

## EFFECT OF PLATINUM IONS ON THE HEAVY METAL IONS IN LOESSIAL SOIL. PART I: COPPER IONS

*M. Bojanowska, I. Jackowska*

Department of Chemistry, University of Agriculture, Akademicka 15, 20-033 Lublin, Poland

**A b s t r a c t.** Studies on the possibilities of activating heavy metal ions by platinum ions in the soil have been undertaken. The present work gives results of research on the copper ions activated in loessial soil by the treatment with solutions containing platinum ions.

Samples of podzolic soil developed from loess were collected from the horizon  $A_p$  (0-20 cm). The samples were treated with re-distilled water or with the same quantity of  $PtCl_4$  water solutions containing 2, 4, 20 mg of platinum ions. Soil reaction (pH) was measured after 1, 2, 3, 4, 5 and 6 months of incubation at 5 and 20 °C temperature. Copper ion content was determined in the filtrates using the technique of atomic absorption spectrometry.

The amount of copper ions activated in the soil material depended on the soil reaction, temperature, quantity of platinum ions introduced and the time duration of the experiment.

**K e y w o r d s:** Platinum ion, loess soil, copper ion.

### INTRODUCTION

Catalytic activity of platinum in connection with palladium and rhodium is utilised in fatty oil production and pharmaceutical industry for the synthesis of ammonia and other chemical products. An important use of platinum is its application in car catalysts to reduce the level of some impurities in exhaust gas, in particular hydrocarbons, carbon and nitrogen monoxides [2,4,9].

The annual amount of platinum production reaches about 100 tons, in that, over 50% is used in the fields with heavy impact on the environment. At present, platinum content in the environment is much higher than its natural content in the earth crust. It is due to the increasing platinum application in medicine, and the fact that it is an active component of exhaust gas converters [1,12].

Platinum compounds, especially soluble salts, are toxic. Exposure to these toxic compounds results in a syndrome called platinosis characterised by cutaneous

hypersensitivity and dyspnoea [10]. Moreover, some platinum complexes used in antineoplasm therapy show a mutagenic activity. At present, information on the metabolism of platinum and its compounds in human organism is insufficient. It is well known, that soluble platinum compounds are easily absorbed by organisms and removed through the kidneys [3,13]. Effects are not harmful if the platinum particles absorbed by the organism are surface-oxidised.

It has been proved that platinum from anthropogenic sources penetrates the soil and then is taken up by plants and cumulated in the roots. It causes disturbances in the plant water balance and results in plant necrobiosis, preterm foliage loss and excessive root growth [5, 6]. The highest platinum concentrations appear in the soils in the vicinity of roads with heavy traffic, in the soil layers up to 10 cm deep as a consequence of platinum emission with car exhaust gas [7,8]. The experimental results demonstrate that relatively small quantities of platinum from the catalysts can be dissolved in various environmental conditions. Platinum in the metallic form becomes inactive. The catalytic form of platinum is completely different [11]. It enables platinum potential to enter chemical reactions after some time spent in the environment and its fast mobilisation.

Information on the long-term reaction of small platinum quantities or platinum compounds with cations of other metals in the soil is scarce. The present studies were undertaken to assess possibilities of initiation heavy metal ions by platinum ions in the soil. The present work gives the results on the copper ions activated in the loessial soil after treatment with the solutions containing platinum ions.

## METHODS

Samples of podzolic soil developed from loess were gathered from the horizon  $A_p$  (0-20 cm) to be examined. An air dry sample was screened through a sieve and fractions under 1 mm were collected.

A soil sample of 0.1 kg was treated with 0.1 dm<sup>3</sup> of re-distilled water and with the same quantity of PtCl<sub>4</sub> water solution containing 2, 4, 20 mg of platinum ions, respectively. The samples were closed tightly in polypropylene beakers and incubated at 5 and 20 °C temperature for 1, 2, 3, 4, 5 and 6 months. After incubation, measurements of soil reaction (pH) were done. Afterwards, each soil sample was mixed, centrifuged and filtered. Copper ion content was determined in the filtrates using a technique of atomic absorption spectrometry. The measurements were taken three times to get average values.

Total content of metals was established by digesting wet soil samples with a mixture of specpure concentrated acids HF, HNO<sub>3</sub> and HClO<sub>4</sub> in the volumetric rate of 4: 3: 1. According to the analytic method employed, identification limit for the copper ions is 0.1 µg/cm<sup>3</sup>.

## RESULTS

The soil used for the present examination had the content of granulometric fractions as follows: 0-0.1mm - 1%, 0.1-0.02 mm - 63%, 0.02-0.002 mm - 27% and below 0.002 mm - 9%. The humus content was 2.13%, pH 4.8 in H<sub>2</sub>O and the specific surface 24 m<sup>2</sup>/g. Total copper content in the soil was equal to 6 mg/kg d.m.

Number of copper ions activated by water and platinum ions during the experiment was presented in Fig. 1.

The process of treatment with re-distilled water activated from 0.016 up to 0.145 mg of copper ions in 1 kg of soil. The highest quantity of copper ions was activated after 1 month at the temperature of 20 °C. After two-months, the number of copper ions recorded was 10 times lower. After other periods of time, i.e. 3, 4, 6 months, the quantity was two-fold higher, and after 5 months three times higher. At the temperature of 5 °C, after 1 and 5 months, water activated the highest amount of copper ions, whereas after 2, 3 and 4 months nearly half less. However, the smallest amount (0.042 mg/kg) was noted after 6 months.

Introduction of 2 mg of platinum ions into the soil, activated a higher greater amount of copper ions then the treatment with re-distilled water. Similar to water application, the highest of copper ions was activated after 1 month, at the temperature of 20 °C. After 2 and 3 months, the number of copper ions was similar at both temperature levels. Lower but similar quantities were recorded after 4 and 5 months, and the lowest after 6 months.

Introduction of a two-times higher amount of platinum ions (4 mg) activated even higher quantity of copper ions after one month. However, in the case of other periods, the number of copper was lower, even though the levels were close.

Soil treatment with 20 mg platinum ions resulted in copper ion mobilisation in even higher amount after one month. The smallest number of copper ions was recorded after 2 months, whereas after 3, 4 and 5 months, the number of copper ions activated increased at the temperature of 20 °C. On the other hand, after 6 months this number decreased to the level of copper ions activated after 3 months. After 2, 3 and 4 months at the temperature of 5 °C, the quantity of copper ions increases to

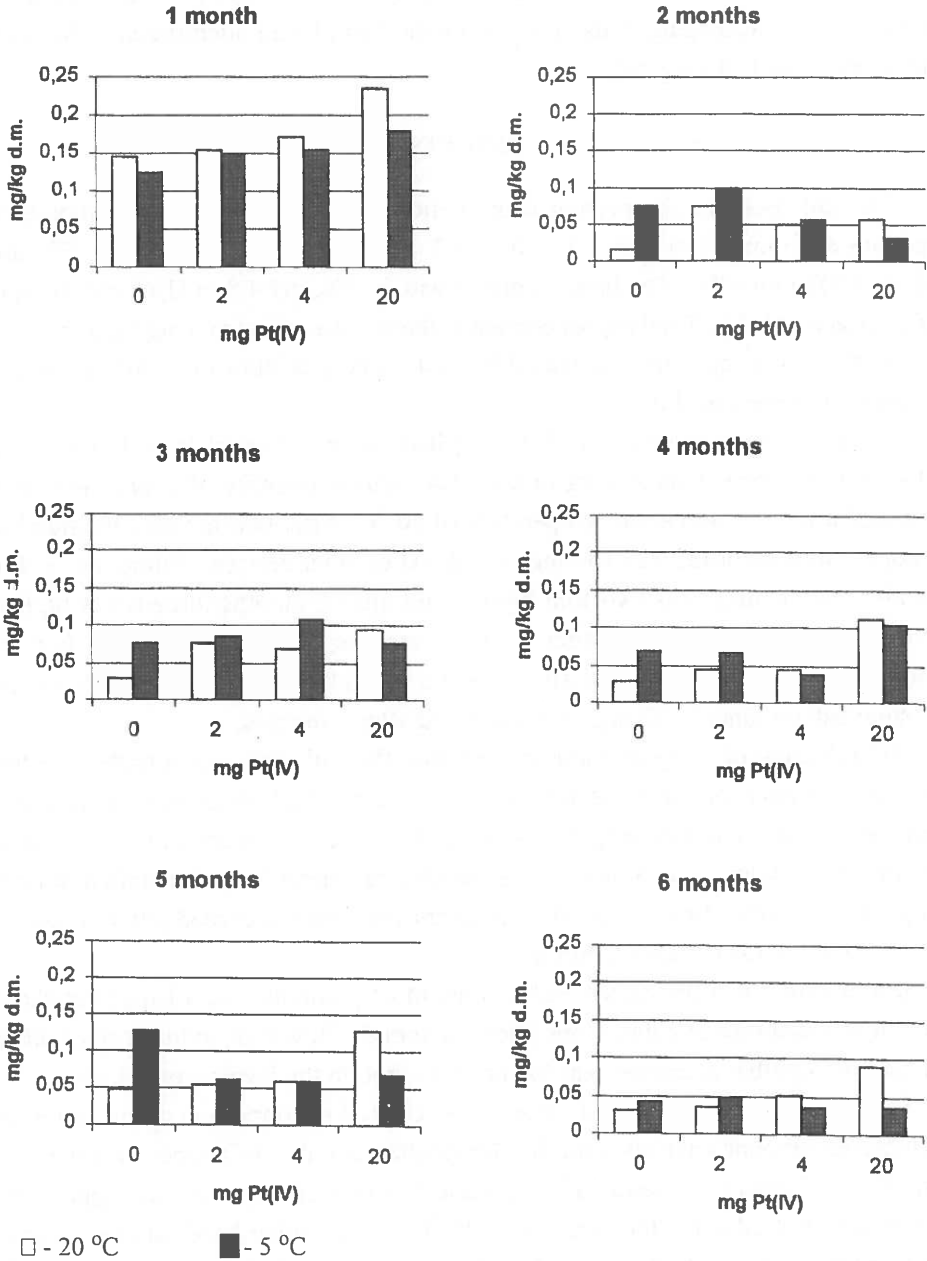


Fig. 1. Mobilization of copper ions from loessial soil with water solutions of Pt (IV).

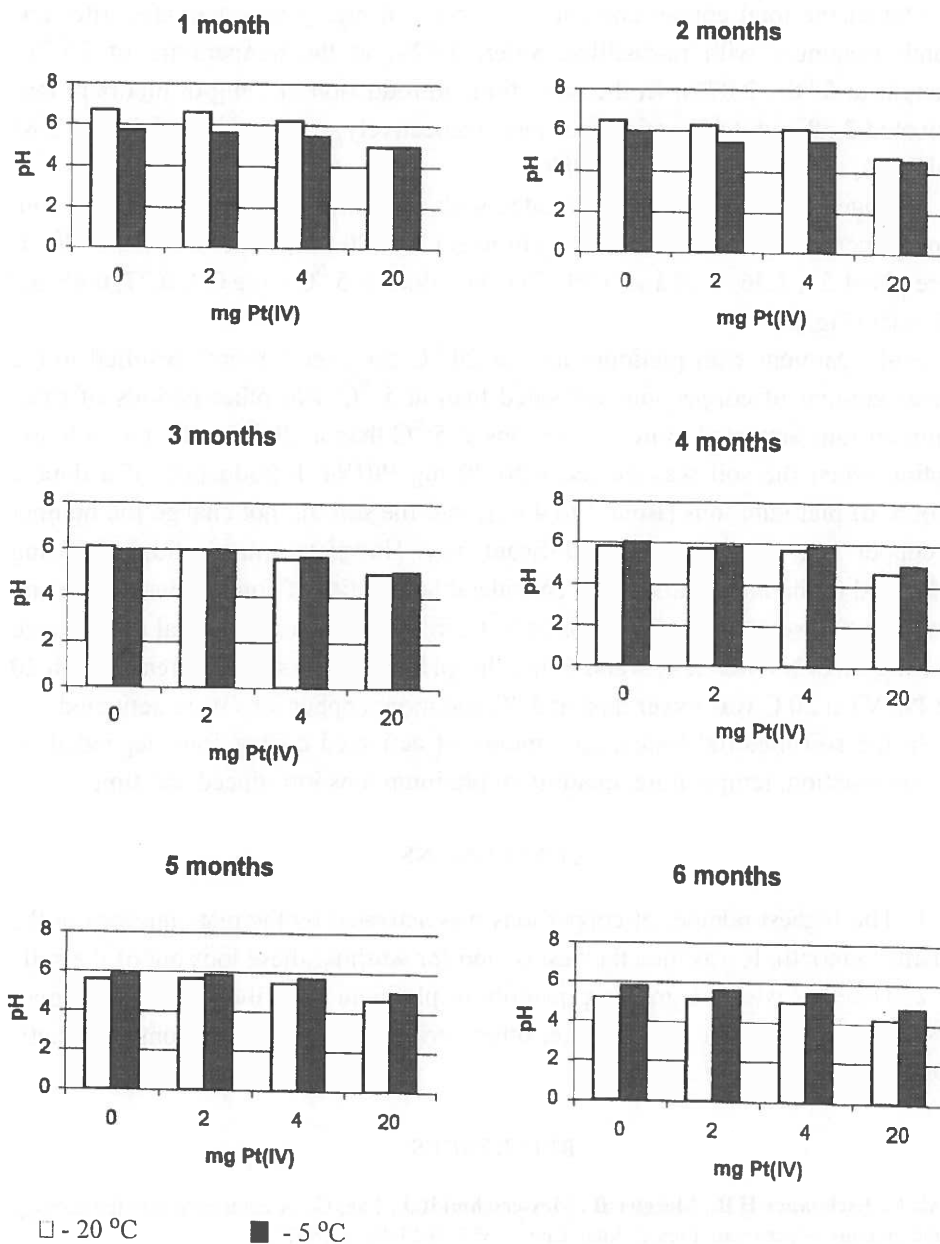


Fig. 2. Changes in the soil after treatments with water solution of Pt (IV).

0.032, 0.077, 0.106 mg/kg, respectively, and after 5 and 6 months it decreased to 0.068 and 0.036 mg/kg.

Out of the total copper content in the soil - 6 mg/kg was activated after one month treatment with re-distilled water, 2.42% at the temperature of 20 °C, whereas at 5 °C - 2.07%. At the same time, introduction of 2 mg of platinum ions activated 2.58 and 2.47% of copper ions, respectively; introduction of 4 mg - 2.85 and 2.5%, and 20 mg - 3.9 and 2.98%.

Changes in the pH of the soil treated with re-distilled water and solutions containing increasing numbers of platinum ions (2, 4, 20 mg) for 6 months, at 20 °C were pH=1.51, 1.46, 1.19 and 0.79. The pH values at 5 °C were 0.3, 0.27, 0.45 and 0.5 units (Fig. 2)

Soil treatment with platinum ions at 20 °C for over 1 month resulted in the higher amount of copper ions activated than at 5 °C. For other periods of time, platinum ions activated more copper ions at 5 °C than at 20 °C, with the only exception when the soil was treated with 20 mg Pt(IV). Introduction of a double amount of platinum ions (from 2 to 4 mg) into the soil did not change the number of copper ions activated in a significant way. However, introduction of 20 mg Pt(IV) led to the mobilisation of a considerable quantity of copper ions after 4 and 5 months. However, after 6 months at 5 °C, this amount was identical as activated by 4 mg Pt(IV). After 3, 4, 5 and 6 months, pH of the soil samples treated with 20 mg Pt(IV) at 20 C was lower than at 5 °C and more copper ions were activated.

In the soil material tested, the amount of activated copper ions depended on the soil reaction, temperature, quantity of platinum ions introduced and time.

## CONCLUSIONS

1. The highest number of copper ions was activated by the platinum ions in the soil after a month. It was then the best period for washing these ions out of the soil.
2. Together with the growing quantity of platinum ions, the amount of copper ions increased after one month. After other periods, changes in the number of activated copper ions were explicit.

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