranes, railway sidings and car parks. Samples were taken from the surface soil layer (0-20 cm). Within each test area 30 individual samples were mixed together to get a weight of about 1 kg of a representative sample (aggregate). The samples were dried. Then, all soils samples underwent the following research:

- analysis of granulometric composition - areometric method by Casagrande in the modification of Prószyński, according to the standard ISO 11277:2009,
- indication of pH - according to the standard ISO 10390:2005, in water and 1-molar KCl,
- determination of iron in the soil in a form similar to the general form - atomic absorption spectrometry (AAS FL) after ignition of samples in a muffle furnace at 550°C to constant mass and dissolving the residue after

ignition in a mixture of hot concentrated acids HCl: HNO_3 relative 3:1 (aqua regia) according to the standard PN-ISO 11466:2002.

In 2010 from all the 10 test sub-areas samples were collected from the above-ground parts of grasses. The study had been taken all the species of grasses growing in the industrial plant. They were dried and then ground. In the plant material obtained in this way the following research was carried out:

– the examination of losses after ignition by means of the weight method - after ignition of samples in a muffle furnace at 550°C.
– the specification of the quantity of iron in a form similar to the general form- atomic absorption spectrometry (AAS FL) after ignition of samples in the muffle furnace at 550°C to constant mass and dissolving the residue after ignition in a mixture of hot concentrated acids HCl: HNO_3 over 3:1 (aqua regia) according to the standard PN-ISO 11466:2002.

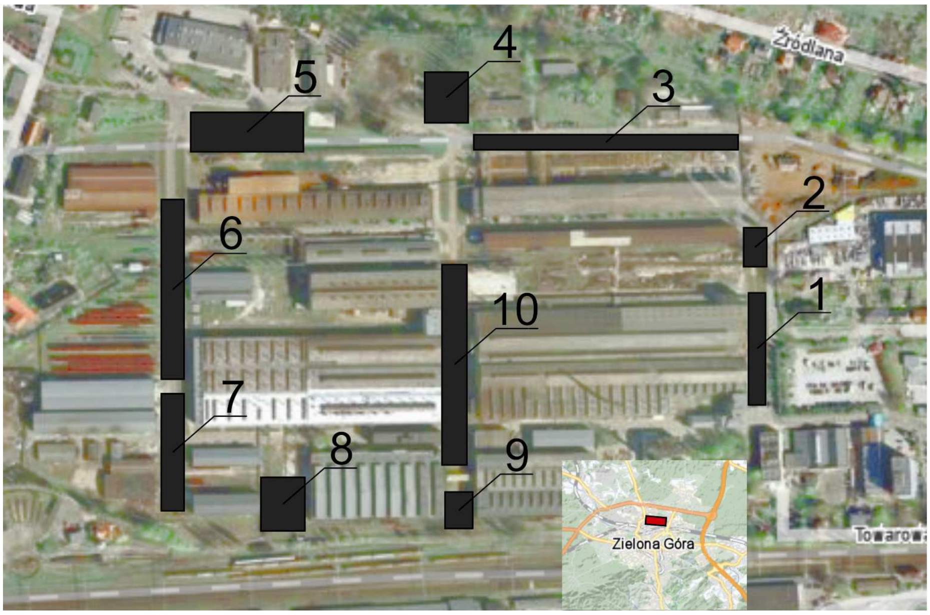

Fig. 1. Location of sampling sites in the factory area
[Fruzińska 2011 based on Zumi.pl map]

Results of the analysis of the iron content in soils and plant material are presented in the percentage of dry matter. Figure 1 presents the sampling of soil and plant material.

4. RESULTS

On the basis of the particle size it has been determined that all the soil samples obtained from the area of the metal industry belonged to loose sands. All the soils used in the tests belonged to grainy forms, the smallest content of the soil skeleton was found in sample 4.1 – 6,53%, while sample 9.1 contained the largest percentage of the soil skeleton – 31,38%. The sand content in the samples analyzed ranged from 86 (sample 9.1) to 96% (samples 4.2 and 6.2). Other fractions were dust: 3-14%, and clay: 0-3%.

Both the soil samples and plant material were analyzed for the iron content in the form similar to the general form. The results are presented in Table 1.

Table 1. The results of the iron content in a form similar to the general form in the soil and grasses

Field Number	Designation	Iron content in soils (% of dry mass)	Iron content in grasses (% of dry mass)
1	a	-	-
	b	5,79	0,027
2	a	-	-
	b	-	0,042
3	a	2,77	-
	b	2,66	0,030
4	a	1,06	-
	b	1,41	0,029
5	a	1,80	-
	b	1,52	0,028
6	a	3,04	-
	b	1,70	0,104
7	a	4,72	-
	b	5,56	0,063
8	a	5,70	-
	b	8,13	0,053
9	a	5,48	-
	b	5,17	0,054
10	a	-	-
	b	4,89	0,074

"-"– results in development or no sample
a – samples taken in June 2009
b – samples taken in June 2010

The iron content in soils and plant materials depended on the location of sampling. Sample 8.2 had the highest iron content in the soil (on dry basis), the lowest content of iron was found in sample 4.1. These values were 8,13% for sample 8.2 and 1,06% for sample 4.1.

The lowest content of iron in the general form in the grass was 0,027% for sample 1.2, while the largest was 0,104% for sample 6.2

5. DISCUSSION OF RESULTS

Iron is present in the soil in varying quantities, it depends on the type of soil. The average iron content in light soils is 0,6% [Kabata-Pendias and Pendias 1999, 2001].

Iron in the soil has different functions depending on the valence of the element. In general, the presence of iron has a positive effect on the soil structure, it plays a significant role in the processes of soil formation. It affects the chemistry of other elements present in the soil. Amorphous iron oxides are characterized by the sorption capacity in relation to heavy metals. They may affect their distribution and bioavailability [Lityński and Jurkowska by E. Schlichting 1976], for example, arsenic contained in soils is primarily bound by amorphous iron oxides [Karczewska et al. 2004]. An increased iron content in the soil can cause silting soil pores hindering the flow of water and air penetration. A high iron content in soil can cause hard concretions disrupting plant growth.

All the analyzed soil samples showed a higher iron content in comparison with light soil unaffected by direct anthropressure. The highest iron content was 8,13% for sample 8.2 and the lowest was 1,06% for sample 4.1. The soil conditions of the area from which samples are obtained should be taken into account in the assessment of the risk connected with a higher iron content. Only then can it be determined whether the iron accumulated in the soil will adversely affect the growth of plants in the area under research.

In the grasses tested, growing in the premises of an industrial plant, the iron content was higher in the aboveground parts of plants. The average content of iron in the grass growing in areas of Poland which are not subject to direct anthropopressure is 0,006-0,014%, with an average of 0,009% [Kabata-Pendias and Pendias 1999, 2001]. The lowest content of iron in the grass in the industrial area under research was 0,027% for sample 1.2% and the highest was 0,104% for sample 6.2.

Iron is essential for the proper development of plants. This microelement is absorbed from the soil in different amounts depending on the species and varieties of plants. It is absorbed from soil solutions in the form of ferric ions, Fe^{3+}, Fe^{2+}, and ferrous Fe in the form of chelates [Gliński 1999].

The function of iron in higher plants is mainly participation in redox processes occurring in cells, mainly in the process of respiration. Iron is located in ferredoxine, which can pass from the form of a two-to trivalent[1] [Brady 1982, Lityński and Jurkowska by Arnon et al. 1961, 1965], it also participates in the metabolism of nitrogen.

[1] Ferredoksyna participates in the transfer of electrons in the processes of cyclic and non-cyclic phosphorylationic during photosynthesis

Both deficiency and excess of iron in the soil impairs the extraction of nutrients by plants. The result is a system disorder in development and operation of the plant [Kabata-Pendias and Pendias 2001]. Deficiency of iron ions in the soil may cause a reduction of chlorophyll content in leaves - interviscicular chlorosis[2] [Kabata-Pendias and Pendias 1999].

Deficiency or excess of elements is not the only obstacle to the proper functioning of plants. Micronutrients in the soil under certain conditions, take physical and chemical forms toxic or unabsorbable for plants. The bioavailability of micronutrients, including iron, is determined, among other things, by the pH. In soils with a high pH iron precipitates. The limit of participation for iron hydroxides (III) is pH 6,0 [Brady 1984, Lityński and Jurkowska by Lucas and Knezek 1972, Lityński and Jurkowska by Lindsay 1972]. Other factors influencing on the form of iron ions in the soil are: soil aeration, oxidation-reduction potential, the content of organic matter and minerals (especially clay). In conditions of iron-oxidizing and alcaline coditions iron is subject to precipitation processes but reductive and acidic conditions favor the formation of soluble forms of iron in the soil, which are available to plants [Kabata-Pendias and Pendias 1999]. According to this principle, wetland soils are rich in available forms of micronutrients. If, however, simultaneously with the occurrence of severe waterlogging in the soil there is a low pH, then micronutrients, including iron, can reach a toxic dose for plants.

In soils with a low moisture content, good aeration and a high pH micronutrients, in spite of their sufficient quantity for plants, occur in forms unavailable to plants. In the case of iron they are iron-hydroxides (III) [Lityński and Jurkowska 1982]. Changing forms of iron in the soil are presented in the following diagram:

$$Fe^{3+} \xrightarrow{OH^-} Fe(OH)^{2+} \xrightarrow{OH^-} Fe(OH)_2^{+} \xrightarrow{OH^-} Fe(OH)_3 \downarrow$$

Simple cation (soluble) $\xrightarrow{OH^-}$ hydroxy metal cations (soluble) $\xrightarrow{OH^-}$ hydroxide (insoluble) $\downarrow$

Diagram 1. Changing forms of iron in the soil [Brady 1982]

The above diagram illustrates that the alkaline hydroxides of iron (III) precipitate, so it is impossible for plants to absorb iron from soil solutions. However, to some extent, plants have evolved the ability to cope with shortages of iron in an assimilable form [Olsen et al. 1981]. Therefore, the efficiency of iron absorption from the soil depends on the ability of roots to reduce Fe^{3+} to

[2] The disease manifests itself by the blanching of the leaf with the exception of the leaf tissue along the major sieve-vascular bundles [Lityński and Jurkowska 1982].

Fe^{2+} [Chaney et al. 1972] by secrete of mugineic acid from the roots, which changes the soil conditions and causes reduction. Unfortunately, simultaneously with the increase of soil acidity around the roots, used to absorb iron, there appear other micronutrients, including heavy metals, which adversely affect plants [Kabata-Pendias 1999].

All the soils in the area under research had alkaline reaction. The highest pH, measured both in water and 0,1 M KCl was observed for sample 6 (8,16 and 8,00 pH_{H2O} pH_{KCl}), the lowest for sample 9 (7,72 and 7,29 pH_{H2O} pH_{KCl}) [Fruzińska 2010]. Soil samples tested belonged to the granulometric group of loose sands.

The results for the soil obtained from the area of the industrial plant have a high reaction. A granulometric composition classifies the soil among loose sands and a high content of skeletal forms provides soil aeration. The results obtained make it possible to claim that the iron in the soil has assumed a form unavailable to plants. A significantly higher iron content in the soil in the form similar to the general form is accompanied by a relatively lower increase in the iron content in the grass. It means that a significant proportion of iron in the soil is hard to absorb, because it appears in the form of trivalent iron and metallic iron [Gurzau et al. 2003]. This is typical of industrial areas of the metal and metallurgical industry. There are known cases of difficulty in iron absorption by plants because of phosphates found in the soil [Ayed 1970], but because of the character and industrial use of the area under research it is considered much less likely.

6. CONCLUSIONS

The results of the laboratory analysis indicated a change in soil chemistry in the area of metal industry in comparison to areas unaffected by industrial use. The change was illustrated, among other things, by a higher iron content in soils. The consequence of a higher iron content in soils was an increase in the accumulation of iron in the grass. Plants did not show symptoms of iron toxicity, which could be associated with a slight alkaline reaction and loose granulometric composition of the soil (facilitating the maintenance of Fe on the third level of oxidation).

The iron content in the soil depended on the location of sampling. The highest iron content was found in soils located near the production facilities - sample 9, while the lowest iron content was found in sample 4 obtained from a green area located near disused wooden cooling towers. The highest iron content was found in the grass growing on soils with a high iron content.

REFERENCES

1. Ayed I. A.: *A study of the mobilization of iron in tomato roots by chelate treatments*, Plants and soil, **32**, 1-3 (1970) 18-26.
2. Bezak-Mazur E.: *Elementy toksykologii środowiskowej*, Kielce, Politechnika Świętokrzyska w Kielcach 2001, 23-56.
3. Borkowski W., Fedorowicz C., Kapała J., Koziorowski A., Łuczkiewicz Z., Rutkowski H.: *Zastal 1945-1985*, Zielona Góra, Zaodrzańskie Zakłady Przemysłu Metalowego im. M. Nowotki ZASTAL w Zielonej Górze 1985.
4. Brady N. C.: *The Nature and Properties of Soil*, New York, Macmillan Publishing Company 1984.
5. Chaney R. L., Brown J. C., Tiffin L. O.: *Obligatory reduction of ferric chelates in iron uptake by soybeans*, Plant Physiology **50**, 2 (1972), 208-213.
6. Chmielnicka J., w: *Toksykologia*, red. W. Seńczuk, Warszawa, Wydawnictwo lekarskie PZWL 2002, 511-516.
7. Eckert M.: *Zastal 1876-1976*, Zielona Góra, Wyższa Szkoła Pedagogiczna 1980.
8. Fruzińska R.: *Właściwości fizyczno-chemiczne gleb terenu przemysłu metalowego*, Zeszyty Naukowe Uniwersytetu Zielonogórskiego Inżynieria Środowiska, **138**, 18 (2010) 146-157.
9. Gliński J.: *Chemiczne i fizykochemiczne właściwości gleb*, w: *Gleboznawstwo*, red. S. Zawadzki, Warszawa, Państwowe Wydawnictwo Rolnicze i Leśne 1999, 183-236.
10. Gurzau E. S., Neagu C., Gurzau A. E.: *Essential metals – case study on iron, Ecotoxicology and Environmental Safety*, Ecotoxicology and Environmental Safety, **56** (2003) 190-200.
11. Hüttl R.F.: *Ecology of post strip-mining landscapes in Lusatia, Germany*. Environmental Science and Policy, **1** (1998) 129-135.
12. Kabata-Pendias A., Pendias H.: *Biogeochemia pierwiastków śladowych*, Warszawa, Wydawnictwo Naukowe PWN 1999, 329-336.
13. Kabata-Pendias A., Pendias H.: *Trace elements in soil and plants*, Boca Raton, CRC Press 2001, 65-87, 310-317.
14. Karczewska A., Bogda A., Gałka B., Krajewski J.: *Ocena zagrożenia środowiska przyrodniczego w rejonie oddziaływania złoża rud polimetalicznych Żeleźniak (Wojcieszów – Góry Kaczawskie)*, Wrocław, Wydawnictwo Akademii Rolniczej we Wrocławiu 2005, 152-166.
15. Lesley B., Hooley D., Younger P.: *Iron and manganese removal in wetland treatment systems: Rates processes and implications for management*, Science of the Total Environment, **394** (2008) 1-8.
16. Lityński T., Jurkowska H.: *Żyzność gleby i odżywianie się roślin.* Warszawa, Państwowe Wydawnictwo Naukowe 1982, 283-292.

17. Olsen R. A., Clark R. B., Bennett J. H.: *The enhancement of soil fertility by plant roots*, American Scientist, **69**, 4 (1981) 378-384.
18. PN-ISO 10381-1:2008 *Jakość gleby. Pobieranie próbek. Część 1: Zasady opracowywania programów pobierania próbek.*
19. PN-ISO 10381-2:2007 *Jakość Gleby. Pobieranie Próbek. Część 2: Zasady dotyczące technik pobierania.*
20. PN-ISO 10381-5:2009 *Jakość gleby. Pobieranie próbek. Cześć 5: Zasady postępowania podczas badań terenów miejskich oraz przemysłowych pod kątem zanieczyszczenia gleby.*
21. ISO 10390:2005 *Soil quality - Determination of pH.*
22. ISO 11277:2009 *Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation.*
23. PN-ISO 11466:2002 *International Standard, Soil Quality—extraction Of Trace Elements Soluble in aqua regia.*
24. Polański A., Smulikowski K.: *Geochemia,* Warszawa, Wydawnictwa Geologiczne 1969, 431-441.
25. Polański A.: *Geochemia i surowce mineralne*, Warszawa, Wydawnictwa Geologiczne 1988, 312-325.
26. Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi (Dz.U. 2002 nr 165 poz. 1359).
27. Ustawa Prawo Ochrony Środowiska z dnia 27 kwietnia 2001 r. (Dz.U. 2001 nr 62 poz. 627).

KUMULACJA ŻELAZA W UKŁADZIE GLEBA-ROŚLINA NA TERENIE PRZEMYSŁU METALOWEGO

S t r e s z c z e n i e

W pracy przedstawiono wyniki badań zawartości żelaza w formie zbliżonej do ogólnej w glebach terenu przemysłu metalowego oraz zawartości żelaza w trawach porastających badany obszar. Badania zawartości żelaza w glebach i trawach realizowano w latach 2009-2010. Otrzymane wyniki badań wskazały, że zawartość żelaza w glebach pobranych z terenu zakładu przemysłu metalowego była większa niż w glebach z obszarów nieobjętych bezpośrednią antropopresją. Stwierdzono zawartość żelaza w glebach od 1,06% s.m. do 8,13% s.m. przy zawartości 0,6% s.m. na obszarach kontrolnych. W badanych roślinach wykazano obecność żelaza na poziomie 0,027-0,104% s.m. przy zawartości 0,009% s.m. na obszarach kontrolnych. Kumulacja żelaza w glebach z badanego terenu jest wynikiem długotrwałej działalności przemysłowej (mającej miejsce od roku 1876), opierającej się na produkcji taboru szynowego oraz elementów stalowych.