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Discussion Paper No. 629

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The focus of this research is on the salt/metalliferous pollutants under the harsh arid/semiarid environments. The extent of pollution of surface water and plants by various contents of salts, traces of heavy metals is presented for different regions of Zerafshan River Basin and Kyzylkum Desert. Soils and water are contaminated with cadmium, copper, lead, zinc, selenium, arsenic, molybdenum, manganese, chromium, and various oxidizers (Mn, NO₃⁻, Fe ⁺³, Al ⁺³, ClO₃⁻). This research was supported by a Grant in Aid for Scientific Research, Japan Ministry of Education and Culture, 2003 (Monbusho International Scientific Joint Research Program, No. 15252002), represented by Professor Tsuneo Tsukatani

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Environmental Contaminants of Asiatic Deserts Ecosystems in relation to Plants Distribution and Structure

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Abstract

The focus of this research is on the salt/metalliferous pollutants because of their extreme toxicity, carcinogenicity, wide distribution and slow biodegradation under the harsh arid/semiarid environments. The extent of pollution of surface water and plants by various contents of salts, traces of heavy metals is presented for different regions of Zerafshan River Basin and Kyzylkum Desert. Soils and water contaminated with cadmium, copper, lead, zinc, selenium, arsenic, molybdenum, manganese, chromium, various oxidizers (Mn, NO₃⁻, Fe ⁺³, Al ⁺³, ClO₃⁻), NH₄ and organic pollutants show natural colonization by species that have strategies of avoidance or tolerance to salt/metal toxities. Mapping of plant colonists of salts/metal contaminated soils, seed reproduction and cellular structures of tolerant taxa named as metallohalophytes are examined in the light of present knowledge of such strategies. Electrolytic adsorption and in situ immobilization technologies for cleaning pollutants of mining contaminated soils and underground water are suggested. Phytoremediation technology in the present case may offer a cost-effective and ecologically sound alternative.

Key words: ion/salt contents, ICP-MS, glandular structures, metallohalophytes, phytoremediation, contaminated ecosystem, Kyzylkum Desert.

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Introduction

It is widely recognized (Rauret et al, 1988, Usero et al., 1998, Navas & Lindhorfer, 2002, Toderich at al., 2002) that to assess the environmental impact of water/soil pollution and determine element speciation will give more information about the potential for release the contaminants and further derived processes of migration and toxicity. Several authors have pointed out recently that the use of plants that accumulate or/and excrete salt/ions in their aerial parts could be an economically efficient method for cleaning the soils (Leblane et al., 1999, Escarre et al. 2000, Pillay et al, 2002). Significant progress has been made in recent years in developing native or genetically transformed plants for the bioremediation of environmental contaminants (Rugh et al., 1996, Meager et al., 2000). At many geologically mapped sites of Central and South-Eastern Kyzylkum vegetation. This may be due to a variety of causes: removal of metalliferous soil; superficial (Uzbekistan) with elevated concentrations of metals there is a little discernible effect on covering of overburden materials with low metal content; amelioration of toxities by Ca²⁺ ions from limestone; low availability to plants of metals in insoluble minerals and extremely course-textured and stony desert soils, where drought and nutrient shortages have an overriding influence. It must be admitted, however, that even for these sites the causes (toxities, nutrient deficiencies or physical factors, single or in combination) of distinctive vegetation have never been investigated for Central Asian Desert Flora, and in absence of more information, facile assumptions about salts and metal toxities frequently hold.

Initial exploration of the natural plant cellular mechanisms effecting the bioremediation of elemental and/or organic pollutants suggest great promise for the use of Asiatic desert plants to extract, sequester, and/or detoxify heavy metals and other contaminants. Factors that relate to make-up of chemical compounds, such as tannins, nitrates, metals, and oxalates (some of which may be toxic for plant development) have not been adequately studied for the arid flora of Central Asia. The first survey conducted at a regional scale (Goldstein, 1997, Petukhov & Grutsinov, 2000, Toderich et al. 2002) analyze the spatial distribution of several elements in a wide variety of Kyzylkum Desert soils and indicated to the close relation existing between metal contents, bedrock origin and vegetation.



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A part of a current research focuses on assessment of surface and underground waters contamination of Zerafshan River Valley in relation to the ecology, distribution and structure of salt/metal accumulating plants.

Material and methods

The quantitative assessment of the environmental impact by salinization and industrial mining pollution in the Kyzylkum desert environments was conducted using topographical map at the scale of 1:200,000 and geoecological aerial images of 1:500,000. The study area encloses a heterogeneous landscape comprised of sand dunes, gypsum flats, clay and solontchaks depressions. The species studied undergo extreme, continental, arid conditions that have a limited and unreliable precipitation and a minimal annual precipitation (MAP) = 100-180 mm. Most of the selected sites are located inside or close to gold-uranium and oil-and gas industries complexes of Kyzylkum Desert.

The water samples were taken along the watercourse of Zerafshan River from the settlement of Rahmatabad, through Bukhara oasis into Karakul plateau (south-east part of the Kyzylkum desert). Sampling method is similar to that described by Tsukatani and Katayama (2001). Water samples on heavy metals contents were analyzed by ion chromatography and inductively coupled plasma mass spectrometer (ICP-MS). At each sampling site, the following field data were collected: global position by SONY GPS; pH, electronic conductivity, turbidity, dissolved oxygen, water temperature and salinity by Horiba multiple water quality monitoring system U-20. A cluster analysis was performed to form groups of sites with similar characteristics of the heavy metals in the fractions. The clustering method used was the furthest neighbor (complete linkage, distance metric: Euclidean).

Assimilatory and generative organs of the same species at the different stages of their ontogenesis were studied by light and electron microscopy. Two methods for sample preparation were used for SEM, i.e. chemical fixation and freeze-drying. For chemical fixation, the material was fixed, post-fixed and dehydrated as described for SEM, critical point dried, putter-coated with gold and observed with a Philips SEM 500. The salt secretions on freeze-dried, leaf-like organs of sterile floral organs





(bract/bracteoles and perianth segments) were analyzed by energy disperse X-ray microanalysis (EDAX) with a JEOL JSM –T330A SEM. The elemental composition of crystalline deposits secreted by the salt glands for different ecological groups of arid plants was determined.

Results and discussion

Risk assessment of salts/heavy metal contaminants in arid/semiarid Environments in relation to plant distribution and structure

A survey of 65 water samples taken along Zerafshan River and its tributaries (canals and collectors) are contaminated with high levels of variety of toxic metals, various oxidizers (Mn, NO_3^- , Fe⁺³, Al⁺³, ClO₃⁻), NH₄ and organic pollutants. It was intended to determine similarities between sampled points in relation to quantitative contents and distribution on groups for Pb, Cu, As, Ni, Sr, Cr and Se (Fig.1 a, b). A cluster analysis applied for these traces metals indicate that the points from middle and lower streams of Zerafshan River are separated from the group formed by the remaining sites. As can be observed from Fig.1b the results of distribution of strontium presumed that pollutants are released mostly to the middle and lower parts of Zerafshan River Valley and Kyzylkum Desert.

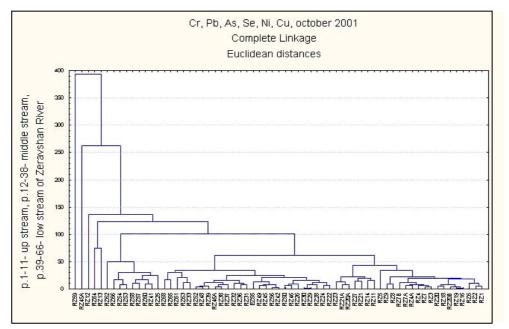


Fig.1a. Dendrogram of traces metal contents alongside the Zerafshan River stream



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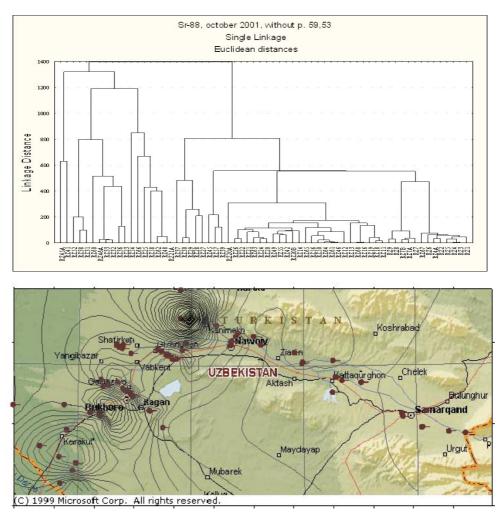


Fig.1b. Distribution of Sr⁸⁸ contents in surface water of Zerafshan Basin





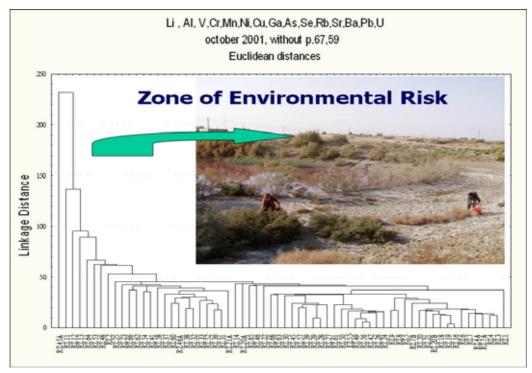


Fig.1b. Distribution of trace metals in surface water of Zerafshan Basin

These regions are often characterized by scrubby, heavy metal tolerant flora. Our experiments demonstrated that only a restrict number of species consistently have ions/salt removal potential simultaneously surviving and reproducing under contaminated Environments. Among them are species from genera *Salsola* (both annuals and perennial) *Haloxylon , Dactylis, Bromus, Kallidium, Tamarix, Artemisia, Cynadon, Peganum, Alhagi, Zygophyllum, Aeluropus, Poa, Allysum, Carex, Euphorbia, Frankennia, Lycium, Eremopyrum, Phragmites.* However many species of bizarre metal ion requirements, most grow poorly even in less contaminated habitats than those where they are found, and few are, as yet, of any agronomic utility as crop, forest or conservation species (Figs. 2 a, b, c).



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Figure 2. a- First stage of plant colonization of contaminated sites in the Central Kyzylkum



Figure 2. b- Rarefied vegetation on foot area of ores dumps after uranium industry



Figure 2. c- Tailings of uranium mining at Uchquduq (Google Earth) as is shown above



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We found out that arid/semiarid metallohalophytes are widespread species that can occur on both contaminated soils (as tolerant ecotypes) and noncontaminated soils (as non-tolerant races) in the same region of Zerafshan River Basin and Kyzylkum Desert. Within group can be recognized further classes: a) electives, taxa that are abundant and often more vigorous on contaminated soils (e.g., many of the common grasses, tamariks, Artemisia colonists of lead/zinc mine spoils); b) indifferent, taxa which frequently colonize metalliferous soils, but show neither abundance nor particular vitality; and c) accidentals, which are usually weedy species or ruderals like species of genera Chenopodium, Frankenia, Zygophyllum, annual chenopods etc., appearing sporadically but showing reduced vigor, and generally avoiding the areas of high metal concentrations. Many taxa among cited groups produce large quantities of small, easily dispersed seeds, so as seen on Fig. 2a facilitating further colonization.

The plant species also exhibited differences in their ions/metals distribution characteristics. From the standpoint of salt/ions accumulation, *Artemisia diffusa* was mostly inferior to *Tamarix hispida, Carex pahystylis, Triticum sp.* and *Salsola sp.* that showed a multi-element accumulation capability with regard to chromium, strontium, cobalt, lead (fig. 3a,b), nickel and iron contents.

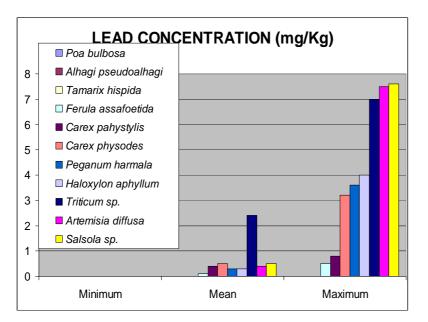


Figure 3 a- Lead levels (mg/kg, dry weight) in overground biomass of various plant species



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ARSENIC CONCENTRATION (mg/Kg)			
2 -			
1.8 -	🗖 Tamarix hispida		
	Poa bulbosa		
1.6 -	Carex physodes		
1.4 -	🗖 Ferula assafoetida		
1.7	Alhagi pseudoalhagi		
1.2 -	🗖 Peganum harmala		
1 -	Carex pahystylis	_	
1	Haloxylon aphyllum		
0.8 -	🗕 🗖 Salsola sp.		
	Triticum sp.		
0.6 -	🗖 Artemisia diffusa		
0.4 -			
0.2 -			
0 -			
	Minimum	Mean	Maximum

Figure 3 b- Arsenic levels (mg/kg, dry weight) in overground biomass of various plant species

Our analyses show that desert plants, grown on the contaminated environments, tend to accumulate the highest ion concentrations in epidermal and subepidermal tissues, including leaf and leaf-like trichomes and various glandular structures. Salt glands are recognized as structures of varying degrees of specialization. They are actively involved in the elimination of solutes and mineral elements on the surface of the vegetative organs and are very common for Asiatic desert plants. Salt glands occur predominantly on the adaxial surface and are uniformly localized along the lateral walls of the grooves. Structurally, SEM methods have revealed a high diversity in the micromorphology of epicuticular wax (epicuticular secretion), mostly occurring as specific crystalloids on the plant surface of the investigated desert plants(Figs. 4,5).



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Figure 4. Salt gland of Salsola paulsenii perianth, comprising flask-shaped basal cell, dome-shaped cap cell and raised cuticular chamber

Figure 5. Micrographs illustrating surface orientation of silicified structures of inflorescence bracts in Eremopyrum orientale (Poaceae)

Electrolytic absorption technology (EAT)

- an alternative means for rehabilitation of contaminated lands and underground waters

This type of technology has been developed by researchers of Navoi Mining Metallurgical Plant and recognized as one of the basic methods for neutralization and/or cleaning of environmental pollutants. The most distinctive sequential procedures of this technology consist of:

- 1- absorption of toxic elements from soil or hard rock material;
- 2- controlled movement of contaminants (ions and particles) towards electrodes -sorbents;
- 3- concentration (linkage) of these pollutants in insignificant volume of sorbent-neutralizer.

For the effective mobilization of toxic elements presenting in cations form it is reasonable to use ions of Al^{+3} and Fe^{+3} at pH = 2-3. This technology already tested in large industrial scale allows effectively cleaning up soil and underground water "in situ".

Conclusion

High concentration of various salts (nitrates, sulfates, oxalates, and chlorides) and trace of toxic metals both in soils, water and vegetation indicate



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environmental problems in the whole Bukhara oasis and South-east Kyzylkum Deserts. It is presumed that pollutants are released mostly from different sources such as municipal wastewater, manufacturing industries, mining, rural irrigation and agricultural cultivation. Tailing-sand soils contaminated with cadmium, copper, iron, nickel, manganese, chromium, lead, zinc and various toxic salts and organic pollutants are colonized firstly by species that have developed strategies for avoidance or tolerance to these metal toxins. One possible avoidance strategy is for plants to prevent the uptake of potentially toxic metals into the plant tissues, especially in the generative organs like embryo. This mechanism, however, is not strongly developed in arid vascular plants, although tolerant plants may restrict metal uptake to a varying degree. This is an indication that in the stems and leaves of many metallohalophytes, as well as in the recreto- and pseudohalophytes from Kyzylkum Desert, there are different mechanisms and strategies for the adjustment and regulation of ion accumulation in plant tissues.

In addition to the use of Asiatic native flora potential for land remediation, there should also be an interest in the possibility of introducing domesticated halophyte species with high adaptability to severe water deficiency and which have protective water-saving mechanisms. The cultivation of metallohalophytes species (both native and introduced) may limit the extent of salt spreading and improve the vitality and growth conditions for the local species, and especially when cultivated in combined plantations.

However our findings require further studies on a wider range of plant material in respect to structural and genetic variation and their relation to bioremediation of contaminated desert/semidesert ecosystems.

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References

- Escarre J., Lefebvre C., Gruber W., Leblane M., Lepart J., Riviere Y., Delay B. (2000). Zinc and cadmium hyperaccumulation by Thlaspi caerulescens from metalliferous and non metalliferous sites in the Mediterranean area: implications for phytoremediation. New Phytologists, 145:429-437.
- Goldshtein, R.I. (1997): Ecological situation in the Kyzylkums in connection with its industrial development. Bulletin of SCST of the Republic of Uzbekistan, 3-4: 70-75.
- Leblane M., Petit D., Deram A., Robinson B.H., Brooks R.(1999). The phytomining and environmental significance of hyperaccumulation of thallium by Iberis intermedia from southern France. Economic Geology, 94:109-114.
- Meagher, R.B., Rugh, C.L., Kandasamy, M.K., Gragson, G., Wang, N.J. (2000): Engineered phytoremediation of mercury pollution in soil and water using bacterial genes. In: *Phytoremediation of contaminated soil and water*, W. Terry and G. Banuelos (editors), Berkeley, California: Ann. Arbor. Pres., Inc., 201-219.
- Navas Ana & Lindhorfer Harald (2003): Geochemical speciation of heavy metals in semiarid soils of the central Ebro Valley (Spain). Environment International, 29: 61-68.
- Petukhov, O.F. & Grutsinov, V.A. (2000): Electroadsorption technology- a new direction of rehabilitation of lands and underground water. Mountain Bulletin of Uzbekistan. 2: 82-85.
- Pillay A.E., Williams J.R., El Mardi M.O., Al-Lawati S.M., Al-Hadabbi M.H., A.Al-Hamdi. (2003): Risk assessment of chromium and arsenic in date palm leaves used as livestock feed. Environmental International, 29: 541-545.
- Rugh, C.L., Wilde, H.D., Stack, N.M., Thompson, D.M., Summers, A.O. and Meagher, R.B. (1996): Mercuric ion reduction and resistance in transgenic *Arabidopsis thaliana* plants expressing a modified bacterial merA gene. Proc. Natl. Acad. Science USA, section Ecology, 93: 3182-3187
- Rauret G, Rubio R., Lopez Sanchez JF, Casassas, E. (1988): Determination and speciation of copper and lead in sediments of Mediterranean river(Rivers Tenes, Catolonia, Spain). Water Resources, 22: 449-455.
- Toderich K.N., Tsukatani T., Black C.C., Takabe K., Katayama Y., (2002). Adaptations of plants to metal/salt contained Environments: glandular structure and salt excretion.



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Discussion paper No 552, Kier, Kyoto University, Japan 18P.

Tsuneo Tsukatani and Yukio Katayama (2001). Baseline Study of Surface Streams of Zerafshan River Basins, Research Report of Water Resources Research Center No.21, pp.75-91.

Usero J., Gamero M., Morillo J., Gracia I. (1998): Comparative study of three sequential extraction procedures for metals in marine sediments. Environmental International, 24: 487-497.