ANNALS OF THE FACULTY OF ENGINEERING HUNEDOARA
2003, Tome I, Fascicole 3

HEAVY METALS FROM DRILLING SLUDGE ADDITIVES IN PLANTS

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Abstract - *MOL Rt. contacted our laboratory and gave us an assignment to conduct studies on the effect of the heavy metal pollution on the local vegetation. From these polluted areas we collected samples from all dominant species that may be potentially harmful to animals (from the point of view of pasture and nectar production). Considering this and the potential to sample contamination due to the loose character of the sandy soil at the location, only above ground plant parts were collected. Control samples, in similar number and distribution, were taken at locations 100-150 m away from the polluted areas. A total of 47 sampling sites were designated and used. The homogenized samples were dried at 120 °C and then weighed into Pyrex-glass digestion vessels in 0.5-0.6 gram portions. The sample digestion procedure consisted of a 12-hour long heating with 10 cm^3 cc. HNO_3under reflux. Cr and Ba contents of the sample solutions were determined using an ICP-AES instrument equipped with a V-groove nebulizer. Pb concentrations were measured by the Zeeman-GFAAS method. As a conclusion, it is to be stated that farming can not be advised in the polluted area as measurement results show an elevated level of the heavy metals in plants.*

1. INTRODUCTION

In 1997 the Research and Management Engineering Office of MOL Rt. (Hungarian Oil and Gas Company) has conducted a careful investigation of soil quality and soil composition in the neighborhood of four production wells drilled between 1977 and 1984 in the Northern East area of the Kiskunhalas field [1].

Among other results, this report established that at the time of the drilling of these production wells about 160-240 m^3 sludgy rock debris, a waste of the drilling process, was deposited around on the top-soil. This sludge, in accordance with the technology in use at the time, contained a significant amount of Cr, Pb and Ba heavy metals in the form of viscosity decreasing and sedimentation additives. Archives and measurements indicated that the top-soil here contains 21-992 mg/kg Cr and 10-92 mg/kg Pb. In possession of the above data, MOL Rt. contacted our laboratory and gave us an assignment to conduct studies on the effect of the mentioned heavy metal pollution on the local vegetation.

The extent of accumulation of heavy metals in plants as well as the distribution of these pollutants in different plant parts varies largely. The general distribution of these pollutants inside a plant is such that the concentration of pollutants decreases in the root, vegetative parts, seeds order. Other factors affecting pollutant concentrations in plants are the age of plant and the chemical-microbiological conditions in the soil. Under certain conditions it is not uncommon that a fully functioning plant contains such a high concentration of pollutants that can be harmful to animals feeding on them and/or to humans eventually consuming these animals.

Chromium is considered to be a mobile element (metal ion) in basic or neutral soils. Uptaken Cr translocates from the roots poorly. Under normal circumstances, plants rarely contain more than 5 ppm of Cr based on their dry weight. 0.1-0.2 mg/kg Cr is allowed in food plants. In greater doses, Cr (VI) in particular, is proven to be cancinogenous to both humans and animals; causing kidney, liver and skin problems [2,3,4].

Lead is characterized with limited mobility in acidic soils, its accumulation typically occurs also in the roots. Its average, typical concentration in a plant grown on normal soil is about 1-7 ppm. Any small quantity of Pb is harmful; its main target organ is the brain and the neural system. The maximum allowed concentration of Pb in food is a few tenths of ppm (dry weight basis) [3,4,5].

Barium occurs in soils sometimes in a surprisingly high concentration; consequently its accumulation in plants is not uncommon either. It is usually not considered to be a toxic heavy element, although acute exposition to Ba may cause problems in the functioning of the digestive and neural systems or in blood circulation [2,4].

2. OVERALL BOTANICAL DESCRIPTION

After the botanical examination of the drill waste sites it can be stated that the vegetation in the KIHA-ÉK-38 and KIHA-ÉK-62 areas can not be said to be significantly different from that of the surrounding areas. In the waste area of KIHA-ÉK-73 however, the vegetation is scarce in spite of the enhanced water supply of this area due to the disturbance of soil caused by works done here at the time of drilling.

In a well defined spot of the KIHA-ÉK-38A waste area, the vegetation is also much different from that of the surroundings. The over-representation of more than one weed species, which are generally known to be highly competitive and less sensitive to pollution, signals a significant disturbing effect of the pollution on the vegetation.

The following plant species were found to be dominant at the four waste sites and therefore sampled. KIHA-ÉK-38A: *Dactylis glomerata, Asclepias syriaca, Salvia nemorosa, Achillea setacea, Poa pratensis, Bromus tectorum.* KIHA-ÉK-38: *Poa pratensis, Dacctylis glomerata, Asclepias syriaca, Achillea setacea, Populus tremula.* KIHA-ÉK-73: *Dactylis glomerata, Populus tremula, Asclepias syriaca.* KIHA-ÉK-62: *Asclepias syriaca, Robinia pseudoacacia, Achillea setacea, Dactylis glomerata, Poa pratensis.*

3. SAMPLE PREPARATION AND MEASUREMENT

We located the waste sites by relying on the descriptions given in the MOL report [1]. From these polluted areas we collected samples from all dominant species that may be potentially harmful to animals (from the point of view of pasture and nectare production). Considering this and the potential to sample contamination due to the loose character of the sandy soil at the location, only above ground plant parts were collected (leaves and leave tips, typically).

Sampling locations were distributed evenly over the areas, where a large number of subsamples -for the purpose of averaging - were taken. Control samples, in similar number and distribution, were taken at locations 100-150 m away from the polluted areas, where the character of soil and vegetation were as close as possible to that of the waste sites. A total of 47 sampling sites were designated and used. Samples were stored in clean PE bags and kept frozen (-18°C) until their preparation.

Plant samples were rinsed with distilled water, dried between clean laboratory paper towels and cryogenically crushed. The homogenised samples were dried at 120°C and then weighed into Pyrex-glass digestion vessels in 0.5-0.6 gram portions. The sample digestion procedure consisted of a 12-hour long heating with 10 cm^3 cc. HNO_3 under reflux. This procedure left the samples fully dissolved except for their silicate content. After filtering, the samples were diluted to mark in 25 cm^3 volumetric flasks. Cr and Ba contents of the sample solutions were determined using an ICP-AES instrument equipped with a V-groove nebulizer. Pb concentrations were measured by the Zeeman-GFAAS method.

4. RESULTS

Found concentrations are shown in the following tables. All concentrations given are to be meant in mg/kg (ppm) units and for dry weight. It can be observed that there actually is a significant increase in the heavy metal content of most plants (82.4%) with respect to the control samples. The amount of increase is notably high, above 50% in most cases. In a small number of instances the control value is higher than the sample value. This is probably explainable in terms of the slightly different soil composition/status, the complexity of biological systems or the possibility that the random sampling covered plants of different age and therefore of different root length. An even higher number of samples may have further clarified the situation, but it is interesting that these cases are almost exclusively connected to *Aslepias syriaca.*

TABLE 1.

KIHA-ÉK-38A		Sample	Control	Increase (%)
Poa pratensis	Cr	0.89	0.71	25
	Ba	23.49	18.75	25
	Pb	2.33	1.35	73
Dactylis glomerata	Cr	0.96	0.6	60
	Ba	30.78	12.75	141
	Pb	1.64	0.46	257
Salvia nemorosa	Cr	1.31	0.68	93
	Ba	23.63	3.19	641
	Pb	3.11	2.01	55
Achillea setacea	Cr	0.87	0.78	12
	Ba	9.34	16.22	-
	Pb	2.67	0.69	287
Asclepias syriaca	Cr	1.07	0.85	26
	Ba	9.43	4.75	99
	Pb	0.97	1.4	-
Bromus tectorum	Cr	2.09	0.87	140
	Ba	57.75	11.57	399
	Pb	1.61	23.93	-

TABLE 2

KIHA-ÉK-38		Sample	Control	Increase (%)
Populus tremula	Cr	0.44	0.28	57
	Ba	16.85	5.88	187
	Pb	0.03	0.04	
Poa pratensis	Cr	0.71	0.71	0
	Ba	20.85	18.75	11
	Pb	1.61	1.35	19
Asclepias syriaca	Cr	0.46	0.83	
	Ba	12.0	4.75	153
	Pb	0.02	1.4	
Achillea setacea	Cr	1.36	0.78	74
	Ba	48.3	16.22	198
	Pb	0.51	0.69	
Dactylis glomerata	Cr	1.02	0.6	70
	Ba	26.08	12.75	105
	Pb	4.11	0.46	793

Sorting the concentration increase results by the plant species it can be furthermore established that *Dactylis glomerata, Robinia pseudoacacia* and *Salvia nemorosa* prone the most to accumulation. Significant accumulation was found in 91-100% of their samples. At the same time and similarly to the general results, none of the elements is preferred to the others from the point of view of accumulation. The range of concentration data for the four areas are similar, they all are in the same order of magnitude.

TABLE 3

IHA-ÉK-62		Sample	Control	Increase %)
Asclepias syriaca	Cr Ba Pb	0.53 20.45 0.77	0.71 2.18 2.25	838
Robinia pseudoacacia	Cr Ba Pb	1.13 16.79 3.33	0.59 5.46 0.78	92 208 327
Achillea setacea	Cr Ba Pb	1.13 26.42 1.47	1.06 5.88 1.39	7 349 6
Dactylis glomerata	Cr Ba Pb	1.19 38.88 1.38	0.82 17.45 0.83	45 123 66
Poa pratensis	Cr Ba Pb	0.94 28.51 4.1	0.63 23.12 2.16	49 23 90
KIHA-ÉK-73		Sample	Control	Increase (%)
Populus tremula	Cr Ba Pb	0.46 8.07 0.76	0.28 5.88 0.04	64 37 1800
Dactylis glomerata	Cr Ba Pb	1.59 27.71 2.38	0.9 11.29 1.02	77 145 133
Asclepias syriaca	Cr Ba Pb	2.12 13.65 1.57	0.5 3.53 1.01	324 287 55

5. CONCLUSION

As a conclusion, it is to be stated that farming can not be advised in the polluted area as measurement results show an elevated level of the heavy metals in plants. However, the use of the plants grown here for pasturing is not directly dangerous if the distant possibility that animals consume the polluted plants *only* can be excluded (the small capacity of soil to support vegetation alone ensures this).

Based on this, recultivation by soil change does not seem to be necessary, plantation of tree species like *Robinia pseudoacacia* or *Populus alba/tremula* in the polluted areas can be suggested instead. These plants cope well with the climatic conditions typical of the region, put a shade on the area beneath them - thus further decreasing the amount of pasturable vegetation - and their plantation is relatively cheap.

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