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INFLUENCE OF SELECTED CHEMICAL, TIMBER, AND PAPER PLANT EMISSIONS IN POLAND ON THE TOTAL SULFUR AND SULFATE CONTENT IN PLANTS, SOIL, AND GROUND WATER

The research project on the impact of emissions from three types of industrial plants, i.e., chemical fibre, petrochemical, cellulose and paper industries, on the content of total sulfur and sulfates in various plants, soils and ground water has been recently completed. The results have shown wide differentiation of such an impact which becomes a function of a distance from an emission source as well as depends on the species of the plants concerned. The content of sulfates was a better indicator of interdependence than the content of total sulfur. At the same time, it has been discovered that soils have accumulated much more of such compounds than plants and ground water.

1. INTRODUCTION

The excessive emission of sulfur compounds, mainly SO_2, is the basic problem of environment protection in Poland at the moment. The total sulfur dioxide emission in our country has been estimated to be 4.3 million ton [9]. The participation of industrial emissions in environmental pollution is very high, for example the total emission of sulfur dioxide by industrial plants in Poland was found to be 2652.4 thousand ton in 1985. The most of sulfuric pollution comes from power and metallurgical industries. The chemical, timber and paper plants also create a serious threat to the environment and produce 6.2 and 1.5% of all industrial SO_2 emission in 1985, respectively [4]. That fact induced our Department to carry out research in 1981–1985 around three selected plants, two chemical plants and one timber and paper plant.

The research covered the Mazovian Refinery and Petrochemical Plant in Płock (SO_2 emission – 70.6 thousand ton in 1985 [4]), the Chemical Fibre "Chemi-

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tex-Elana" Plant in Toruń (SO_2 emission – 10.4 thousand ton in 1985 [4]), and the Cellulose-Paper Plant in Ostrołęka. The observations were conducted in Płock (1981–1985), in Toruń (1981–1982), and in Ostrołęka (1983–1984). The total sulfur and sulfates content in plants and soil have been estimated (the sulfates in soil have been determined in Płock only). Seven vegetable species (red beet, carrot, lettuce, spinach, radish, tomato, and broad bean), six agricultural crops (potato, barley, wheat, field pea, vetch, and lupin), four fruit plants (apple-tree, pear-tree, strawberry, and red currant) have been examined and the results related to six selected species very sensitive or sensitive to SO_2 [2], [3], [5] have been presented. The soil in the arable layer of 0–40 cm depth has been also thoroughly investigated. In addition, the sulfates content in ground water has been analysed in Płock. Totaly, 1017 plant, 210 soil, and 70 ground water samples have been analysed.

The aim of research was to estimate the emission effect of three mentioned industrial plants on the total content of sulfur and sulfates in plants, soil, and ground water.

2. MATERIAL AND METHODS

The samples of plants, soil, and ground water were taken from the experimental plots in allotment gardens located closely to the refinery and petrochemical plant in Płock, chemical fibre plant in Toruń or cellulose-paper plant in Ostrołęka. The samples taken from plots located around Płock, beyond the zone of direct refinery emissions, served as a control.

Eight varieties of plants belonging to six species have been analysed, i.e., leaves and roots of red beet (*Beta vulgaris* L.) var. Czerwona Kula (Płock) and var. Okrągły Ciemnoczerwony (Toruń, Ostrołęka), leaves and roots of carrot (*Daucus carota* L.) var. Nantejska (Płock) and var. Perfekcja (Płock, Toruń, Ostrołęka), butterhead lettuce leaves (*Lactuca sativa* L.; Toruń, Ostrołęka), spinach leaves (*Spinacia oleracea* L.) var. Matador (Płock, Toruń), straw and grain of spring barley (*Hordeum vulgare* L.) var. Aramir (Płock) and shoots, leaves, stems and seeds of field pea (*Pisum arvense* L.; Płock).

The soil samples were taken in Płock from the depth of 0–5 cm and 5–10 cm (1981–1982) and 0–10 cm, 10–20 cm, 20–40 cm (1983–1985) and from arable layer in Toruń and Ostrołęka. The samples of ground water came from the piezometers and abyssal wells around the refinery plant.

To determine the total sulfur concentration, dried plants and soil were mineralized in the mixture of concentrated nitric and perchloric acids and then extracted in 2% acetic acid to allow estimation of sulfates. The sulfate concentrations in ground water were determined directly in collected samples. The total content of sulfur and sulfates was determined nephelometrically, using barium chloride [8]. The results related to sulfates were recalculated in terms of pure sulfur.

All average values have been statistically analysed in order to count least significant difference according to the Tukey's distribution for the significance level of 0.05.

3. RESULTS

The average total sulfur content in plants varied depending on species, variety, organ, site, and also time of research (figs. 1–3). The lowest sulfur content (0.09% of d.m.) has been found in roots of red beet var. Czerwona Kula in Płock in 1985 (fig. 1),

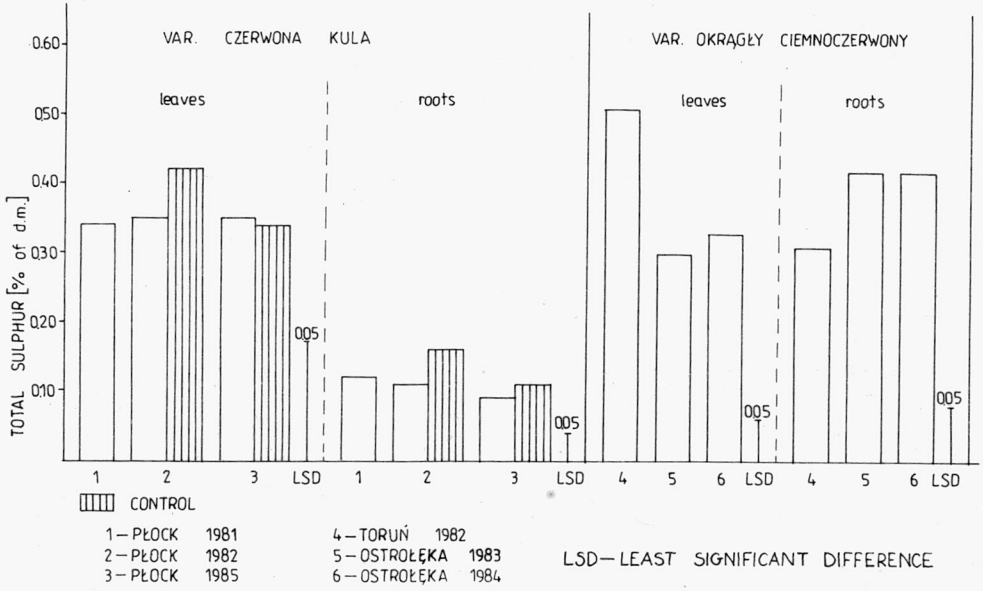

Fig. 1. Total sulfur in red beet

and the highest (0.97% of d.m.), in the leaves of carrot var. Perfekcja in Ostrołęka in 1983 (fig. 2). In the case of the red beet and carrot the content of sulfur in their leaves was considerably higher than in the roots, which confirmed the observations of the other authors [6], [12]. From among all the investigated plant organs, the considerably higher accumulation of sulfur, in comparison with the control sample, has been found only in the case of the field pea leaves in 1984 (fig. 3). Taking into account the differences between the emissions from particular industrial plants, reasonably lower sulfur content was determined in the plants around refinery and petrochemical plant. The ranges of sulfur content (% of d.m.) in the organs of the

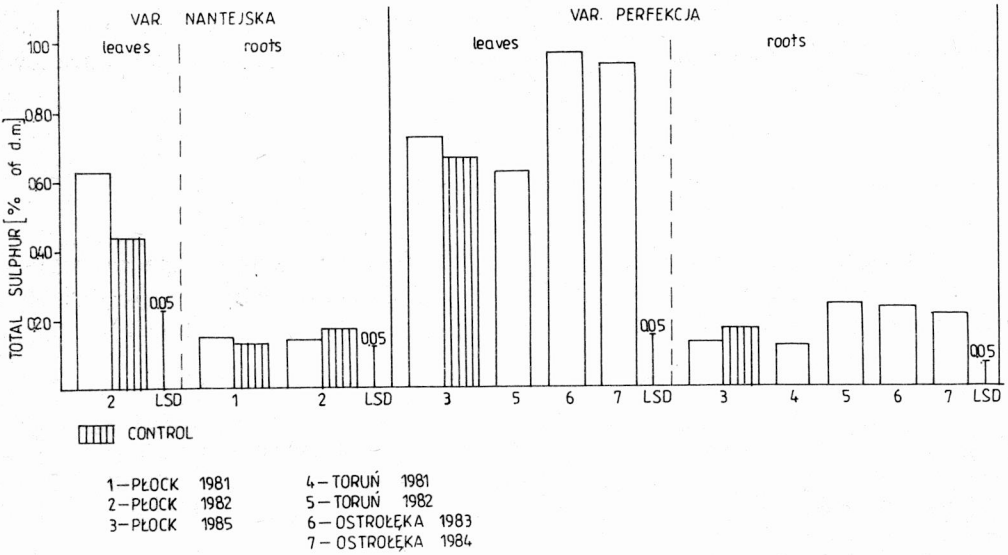

Fig. 2. Total sulfur in carrot

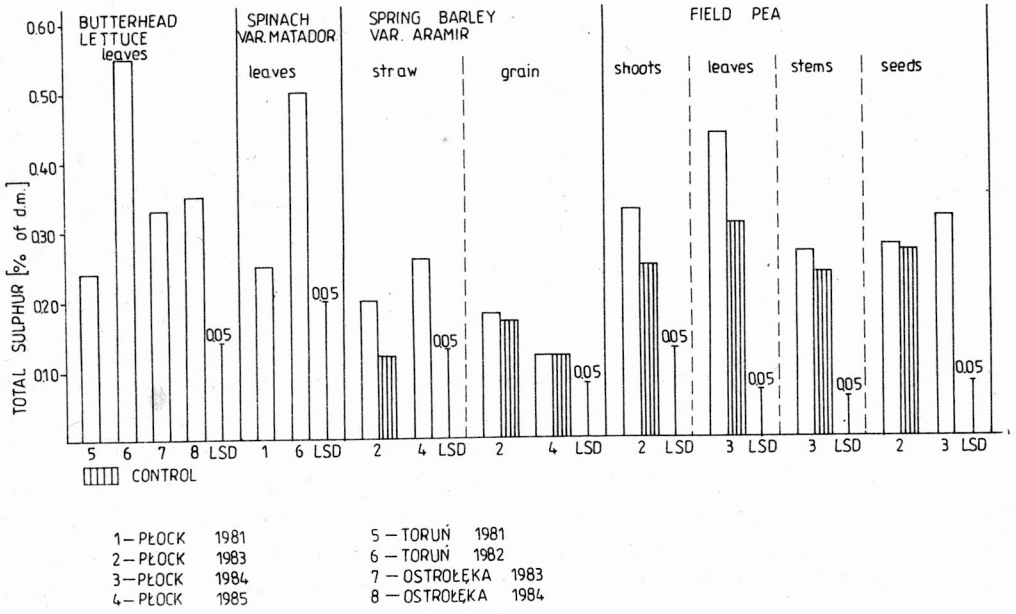

Fig. 3. Total sulfur in butterhead lettuce, spinach, spring barley, and field pea

species investigated were as follows: in leaves of red beet (both varieties) 0.12–0.70; in roots of red beet (both varieties) 0.06–0.97; in leaves of carrot (both varieties) 0.24–1.28; in roots of carrot (both varieties) 0.04–0.92; in leaves of butterhead lettuce 0.09–1.12; in leaves of spinach var. Matador 0.18–0.56; in straw of spring barley var. Aramir 0.16–0.31; in grain of spring barley var. Aramir 0.12–0.18; in field pea shoots 0.31–0.36; in field pea leaves 0.37–0.58; in field pea stems 0.12–0.34, and in field pea seeds 0.26–0.37. The excessive, harmful for the plant growth and development, sulfur content in dry matter, i.e., above 1%, has been found only in the case of few samples of carrot leaves var. Perfekcja around chemical fibre and cellulose-paper plants as well as in the leaves of butterhead lettuce around chemical fibre plant.

The average content of sulfates in other investigated organs showed, similarily to total sulfur content, considerable variations in the particular years and sites (figs. 4–6). The lowest content of sulfates (0.02% of d.m.) has been found in spring barley

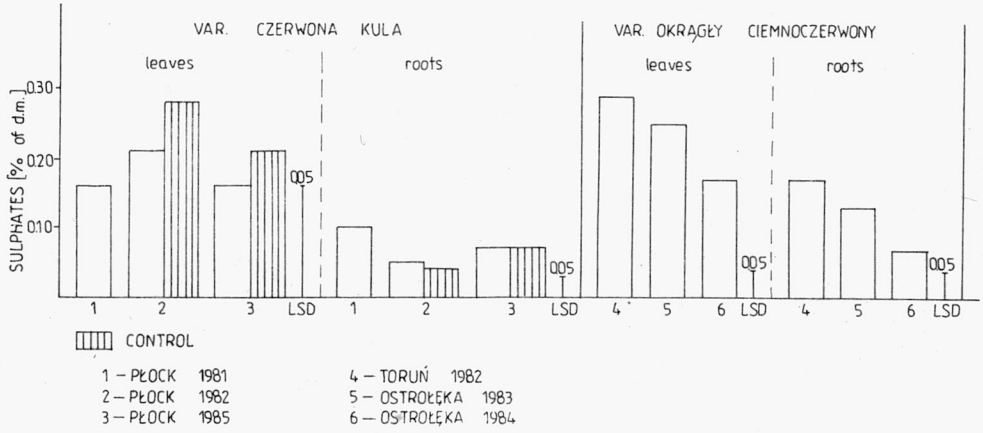

Fig. 4. Sulfates in red beet

grain var. Aramir in Płock (fig. 6), whereas the highest (0.59% of d.m.), in the carrot var. Nantejska leaves in Płock (fig. 5). The notably higher accumulation of sulfates has been observed in the carrot leaves, Nantejska and Perfekcja varieties (fig. 5). In Płock, the accumulation of sulfates in the leaves of two varieties of carrot, i.e., Nantejska and Perfekcja, in the straw of the spring barley var. Aramir, in the leaves of the field pea, and in the seeds of field pea (figs. 5 and 6) was considerably higher than in the control samples. The ranges of sulfate content in the plants have been found as follows: in red beet (both varieties) leaves 0.05–0.54, in red beet (both varieties) roots 0.03–0.33, in carrot (both varieties) leaves 0.15–0.95, in carrot (both varieties) roots 0.02–0.29, in butterhead lettuce leaves 0.08–0.36, in the leaves of spinach var. Matador 0.09–0.37, in the straw of spring barley var. Aramir 0.11–0.21,

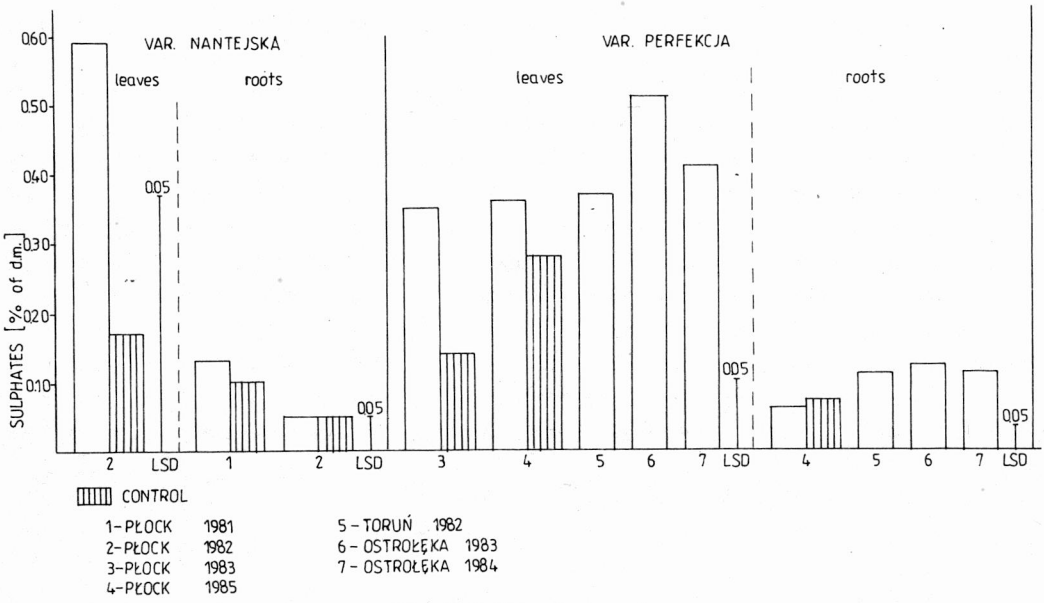

Fig. 5. Sulfates in carrot

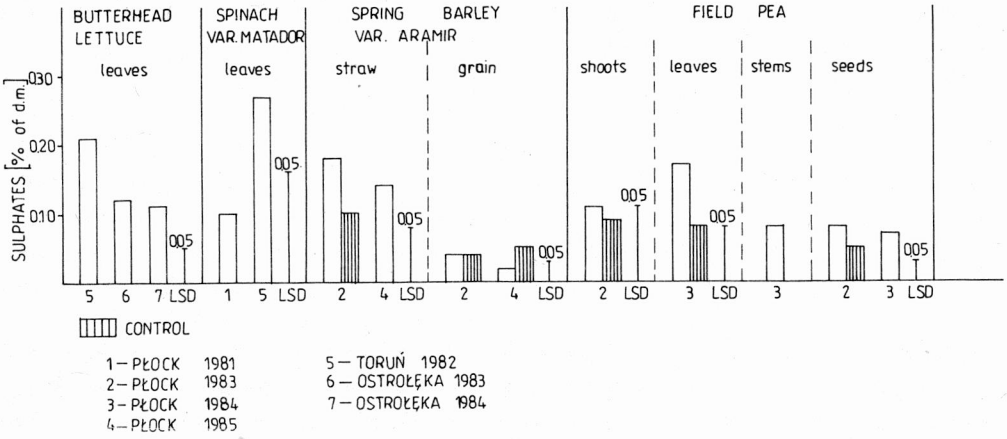

Fig. 6. Sulfates in butterhead lettuce, spinach, spring barley, and field pea

in the grain of spring barley var. Aramir 0.02–0.04, in field pea shoots 0.07–0.16, in field pea leaves 0.08–0.41, in field pea stems 0.03–0.12, and in field pea seeds 0.05–0.10. The excessive sulfate content, probably harmful to the regular plant growth and development ($> 0.50\%$ of d.m.), has been found in the leaves of carrot var. Nantejska and Perfekcja in the vicinity of refinery and petrochemical plant and

cellulose-paper plant as well as in the leaves of the red beet var. Okrągły Ciemnoczerwony around cellulose-paper plant.

Summing up, it should be emphasized that the carrot leaves are highly contaminated both by sulfur and sulfates.

The average total sulfur content in soil at the depths of 0–5 cm and 5–10 cm, 0–10 cm, 10–20 cm and 20–40 cm around refinery and petrochemical plant varied within the range 0.02–0.34% of d.m. (figs. 7 and 8). In the arable layer (fig. 7) around

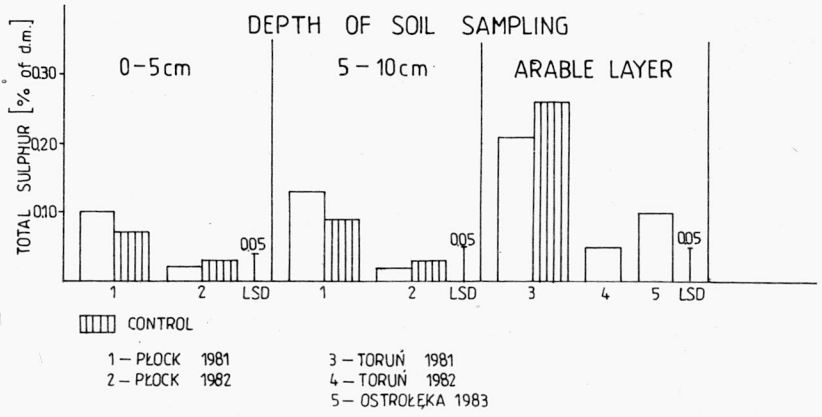

Fig. 7. Total sulfur in soil

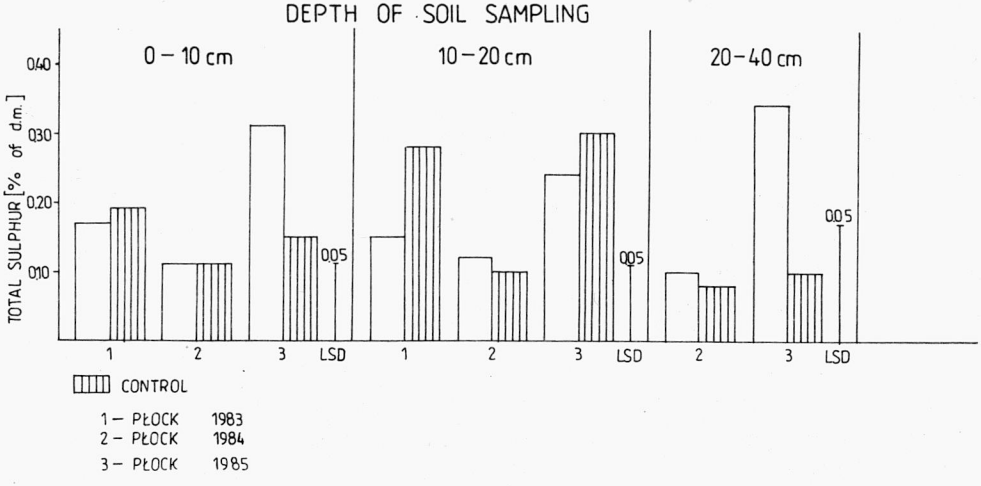

Fig. 8. Total sulfur in soil

chemical fibre plant, the relative contents were found to be 0.05 and 0.21% of d.m. (range 0.02–0.27% of d.m.), and around cellulose-paper plant, 0.10% of d.m. (range 0.06–0.17% of d.m.). In Płock, the following ranges of total sulfur contents 0.01–0.16, 0.01–0.18, 0.01–0.65, 0.01–0.50, and 0.05–0.65 (% of d.m.) correspond with the following depth ranges (cm): 0–5, 5–10, 0–10, 10–20, and 20–40. The accumulation of sulfur in soil was found to be very high in all the cases [1]. Its values have been related to control samples, too. The highest amount of sulfur in soil, considerably higher than those in the control samples, has been stated in Płock (1985) at the depths of 20–40 cm and 0–10 cm.

The average content of sulfates in soil around Mazovian Refinery and Petrochemical Plant was estimated to be 0.006–0.013% of dry mass (fig. 9). The following

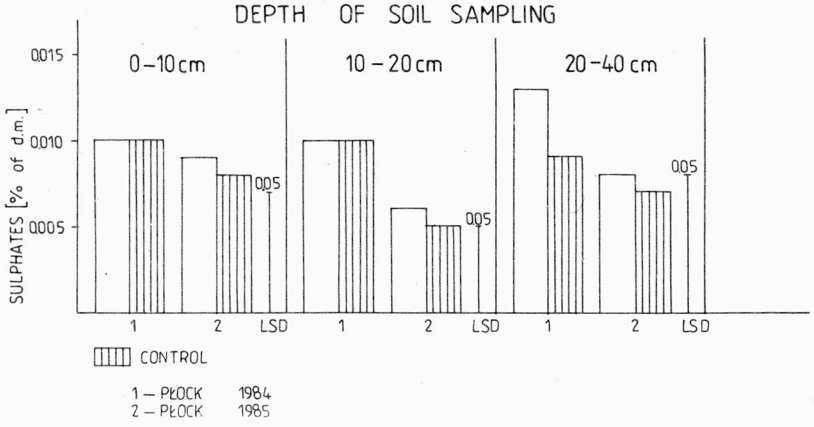

Fig. 9. Sulfates in soil

ranges of sulfate contents in soil, i.e., 0.002–0.030, 0.002–0.025, and 0.003–0.030, corresponded with the following depth ranges: 0–10 cm, 10–20 cm, and 20–40 cm. The accumulation of sulfates as the indicator of sulfur available for plants [11], compared to its average content in Poland [7], was very high both in the case of the plants investigated and control samples. There has not been found any statistically significant difference.

The average content of sulfates in ground water around refinery and petrochemical plant ranged within 34.28–46.95 mg/dm^3 (fig. 10). It was considerably higher in 1983 and considerably lower in 1984, 1985 in comparison with the control sample. The content of sulfates in ground water varied from 6.87 to 73.48 mg/dm^3. When the average content of sulfates in ground water in Poland [10] is taken into account, it should be considered typical, not indicating any pollution with sulfur compounds from the chemical plant.

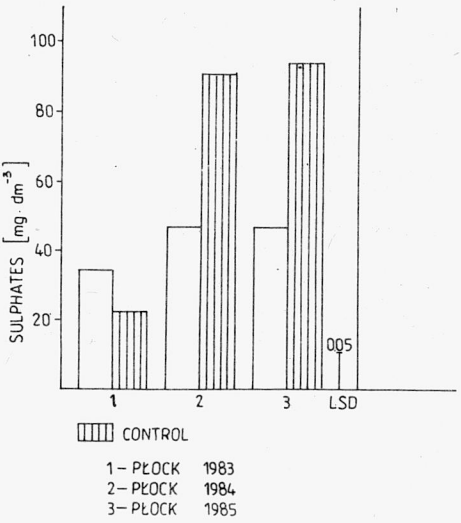

Fig. 10. Sulfates in ground water

4. CONCLUSIONS

1. The emissions of three selected chemical, fibre, petrochemical, and timber and paper plants caused very high pollution of carrot leaves, in which the excessive content of total sulfur as well as sulfates has been found.

2. Due to emissions from the refinery and petrochemical plant the accumulation of sulfates was stronger (e.g., in carrot leaves, barley straw, field pea leaves and seeds) than the accumulation of total sulfur (e.g., in field pea leaves).

3. The accumulation of total sulfur and sulfates in soil was very high in the case of the samples investigated, as well as control ones.

4. There was not stated an increased content of sulfates in ground water nearby refinery and petrochemical plant.

5. It appeared that the most endangered element of the environment around industrial plants was soil, then plants, and the least endangered was ground water.

REFERENCES

[1] ANDRUSZCZAK E. et al., *The effect of emissions of phosphate plant at Ubocz on the fluorine and sulfur content in soil and crops* (in Polish), Roczn. Glebozn., 35, 3–4 (1984), 117–126.

[2] BYTNEROWICZ A., MOLSKI B., *The influence of the atmospheric sulfur dioxide on the vegetation* (in Polish), Wiad. Botan. 18, 3 (1974), 169–183.

[3] CORMIS de L., *Influence de la pollution atmosphérique d'origine industrielle sur les végétaux adventices et cultivés.* "L'arbre dans la ville" journée d'étude FNPMP Paris, 24/2, 1972.
[4] Główny Urząd Statystyczny, *Environment protection and hydrology 1986 (statistics)*, (in Polish), Warsaw 1986, 352 p.
[5] NAEGELE J. A. 1974. *Effect of pollution on plants*, [In:] *Industrial Pollution*, N. Irving Sax Van Nostrand Reinhold Company, New York (Cincinnati)-Toronto (London)-Melbourne 1974, 82–100.
[6] NOWAKOWSKI W., *The influence of the refinery and petrochemical industry pollution on the vegetables growth and their chemical composition* (in Polish), Rozpr. Naukowe i Monografie, Wydawnictwo SGGW-AR, Warsaw 1982, 108 p.
[7] NOWOSIELSKI O., *The available sulfur problem in Polish soils and the available sulfur content depending on soil and fertilization kind* (in Polish), Rocz. Nauk Roln., 84, ser. A, 1 (1961), 35–62.
[8] NOWOSIELSKI O., *The methods of the determination of fertilization requirements* (in Polish), PWRiL, Warsaw 1974, 724 p.
[9] Państwowa Inspekcja Ochrony Środowiska, *The assessment of the environment in Poland* (typescript in Polish), Warsaw 1986, 156 p.
[10] SIUTA J., REJMAN-CZAJKOWSKA M., *Sulfur in biosphere* (in Polish), PWRiL, Warsaw 1980, 396 p.
[11] WALKER D. R., DOORNENBAL G., *Soil sulfate as an index of the sulfur available to legumes*, Can. J. Soil Sc., 52, 2 (1972), 261–266.
[12] WARTERESIEWICZ M., *The effect of air pollution with sulfur dioxide on the selected plant species around Silesian Industrial Center* (in Polish), Arch. Ochr. Środ., part 1, 1979, 95–166.

WPŁYW EMISJI CHEMICZNYCH ZAKŁADÓW PRZEMYSŁOWYCH NA ZAWARTOŚĆ SIARKI OGÓLNEJ I SIARCZANÓW W ROŚLINACH, GLEBIE I WODZIE GRUNTOWEJ

Badano wpływ emisji trzech zakładów przemysłowych; tj. przemysłu włókien sztucznych, petrochemicznego i celulozowo-papierniczego na zawartość siarki ogólnej i siarczanów w różnych roślinach, glebach i wodzie gruntowej. Wyniki świadczyły o dużym zróżnicowaniu tego wpływu w zależności od odległości od źródła emisji i rodzaju rośliny. Zawartość siarczanów była znacznie lepszym wskaźnikiem oddziaływania emisji niż zawartość siarki ogólnej. Stwierdzono również, że gleby akumulowały dużo więcej tych składników niż rośliny i woda gruntowa.

ВЛИЯНИЕ ВЕЩЕСТВ, ЭМИТТИРУЕМЫХ ХИМИЧЕСКИМИ ЗАВОДАМИ, НА СОДЕРЖАНИЕ ОБЩЕЙ СЕРЫ И СУЛЬФАТОВ В ПОЧВЕ И ГРУНТОВЫХ ВОДАХ

Исследовано влияние веществ, эмиттируемых тремья заводами, т.е. заводом производства искусственных волокон, нефтеперерабатывающим комбинатом и целлюлозно-бумажным заводом, на содержание общей серы и сульфатов в разных растениях, почвах и грунтовых водах. Результаты свидетельствовали о большом дифференцировании этого влияния в зависимости от расстояния от источника эмиссии и вида растения. Содержание сульфатов было намного лучшим показателем воздействия эмиссии, чем содержание общей серы. Было также установлено, что почвы аккумулировали намного больше тех составных элементов, чем растения и грунтовые воды.