# Heavy metal transfer to forage material in amended soils in the area of Ptolemais – Greece

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## Abstract

A study of Selenium (Se), Cadmium (Cd), Nikelium (Ni) and Chromium (Cr) uptake by plants, conducted in the reclaimed mine soils of the Ptolemais basin, in North Greece, is reported in this paper. The aim was to estimate the influence of various soil parameters on the concentration of these elements in two plant categories, namely winter cereals and forage species. The results of elemental analysis indicated that the values of Cd, Ni and Cr were much higher than those present in regular soils. The values of bio-available Se in soils were low (< 7.9 ppb), well within the range of regular soils, while they were significantly higher in both plant categories (55-117.5 ppb). Results of multiple and stepwise regression analysis were used to develop models with high $R^2$ (0.82) of predicting Se uptake by plants using easily measured soil parameters such as pH, CEC, EC, clay percentage or Manganium (Mg). These results can be utilized by various local users and land managers, and also to optimize management of grazing livestock and improve their nutrition.

**Key words:** selenium, heavy metals, amended soils, bio-transfer, forage plants

## Introduction

Selenium (Se) is a naturally occurring trace element that can be concentrated and released in the waste materials from certain mining, agricultural, petrochemical and industrial manufacturing operations. One of the primary human activities responsible for mobilizing selenium in the environment is the procurement, processing and combustion of coal for electric power production (Lemly 1985). One of the pathways that provides for direct movement of Se into food chains is the uptake of Se by rooted plants. Mobilization of Se within the soil-plant systems is a highly complex subject (Neal 1990).

Forms and transformation of Chromium (Cr) in soils have great environmental and health implications. Therefore, the speciation of Cr in soils and its solubility in Cr-polluted soils have been widely studied (Barnhart 1997, Rudel et al. 2001). Contents of Cr in plants have recently received much attention due to the knowledge of its importance as an essential micronutrient in human metabolic processes, but also because of its carcinogenic effects. The world soil average content of Cr in soils has been determined as 60 mg/kg.

The concentration of Nikelium (Ni) in surface soils reflects the impact of both soil-forming processes and anthropogenic activities. Soils throughout the world contain Ni in the very broad range; however its mean concentrations are within the range 13–37 mg/kg. Organic matter (OM) exhibits a strong ability to absorb Ni, thus it is likely to be highly concentrated in coal and oil. The mechanism of Ni toxicity to plants is not fully understood, although the restricted growth of plants and injuries caused by an excess of this metal was observed for quite a long time. Increased Ni levels in food plants are associated with health hazards. The ready transfer of Ni from soils to vegetables has been illustrated by Frank et al. (1982).

Cadmium (Cd) is considered as being one of the most ecotoxic metals that exhibit adverse effects on all biological processes of humans, animals, and plants. Although Cd is considered to be a nonessential element for metabolic processes, it is effectively absorbed by both root and leaf systems and is also highly accumulated in soil organisms. The Cd content of plants is of great concern as a pathway of Cd to man and animals. The average Cd content for the Earth's crust is given as 0.1 mg/kg (Kabata-Pendias 2011).

The aim of this paper was to estimate the influence of various soil parameters on the concentration of Se, Cd, Ni and Cr in winter cereals and forage species in the reclaimed mine soils of Ptolemais-Amyntaion, northwest Greece.

## Materials and methods

Ptolemais-Amyntaion basin region is located in the northwest of Greece. The lignite beds of this basin are under intense exploitation by open cast mining (Tsikiritzis et al. 2002). The depleted or abandoned mines are reclaimed and revegatated after being filled with a mixture of fly ash, overburden and inter-bedded sentiments removed from the working mines (Georgakopoulos et al. 2002a, b).

Eight sample sites were selected in the reclaimed mine soils, in two different locations. At each site, soil samples of two depths were collected (0-30 cm and 30-60 cm), as well as plant material. The latter was divided into two categories: winter cereals (wheat and barley) and forage species (*Cynodon dactylon, Briza maxima, Bromus benekenii, Chrysopogon gryllus, Dactylis glomerata, Holcus lanatus and Poa compressa).* The sieved soil was then used to determine the particle size analysis (Gee and Bauder 1986) the chemical properties of the soil and the concentration of Se, Cd, Ni and Cr (Page et al. 1982).

Mean values and their standard deviation were calculated for each plant category and each sampling site. The statistical procedure followed was stepwise multiple linear regression using JMP-7 statistical software of SAS (Sall et al. 2007, Lehman et al. 2005).

## Results and Discussion

Results concerning the properties of soils are shown in Table 1, while the concentrations of Se, Cd, Cr and Ni, are presented in Table 2. Results concerning the concentrations of heavy metals in winter cereals and forage species from each sampling site are shown in Table 3.

**Table 1.** Soil characteristics in 8 sampling sites and 2 depths (depth 1: 0-30 and depth 2: 30-60cm, respectively)

| Sampling site | Depth 1 | | | | | Depth 1 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Clay (%) | Soil type | pH (soil:water ratio 1:1) | pH (KCl, 1N, 1:2.5) | Mn (mg/Kg) | Clay (%) | Soil type | pH (soil:water ratio 1:1) | pH (KCl, 1N, 1:2.5) | Mn (mg/Kg) |
| 1 | 7.2 | SL | 8.48 | 7.62 | 6.04 | 2.0 | SL | 8.55 | 8.24 | 1.14 |
| 2 | 26.4 | LS | 8.42 | 7.58 | 7.18 | 19.2 | LS | 7.91 | 7.88 | 6.56 |
| 3 | 20.0 | LS | 8.21 | 8.20 | 4.38 | 6.0 | SL | 8.32 | 8.05 | 1.70 |
| 4 | 4.0 | SL | 8.64 | 8.14 | 3.72 | 2.0 | SL | 9.39 | 9.59 | 2.20 |
| 5 | 28.4 | SCL | 8.32 | 7.90 | 5.72 | 18.0 | SL | 8.19 | 7.89 | 3.64 |
| 6 | 23.2 | SCL | 7.64 | 7.89 | 0.44 | 48.4 | C | 7.92 | 8.24 | 0.62 |
| 7 | 38.4 | CL | 8.49 | 8.13 | 2.32 | 42.4 | C | 8.26 | 8.15 | 2.52 |
| 8 | 16.0 | SL | 8.28 | 7.76 | 4.30 | 15.2 | SL | 8.16 | 7.63 | 7.08 |

**Table 2.** Soil concentration Se, Cd, Cr and Ni for two depths (depth 1: 0-30 cm and depth 2: 30-60cm, respectively)

| Sampling site | Depth 1 | | | | Depth 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | µg/kg | | | | µg/kg | | | |
| | Se | Cr | Ni | Cd | Se | Cr | Ni | Cd |
| 1 | 2.1 | 53.6 | 1344 | 33.2 | 7.9 | 62.8 | 472 | 25.2 |
| 2 | 3.8 | 578 | 678 | 117.6 | 4.5 | 244 | 3696 | 49.8 |
| 3 | 2.6 | 42.8 | 224 | 15.6 | 3.1 | 45.2 | 130 | 52.0 |
| 4 | 5.4 | 42.6 | 1054 | 14.4 | 5.4 | 154.8 | 1064 | 12.6 |
| 5 | 1.9 | 55.6 | 1056 | 25.4 | 2.6 | 99 | 952 | 49.8 |
| 6 | 2.0 | 65.6 | 1068 | 18.8 | 4.4 | 51.4 | 3696 | 22.2 |
| **7** | 2.3 | 226.0 | 840 | 59.8 | 2.9 | 86.8 | 1206 | 66.6 |
| 8 | 4.9 | 188.0 | 1686 | 51.2 | 2.5 | 184.2 | 6586 | 52.3 |

**Table 3.** Results of plant tissue analysis

| Site | **Winter cereals** | | | | **Forage species** | | | |
|---|---|---|---|---|---|---|---|---|
| | µg/kg | | | | µg/kg | | | |
| | Se | Cr | Ni | Cd | Se | Cr | Ni | Cd |
| 1 | 85.00 | 2295 | 2650 | 50 | 92.50 | 2387 | 2231 | 52 |
| 2 | 74.50 | 4825 | 2750 | 40 | 117.50 | 3978 | 2861 | 47 |
| 3 | 92.50 | 8250 | 7250 | 60 | 92.25 | 7513 | 7311 | 58 |
| 4 | 81.75 | 14750 | 2600 | 80 | 91.25 | 10691 | 2543 | 83 |
| 5 | 78.75 | 2584 | 2870 | 65 | 85.00 | 4282 | 3100 | 68 |
| 6 | 85.25 | 3128 | 4800 | 52 | 84.00 | 3244 | 4520 | 50 |
| 7 | 55.00 | 5125 | 5240 | 85 | 80.00 | 4990 | 5500 | 63 |
| 8 | 97.50 | 6217 | 3600 | 49 | 85.00 | 6005 | 3910 | 56 |

Results indicated that the values of Cd, Ni and Cr were much higher than those present in regular soils. For the water soluble, and thus plant available, Se concentrations were low in soils but high in plant tissues. Therefore, for these highly disturbed soils, Se was transferred to plant species in very high rates, compared to the other three metals which showed a normal bio-transfer rate from soils to plants.

Means comparison using the student's *t*-test showed that there are no significant differences among the 8 sampling sites, between the two depths or between the two plant types. The next step was to use the multiple linear regression analysis, in a forward process. The final multiple regression model for Se is shown below:

$$Se_{plant} = 167.14 – 0.23(Clay\%) – 47.93(pH1) + 30.41(pH2) + 5.09 (Mn) + 6.79 (Se_{soil})$$

In this model the stepwise values of $R^2$ are shown in Table 4.

**Table 4.** The stepwise values of $R^2$

| Step | Parameter | Estimate | $R^2$ |
|---|---|---|---|
| | Intercept | 167.14 | |
| 1 | Clay (%) | -0.23 | 0.1694 |
| 2 | pH 1 (1:1 water) | -47.93 | 0.3666 |
| 3 | pH 2 (1:2.5 KCl) | 30.41 | 0.5066 |
| 4 | Mn (soil) | 5.09 | 0.6765 |
| 5 | Se (soil) | 6.79 | 0.8296 |

## Conclusions

The results indicate that the model derived for bio-available Se has a strong probability (up to 82%) to predict the measured value of Se uptake in plants using parameters that are common in basic soil analyses, relatively easy and economic to measure, as opposed to the expensive and time consuming measurement of Se in plants. Some precaution should be taken to utilize such a model beyond the range of the measured properties of the studied area and extrapolate it in similar areas. The results of this study can be utilized by various local users and land managers, and also to optimize management of grazing livestock and improve their nutrition.

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