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# THE INFLUENCE OF SOIL REACTION ON NICKEL AND ZINC UPTAKE BY CLOVER

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A b s t r a c t. The effect of soil reaction on nickel and zinc availability to red clover has been determined through an analysis of 223 samples of soil and red clover collected in all communes of Cracow province.

The content of total nickel in topsoil ranges from 2.8 to 50.0 mg/kg with a geometric mean concentration 15.2 mg/kg. The values for zinc are respectively 48.8-600 mg and 87.5 mg/kg. The amounts of metals assayed in the investigated clover samples are much smaller and they range for nickel from 0.4 to 16.3 mg/kg, on an average 2.3 mg/kg and for zinc 21.6-174 mg/kg, on an average 47.7 mg/kg d.m.

The absorption of the investigated metals by clover depended not only on their content in soil but also on different soil properties, mainly its reaction. Relation between nickel content in clover and in soil has been expressed as a simple correlation ceofficient - r=0.33 and r=0.20 for zinc. The relation has been more explicitly described by multiple regression equations which determine the metal content in clover based on its concentration in soil and soil pH or soil hydrolytic acidity.

K e y w o r d s: soil reaction, nickel in soil, zinc in soil, red clover

## INTRODUCTION

Metallifereous dusts emitted into the atmosphere, having moved to longer or shorter distances, became deposited on the surface of soil, plants or surface waters. On the other hand, an increase in heavy metals content in soil may result from various materials containing certain amounts of them and used in agriculture [13]. Thus, a raise in heavy metals content in arable lands has been observed not only close to industrial plants but also in the areas further away [4,5].

The uptake of those metals by plants depends on both plant ability to absorb them from the soil [6,10] but also on soil properties. Soil sorption capacity and reaction are said to be the factors most influencing heavy metals solubility in soil and their availability to plants [7,12].

The aim of the presented investigations was to evaluate the influence of soil pH on nickel and zinc uptake by red clover cultivated in the Cracow province.

## MATERIALS AND METHODS

The investigations were based on the results of an analysis conducted on 223 samples of red clover tops and samples of soil collected from 0-20 cm horizon at the same sites as clover. The materials - 3 to 9 samples - were gathered in all communes of Cracow province, usually one sample from one village.

In order to reduce the effect of petrol fumes on the content of heavy metals in soil and plants, the samples were collected from the sites localized at least 50 m from local roads and at least 70 m from more important highways.

The content of nickel and zinc in soil was determined after digesting soil sample in a

mixture of concentrated nitric and perchloric acids on a water bath. The concentration of the investigated metals in soil filtrate as well as in plant material after its dry decomposition, was assayed with flame technique with the use of an atomic absorption spectrophotometer. Soil reaction (pH) was measured potentiometrically in a suspention of 1 mol/dm$^3$ KCl solution and hydrolytic acidity (Hh) was determined with Kappen method.

## RESULTS AND DISCUSSION

The examined soil samples collected in the Cracow province present a whole range of pH changes (pH=3.8-7.3), from very acid to base soils. On an average, more acid soils are found in the southern and eastern parts of the province. The soils localized in the western and northern regions mostly developed from carbonate rocks, so they are mostly neutral or slightly acid.

The most often noted total Ni content in topsoil of arable lands is 10-40 mg/kg [1]. In 223 investigated samples, there were assayed: 2.8 to 50.0 mg Ni, with an average concentration 15.2 mg/kg d.m. (Table 1). The content mentioned, with a relatively slight differentiation of nickel content in soil in the Cracow province, allow an assumption that the metal comes mainly from the weathering of natural soil minerals. Slightly raised nickel content (>25 mg/kg) was noted first of all in soils in the south-eastern part of the province and locally in the south in Pcim commune (Fig. 1). The soils on these territories developed mostly from clay, sandclay and marlclay [11]. According to Cannon (quoted after [1]) the materials are generally abundant in nickel, they usually contain from 20 to 250 mg Ni/kg with an average concentration 68 mg/kg d.m.

An average total content of zinc in the topsoil of the investigated arable lands is 87.5 mg/kg and ranges from 48.8 to 600 mg/kg d.m. (Table 1). Arable lands, not liable to pollution with heavy metals usually contain 5-100 mg/kg [1,11]. According to Brümmer [2] toxic effect of zinc on plant should be expected when its content ranges 100-500 mg/kg, depending on a plant species and soil properties. Among the examined samples 26 % contained over 100 mg Zn/kg d.m. but only in two cases the content exceded 300 mg/kg.

Spacing of zinc in arable topsoil in the province clearly marks the terrains where soil has been contaminated with this metal in result of pollution (Fig. 2). These are areas close to the mines of lead-zinc ores near Olkusz (northwestern part of the province, mainly Alwernia, Krzeszowice, Jerzmanowice-Przeginia and Sułoszowa communes), and first of all Nowa Huta region together with the area eastward.

Nickel concentration in red clover ranges from 0.4 to 16.3 mg/kg, with an average 2.3 mg/kg d.m. (Table 1). If we assume, according to Kabata-Pendias *et al.* [9], the level 50 mg Ni/kg d.m. of plants as the critical content determined from the point of view of fodder utility, it can be seen that all the examined samples meet the demand. Differentiation of nickel content in clover is far more than in soil. The fact is confirmed by coefficients of variations presented in Table 1. The values suggest that this element uptake by plants depends not only on its content in soil but also, to a great extent, on the other soil properties.

**Table 1.** The content of nickel and zinc in clover and soils and soil $pH_{KCl}$ in the Cracow province

| | Red clover | | Soil | | |
|---|---|---|---|---|---|
| | Ni | Zn | Ni | Zn | pH |
| Geometric mean | 2.3 | 47.7 | 15.2 | 87.5 | 5.3 |
| Range | 0.4-16.3 | 21.6-174 | 2.8-50.0 | 48.8-600 | 3.8-7.3 |
| Coefficient of variation | 74 | 52 | 49 | 56 | |

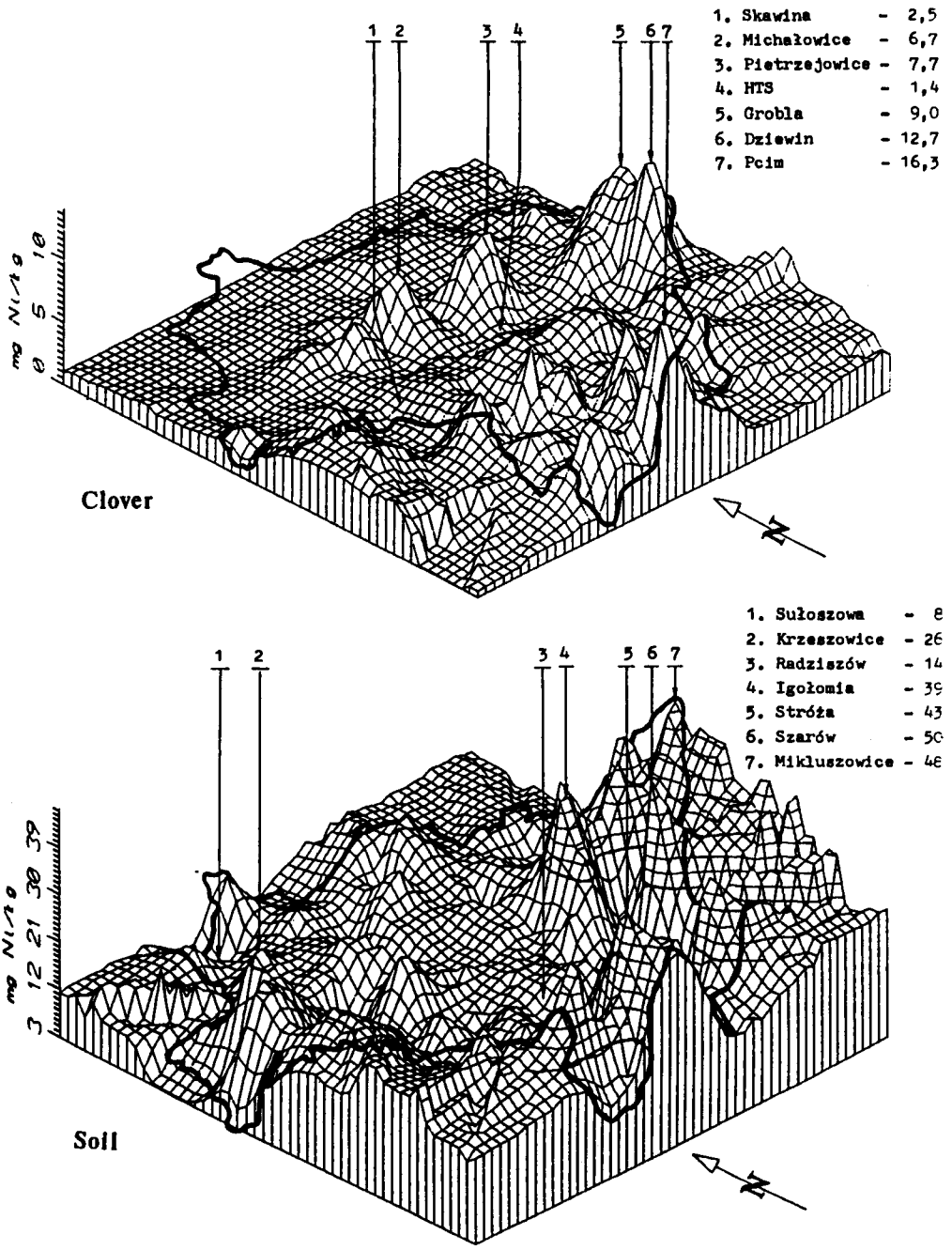


**Fig. 1.** The content of nickel in red clover and soils of Cracow province.

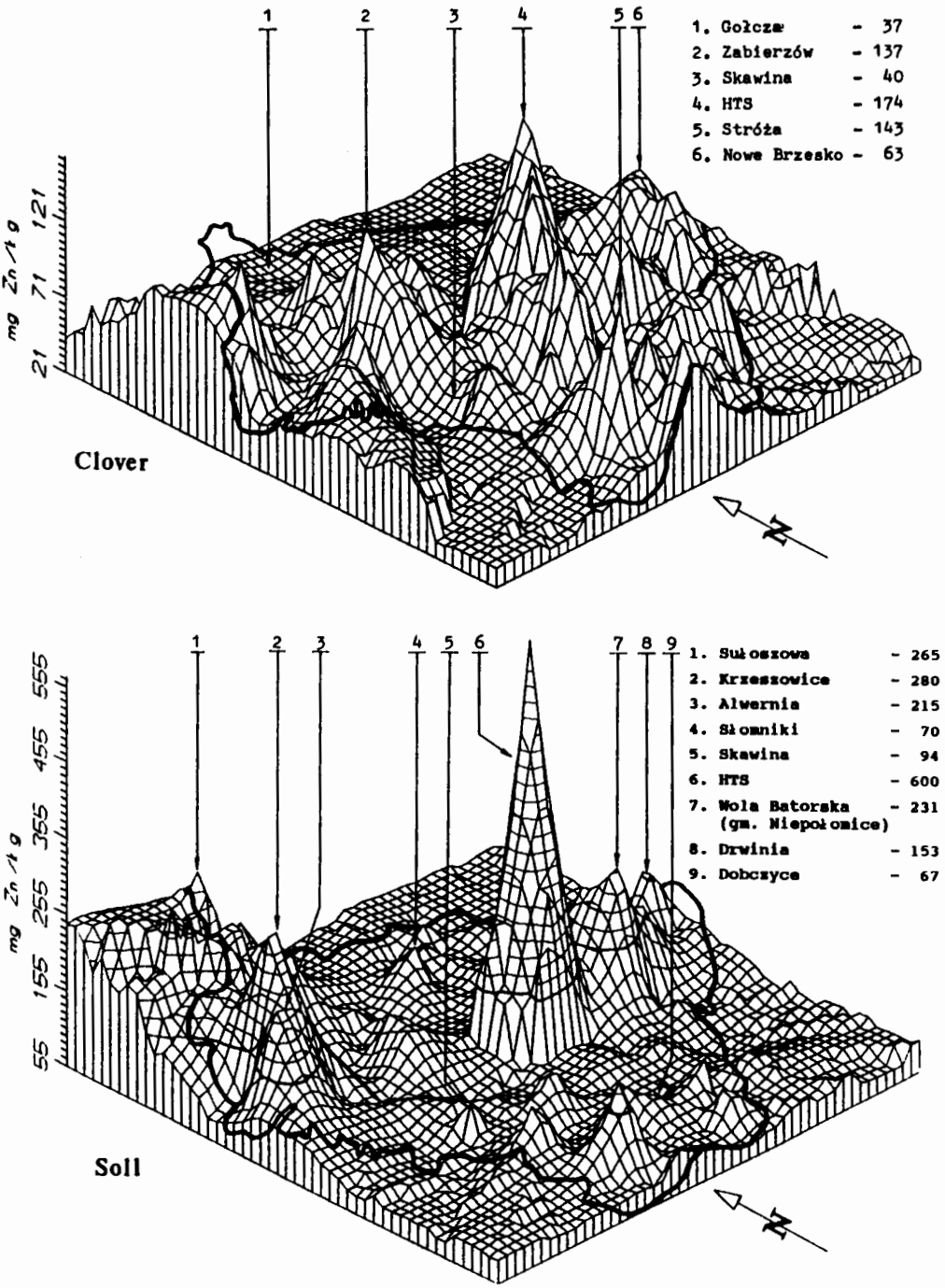


**Fig. 2.** The content of zinc in red clover and soils of Cracow province.

The content of zinc in the studied clover was on an average 47.7 mg/kg and ranged from 21.6 to 174 mg/kg d.m. (Table 1). The critical content of zinc - 100 mg/kg d.m. determined from the point of view of clover fodder utility [9], was exceeded in 5 % of the analysed samples. Spacing of zinc in clover points to an increased concentration of this metal mainly in the samples from the south-eastern part of the province (Fig. 2). It seems clear that where is more zinc in the topsoil (e.g., in the region under the influence of Sendzimir iron works) and soils are more acidified (in southern part of the province), content of zinc in clover is much higher.

These observations confirm the correlation coefficients presented in Table 2. Although clover roots well penetrate all arable layer of soil where usually over 80 % of root mass develop [5] and this horizon is the basic source of heavy metal supply to the plant, the relation between the content of both nickel and zinc in soil and in plant is weak. Simple correlation coefficients which describe the relations, though statistically significant, assume low values: 0.33 for nickel and 0.20 for zinc. The concentration of nickel and zinc in clover depends to a greater degree on the reaction of soil on which it is grown than on the content of the metals in soil. The higher soil pH value, the more limited is Ni and Zn uptake by clover.

The mechanism of the phenomenon may lie in a decrease in the investigated metal solubility in soil, or in limiting of nickel and zinc absorption by clover roots with an increase in soil pH. In the cases under discussion most probably the first mechanism operates. Nickel and zinc are being adsorbed in soil, mainly by amorphous Fe, Mn and Al oxides, as well as by clay minerals. However, sorption capacity of these materials in relation to heavy metals depends to a major extent on soil reaction [3,8]. In the studies by Herms and Brümmer [8] pH influence on heavy metals solubility in soil decreased in the following order: Cd>= Zn>Ni>Cu>Pb.

The hypothesis has been confirmed by multiple regression equations which determine the metal content in clover ($Me_{CL}$) basing on its concentration in soil ($Me_{SO}$) and soil $pH_{KCl}$ or hydrolytic acidity (Hh).

$$Ni_{CL}=0.012+0.057Ni_{SO}+0.982Hh \qquad R=0.82;\ F=227.5$$

$$Zn_{CL}=138.675+0.187Zn_{SO}-18.291pH \qquad R=0.65;\ F=81.6$$

The values of multiple correlation coefficients (R) which describe these equations are statistically significant with the significance level P=0.001. Basing on an interaction between nickel and zinc content in soil and soil reaction, phytoavailability of those metals for clover may be most probably predicted.

## CONCLUSIONS

1. The contents of nickel assayed in soils and red clover of the Cracow province does not point to contamination of the region with this metal.

2. Among areas where the content of zinc in soil and plants is significantly higher, there are the neighbourhood of Sendzimir iron works and the terrains immediately to the east. In soil, the content of zinc has been increased also in the north-western part of the province, close to the mines of lead-zinc ores near Olkusz.

3. The content of the investigated metals

**Table 2.** Relations between total Ni and Zn content in soil and soil reaction, and the concentration of those metals in clover

| Metal | Metal content in soil | $pH_{KCl}$ | Hh |
|---|---|---|---|
| Ni | 0.33** | -0.69** | 0.78** |
| Zn | 0.20* | -0.52** | 0.47** |

r significant at: *P = 0.01; **P=0.001.

in clover depends to a major extent on the reaction of soil on which it is grown than on the soil abudance in nickel and zinc.

4. Maintaining of neutral soil reaction in agricultural practice may at least partially protect it against excessive accumulation of nickel and zinc in plants grown in the areas where soils are contaminated with heavy metals.

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WPŁYW ODCZYNU GLEBY NA POBIERANIE NIKLU I CYNKU PRZEZ KONICZYNĘ

Oddziaływanie odczynu gleby na dostępność niklu i cynku dla koniczyny czerwonej określono w oparciu o analizę 223 próbek gleby i koniczyny pobranych we wszystkich gminach województwa krakowskiego.

Zawartość ogólnego niklu w wierzchniej warstwie gleby waha się od 2.8 do 50.0 mg/kg, przy średniej geometrycznej koncentracji 15.2 mg/kg. Odpowiednie wartości dla cynku wynoszą: 48.8-600 mg i 87.5 mg/kg. Ilości tych metali oznaczone w badanych próbkach koniczyny są znacznie niższe i w przypadku niklu mieszczą się w zakresie 0.4-16.3 mg/kg, średnio 2.3 mg/kg, a cynku 21.6-173.8; średnio 47.7 mg/kg s.m.

Absorpcja badanych metali przez koniczynę zależała nie tylko od ich zawartości w glebie, ale również od innych jej właściwości, głównie od odczynu gleby. Relacja pomiędzy zawartością niklu w koniczynie i glebie wyrażona jest współczynnikiem korelacji prostej r=0.33, a w przypadku cynku r=0.20. Zależność tę znacznie dokładniej opisują równania regresji wielokrotnej określające zawartość metalu w koniczynie w oparciu o jego koncentrację w glebie oraz jej pH lub kwasowość hydrolityczną.

S ł o w a k l u c z o w e: odczyn gleby, nikiel w glebie, cynk w glebie, koniczyna czerwona.