POSITIVE AND NEGATIVE ASPECTS OF PHYTOREMEDIATION MEASURES APPLIED TO MOLDOVA NOUA STERILE DEPOSIT

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Abstract.

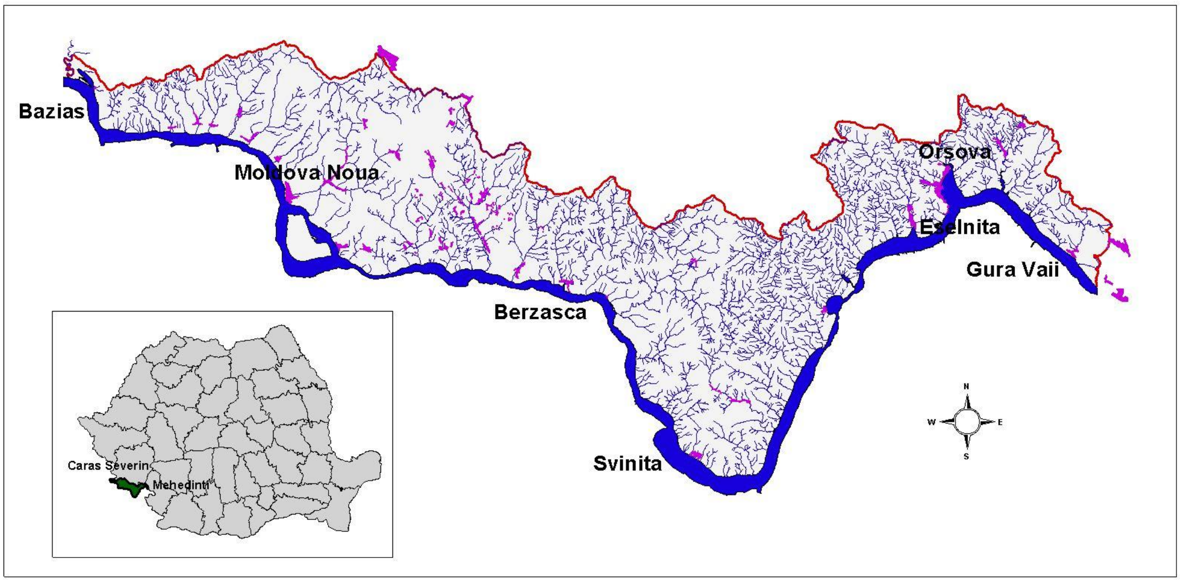
The region of Moldova Noua (South-Western Romania, at the entrance of Danube river on Romanian territory, in the area of the Iron Gates Natural Park) is hosting important mining and quarrying activities, especially for metallic ores exploitation (pyrite, calcopyrite etc.). Presently, still active are the centres from Vărad, Valea Mare, Suvarov and Florimunda. The plant from Moldova Noua also performs primary processing of the copper ores (crushing, milling and wet flotation).

Sterile depositing started in 1965, the total surface occupied at the moment being over 250 ha. Despite sterile deposit immobilisation with different species of plants (*Elaeagnus angustifolia*, *Robinia pseudaccia*, *Hippophae rhamnoides*), copper contamination of Danube river sediments were reported.

The present study is trying to emphasise both good and bad aspects related to phytoremediation techniques in the region. Analyses of heavy metals content in sterile and species used for remediation mentioned above (fruits and leaves) were performed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

Introduction.

Iron Gates Natural Park is the second Romanian protected area (in surface). Localised in the South-Western part of Romania, it is bordered by the Danube River in the South and includes most part of the Danube River tributaries watersheds in the North (Berzasca, Bahna, Radimna, Valea Mare) (1-2) (see map below).



Several strictly protected species are hosted in the park area: *Testudo hermanni*, *Vipera ammodytes, Phalacrocorax pygmaeus*, *Egretta garzetta*, *Ciconia nigra* (3-5).

The region of Moldova Noua showed an increased importance during the industrialisation process starting at the beginning of 1960s due to its important mineral resources. Thus, mining and quarrying centres appeared to Varad, Valea Mare, Suvarov, Florimunda.

In order to perform a primary processing of the ores (crushing, milling, wet flotation), a plant was established nearby Moldova Noua city. For the resulted sterile and wastewater, a system of sterile deposits and settling ponds was created in 1965 (6) (Figure 1).

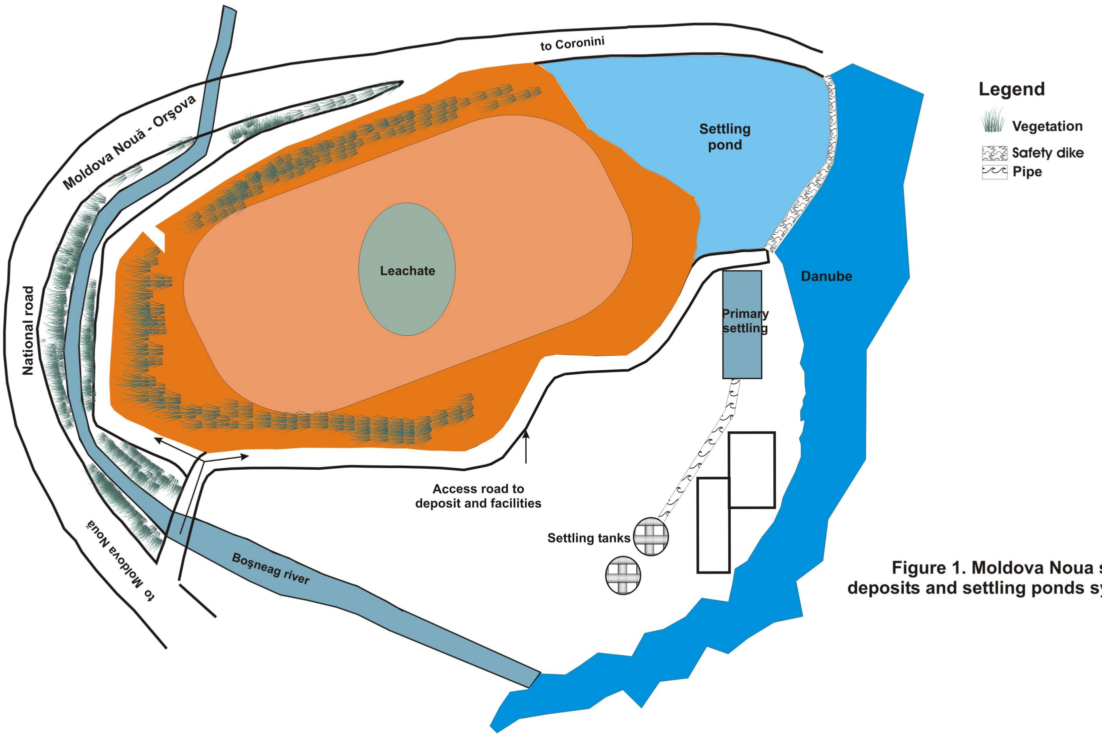


Figure 1. Moldova Noua sterile deposits and settling ponds system

Restoration of mine-degraded soils using plant species can fulfil the objectives of stabilisation, pollution control, visual impact and removal of factors threatening the ecosystem (7).

Salt et al. (1998) defines phytoremediation as the use of plants for removing pollutants from the environment (8). Phytoremediation can be subdivided in

- phytoextraction: plants remove metals from the soil, concentrating them in the aerial parts available for harvesting (9);
- phytodegradation: organic pollutants are degraded by plants and associated microbes (Burken and Schnoor, 1997) (10);
- rhizofiltration: plant roots placed in wastewaters streams absorb metals within it (Dushenkov et al., 1995) (11);
- phytostabilisation: plants reduce contaminants mobility and/or bioavailability (by immobilisation or by preventing the migration) (Vangronsveld et al., 1995; Smith and Bradshaw, 1972) (12);
- phytovolatilisation: volatilisation of pollutants into atmosphere via plants (Burken and Schnoor, 1999; Bañuelos et al., 1995) (13, 14).

In the late 90’s, phytoremediation techniques concentrate attention of scientists working in the field of waste management, used land reclamation, ecological restoration etc. Phytoremediation has some advantages by comparison with other remediation techniques, primarily the low costs involved, as well as the desire of using “green” sustainable processes (Pulford and Watson, 2003) (15).

Conditions enforced for a plant species to be used as a phytoremediation agent are a high pollutant uptake and a high biomass production (Romkens et al., 2002) (16). The process can be enhanced by

(1) addition of chelating agents, of natural or anthropogenic origin (humic substances, EDTA, EDGA, DTPA) which increase the solubility of the metal (metal uptake is achieved by the roots which take up the metals from the soil solution) (16, 17)
(2) presence of microorganisms (which facilitate plants development in stressful conditions) (18).

Materials and methods.

For the remediation of the sterile deposit in Moldova Noua, three species were mainly used: *Elaeagnus angustifolia*, *Robinia pseudaccia*, *Hippophae rhamnoides*.

Samples of sterile material and plants (leaves and fruits) were collected. All samples were firstly dried at 95 ^{o}C for 12 h. Sterile samples were digested in an open system using concentrated acids (HF, HCl, HNO_3 and $HClO_4$). Plants samples were digested using HNO_3 and $HClO_4$. All reagents were of analytical purity (Merck).

The technique used for the determination of the analytes was Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). Instrumentation and operating conditions for the ICP-OES spectrometer are listed in Table 1. The detection limit of the method was 1 ppm (ppm = μg/kg).

Table 1. Operating conditions for the ICP-OES instrument

Plasma generator	Nebulizer	Meinhard	Spectrometer	Air polychromator	210-480 nm
	Cooling gas flow-rate	12 ml/min		Air polychromator	210-590 nm
	Auxiliary gas flow-rate	0,8 l/min		Vacuum polychromator	165-210 nm
	Nebulizer gas flow-rate	1 l/min		Air monochromator	210-480 nm
	Coil Radio frequency	27,12 MHz		Height observation	12 mm

Results and discussions.

The phytoremediation techniques had two main goals:

– to limit the sterile dust transport across the Danube on the Serbian shore and to the north-western part to Moldova Noua city;
– to phytoextract the metals from the sterile in order to avoid Danube river water contamination to be caused by the leachate resulting from the sterile.

For the first aspect, despite the immobilisation of the deposit, when the wind intensity exceeds a certain level, important amounts of sterile dusts are transported outside the deposit area (Figure 2).

Fig 2. Sterile Dust Generation

For the second aspect, the following metals were considered of interest: Cd, Cr, Cu, Mo, Ni, Pb, Zn, with a special emphasis to Cu (the target component of the exploitations in the region). For all seven metals, a bioconcentration factor (BCF), as computed in Equation 1, will be used in discussing the study results:

$$BCF = \frac{C_{aerial}}{C_{sterile}} \quad (Eq.1)$$

where: C_{aerial} is the metal concentration in the leaves or fruits

$C_{sterile}$ is the metal concentration in the sterile material (Mattina et al., 2002) (19).

In Table 2 are displayed the concentrations of metals in plants and sterile. For cadmium, chromium and nickel and lead, the concentration in sterile samples is at a low level, not requiring any intervention for contaminants removal.

Table 2. Metals concentration in sterile and plants samples (ppm)

Metal	Sterile	Eleagnus		Robinia		Hippophae	
		Leaves	*Fruits*	*Leaves*	*Fruits*	*Leaves*	*Fruits*
Cd	0.54	0.18	0	0	0	0.47	0.26
Cr	1.28	0	0	0	0	0	0
Cu	29.42	15.42	28.72	9.25	13.62	7.54	12.82
Mo	0.67	1.2	1.24	5.18	3,61	3.23	0.87
Ni	1.08	1.41	1.38	0.62	0.57	2.82	1.58
Pb	3.96	5.64	9.39	7.22	7.14	9.66	6.98
Zn	26.44	27.2	10.77	32.92	27.32	78.35	13.85

Copper is the main component extracted from the ores exploited in the region, its concentration being high in soils surrounding the deposit (20). Unfortunately, the efficiency of contaminants extraction from the sterile is rather low for all three species of plants, simultaneous to a low biomass production. The poor proofing of deposit and its location in an inappropriate area (Danube river wetland) determined continuous contamination of Danuber river sediments (21). Molybdenum is a special case. Its concentration in sterile is not exceeding 4 ppm but excellent BCF were registered for all three species of plants, in both fruits and leaves. Important amounts of zinc were also detected In Figure 3 shows the BCF for Cu, Mo and Zn.

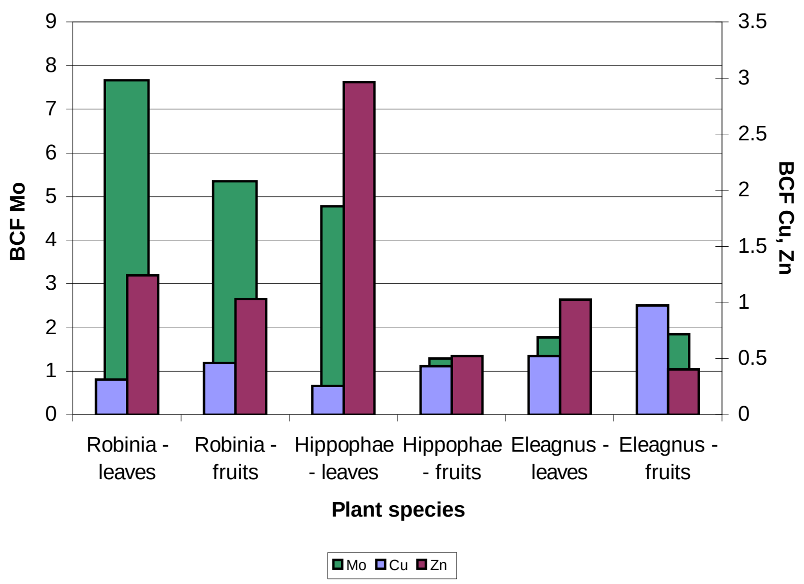


Figure 3. BCF for Mo, Cu and Zn

Conclusions.

The sterile deposits and settling ponds system in Moldova Noua is a significant threat for the environment quality in the region. Its poor management (positioning, conservation, remediation) generated contamination of surrounding soils and of the Danube River sediments. Although the phytoremediation techniques partially reduced sterile dusts transportation, the chosen species are not effective in copper extraction from the sterile. Also, the following steps of the phytoremediation process (harvest, burning of the harvest and re-extraction of metals from the ash) were not considered at all.

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