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Geobotany–biogeochemical prospecting

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ABSTRACT

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Sediment and soil functions show close semblance. Without soil no plant can exist. Thus, correlation and analysis of plant occurrence on sediment/soil provides useful information about edaphic conditions and mineral richness in the substratum. Plants can accumulate metals and may play a significant role in biogeochemical prospecting. In this article the following aspects are dealt:

a) What are the metallophytes and their–significance
b) How can metallophytes be applied to economic geology
c) The potential of geobotanical studies for phytomining?
d) The significance of the role of metallophytes in environmental management
e) The role of "metallophytes" in emerging phytotechnologies (= plant based technologies) with elected examples

Key–words—Biogeochemical Exploration, Economic Geology, Hyperaccumulatiors, Industrial Deserts, Metallomics, Phytomining.

भू–वनस्पतिविज्ञान – जैवभूरासायनिक पूर्वेक्षण

एम.एन.वी. प्रसाद

सारांश

अवसाद एवं मृदा फलन संवृत समानता दर्शाते हैं। इस प्रकार अवसाद/मृदा पर पादप प्राप्ति का सहसंबंध अधःस्तर में मृदीय स्थितियों एवं खनिज प्रचुरता के बारे में लाभदायक जानकारी प्रदान करता है। पादप धातुओं का संचय कर सकते हैं और जैव भू–रासायनिक पूर्वेक्षण में अहम भूमिका निभा सकते हैं। इस लेख में नीचे दिए गए पहलुओं पर विचार किया गया हैः–

क)धातुपादप तथा उनकी महत्ता क्या हैं।
ख)धातुपादपों को आर्थिक भू–विज्ञान पर कैसे अनुप्रयुक्त कर सकते हैं।
ग) पादप खनन हेतु भू–वानस्पतिक अध्ययनों की संभावना।
घ) अंततः पर्यावरणीय प्रबंधन में धातुपादपों की भूमिका।
ड.)चुनिंदा उदाहरणों सहित अभरती पादप प्रौद्योगिकियों (= पादप आधारित प्रौद्योगिकियों) में धातुपादपों की भूमिका।

सूचक शब्द—जैव भू–रासायनिक अन्वेषण, आर्थिक भू–विज्ञान, अति संचायक, औद्योगिक निर्जन मेटलोमिक्स, पादप खनन।

INTRODUCTION

TWO papers published in "Nature" have revolutionized the field of plant and metal interactions. One paper highlight "Harvesting a crop of gold in plants" (Anderson *et al*., 1998); and the other "A fern that hyperaccumulates arsenic" (Ma *et al*., 2001). Metallophytes are plants that successfully complete life cycle in metalliferous soil. The tolerance to extreme metal concentrations makes them ideal for a variety of applications and relevant to a number of basic and applied

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sciences (Prasad *et al*., 2008). For more detailed background on "Metallophytes–properties, functions and applications" reference may be made to Prasad, 2013.

There are plants that have the ability to accumulate very high concentrations of metals (1–6%) such as nickel, cobalt, zinc or copper in their biomass are called hyperaccumulators. These plants are considered to be invaluable resources for 'biogeochemical prospecting.' (Fig. 1)

Recent studies in this field highlighted the importance of phytoextraction and phytomining of precious metals. Gold phytoextraction has created huge demand for these technologies (Sheoran *et al*., 2013).

Metallophytes are classified as follows (Baker *et al*., 2010): Absolute (Obligate) and Local (facultative).

Pseudo metallophytes can occur on metalliferous and normal soils–(a) Elective (b) Indifferent and (c) Accidental.

Metallophytes form a key resources for the mineral industry and mineral exploration (Pratas *et al*., 2005). Detection of subsurface mineralisation by correlation with its vegetative cover has relevance of mineral exploration. Metallophytes are predominated in Brassicaceae, Cyperaceae, Cunoniaceae, Caryophyllaceae, Fabaceae, Flacourtiaceae, Euphorbiaceae, Lamiaceae, Poaceae, Violaceae, etc.

The primary habitats for metallophytes include metal rich areas in the vicinity of ore bodies and mineral outcrops.

The secondary habitats include anthropogenic and technogenic sites where ores are processed.

The tertiary sites could be locations where atmospheric deposition occurs for, e.g. vicinity of metal smelters and depositions of leachates from mines.

Plants metal interactions can be classified into 5 categories (a) Hyperaccumulators (b) accumulators (c) indicators (d) excluders and (e) Pseudoaccumulators.

Hyperaccumulators have potential to find buried metal ores, and also help to reduce the risks of metal–contaminated substrates in the management of phytoremediation of mine waste.

APPLICATIONS OF METALLOPHYTES

Metallophytes are important in locating ore–bodies using indicator species, 'phytoextraction' (cleaning up of metal–contaminated soils by removing metals), and 'phytomining' (commercially producing metals from phytomass). The latter technology entails growing selected hyperaccumulator plants on sub–economic ore bodies or mineral wastes with subsequent harvesting and incineration generating a high–grade bio–ore. The concentration of nickel, for example, in bio–ore (10–25%) is far greater than in current mineable lateritic ores. In essence this is called 'metal farming'. In addition, induced phytomining has also been successfully demonstrated for gold. Despite the scientific validation of the concept of phytomining in the last two decades, the mining industry has yet to exploit the potential of phytomining in India. Lack of awareness in research and development in this field is one of the reasons.

Metallophytes also serve as invaluable plant resources for Green Chemistry. Recently metal accumulators, viz. *Noccaea caerulescens* and *Anthyllis vulneraria* are used as starting raw materials to prepare novel poly–metallic catalysts useful for Lewis acid catalyzed reactions. The synergetic catalysis of these systems leads to efficient syntheses of complex biomolecules. Thus, these new polymetallic catalysts bring new possibilities in green catalysis, and green chemistry and therefore are named as "Ecological Catalysis" (Grison, 2015).

BIOAUGMENTED / BIOASSISTED PHYTOMINING

Growing bioeconomy is an integral component of sustainable development. Availability of clean soil is rather scarce. Pressure on available land is steeply increasing. Under the circumstances appropriate use of contaminated land for boosting bioeconomy and environmental cleanup of contaminated soils via bioremediation an environmental remediation technology are relevant (Prasad, 2015a, b).

Bioassisted phytomining implies targeted use of microorganisms and plants for the selective recovery of the metal. Metals from undissolved compounds are dissolved by applying specially chosen microorganisms and therefore become available to the hyperaccumulating plants (Maluckov, 2015).

METALLOPHYTES FOR PHYTOTECHNOLOGIES

a) Metallophytes for Biological Recultivation of "Industrial Deserts"

b) Metallomics: a novel tool for functional biochemistry of trace elements

c) Biofortification of food products in case of trace elements that of nutritionally important, viz. Zinc and Iron.

Table 1—Metal hyperaccumulator plants (after Baker, 2010)

Metal	% in leaf dry matter	No of taxa	No of families
Antimony	> 0.1	2	2
Arsenic	> 0.1	5	1
Cadmium	> 0.01	2	2
Cobalt	> 0.03	30	11
Copper	> 0.03	32	15
Lead	> 0.1	14	7
Manganese	> 1.0	12	6
Nickel	> 0.1	450	42
Selenium	> 0.01	20	7
Thallium	> 0.01	2	1
Zinc	> 0.3	12	6

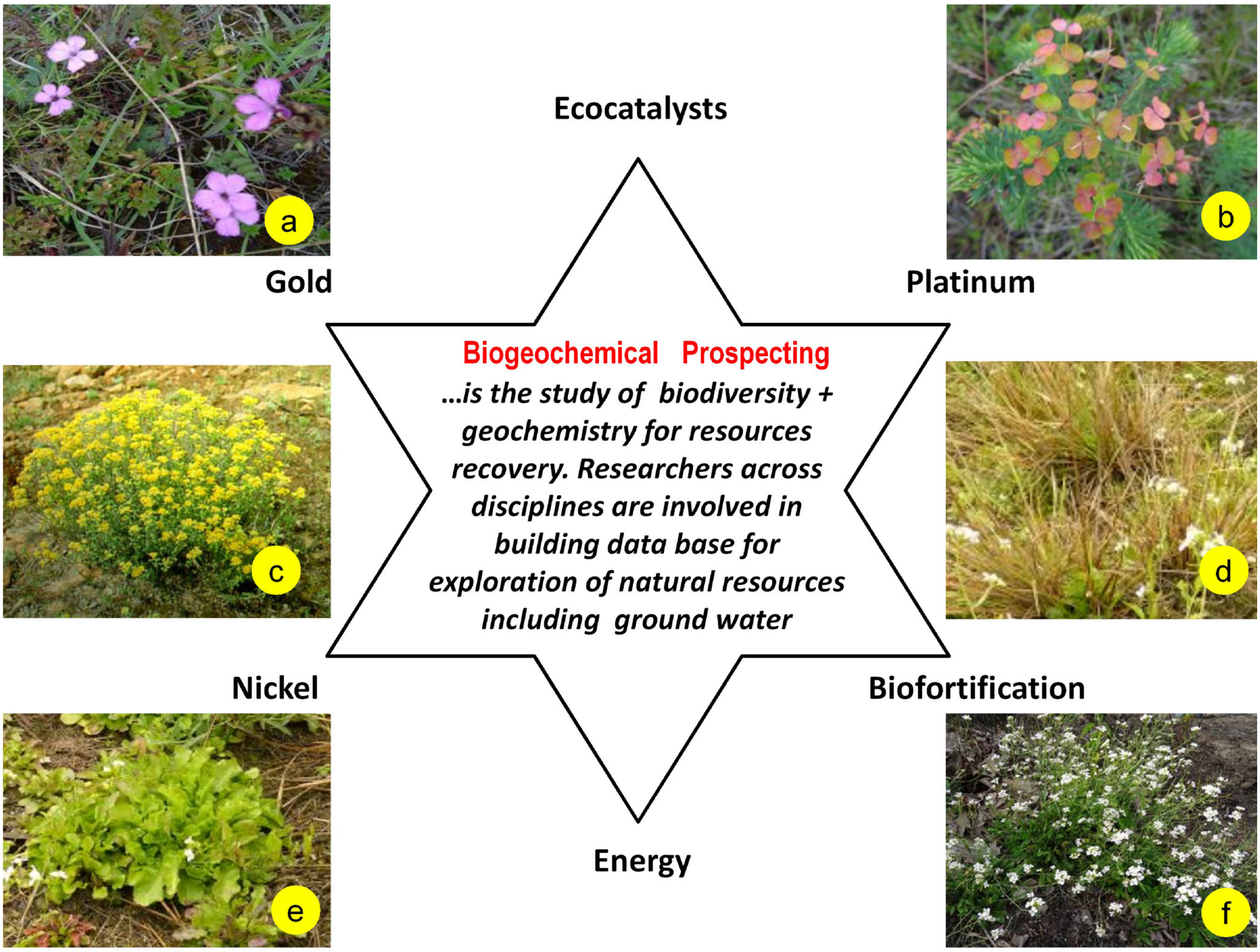

Fig. 1—Biogeochemical prospecting and classic metallophytes, (a) *Dianthus carthusianorum*, (b) *Euphorbia cyparissias*, (c) *Alyssum serpellifolium*, (d–f) *Arabidopsis arenosa*.

"Metallomics" is a new frontier in the field of trace elements in biology highlighting the role of biometals in biological, environmental and clinical investigations since several of the trace elements play as co–factors in several biomolecules. This area is emerging as an interdisciplinary science complementary to genomics and proteomics with cutting edge applications.

''Metallomics'' is the metal assisted functional biogeochemistry, a new scientific field proposed to integrate the research fields related to metal biomolecules. Metallomics is the scientific field of symbiosis with genomics and proteomics, because syntheses and metabolic functions of genes (DNA and RNA) and proteins cannot function without the coordination of various metal ions and metalloenzymes. In metallomics, metalloproteins, metalloenzymes and other metal–containing biomolecules are defined as ''metallomes'' with functional complementarity to genomics and proteomics (Prasad, 2006).

These eco–innovative phytotechnologies can in–situ and ex–situ remediate soil layers explored by roots and at the same time provide plant biomasses, contributing towards achieving envisaged targets on the use of renewable plant–based feedstock for various purposes (renewable energy sources, ecomaterials, biomass for biorefineries, green fine chemistry, bioplastics, etc.) in substitution to fossil fuels and other non–renewable raw materials. They can also reduce the diversion of croplands to bioenergy and other non–food crops.

Major hindrances to the development of phytotechnologies for soil remediation are the non–existence of a complete chain, from the biomass production to its valuation, the focus of research programmes on only a few previously identified plant species with high phytoproductivity. Lack of economically–sound valorisation pathways is another lacuna.

Conversion of phytoremediation–borne phytomass

1. for green–fine chemistry (catalyst production from metal accumulating biomass)
2. for biorefinery (prehydrolysis and organosolv pre–treatment from metal

3. accumulating woody lignocellulosic biomass) and
4. by increasing the panel of plant species cultivated on metal contaminated soils usable for biomass conversion.

CONCLUSIONS

Metal accumulators have a role in phytomining. Phytoextraction may be economical when applied to expensive metals like gold, palladium and platinum. Antarctic snow and crustal enrichment for Platinum [Pt] suggests global transporation could contribute to platinum pollution in the atmosphere during the last decades (Soyol–Erdence *et al*., 2011). Platinum is used as automobile and industrial catalytic converters. Platinum [Pt] is excreted through urine of cancer patients subjected to chemotherapy (Dubiella–Jackowska *et al.*, 2009). Pt is more expensive than gold, it can be beneficial to remove Pt from wastewater by biosorption (Lalhruaitluanga & Prasad, 2015). Phytoextraction and phytomining using the metal accumulating ecotypes of plants has attained global attention (Bani *et al*., 2015; Chaney *et al*., 2004; Leitenmaier & Küpper, 2013; Losfeld *et al*., 2014; Sheoran *et al*., 2013; van der Ent *et al*., 2015; Zhang *et al*., 2014). There are blue and dark skies for application of metallophytes as follows:

Blue skies—The grand success of the Phytomining Workshop 21–22 July 2014, Brisbane, Australia From discovery to full–scale application held at the The University of Queensland, St Lucia Campus, Brisbane, Queensland Organised by the Centre for Mined Land Rehabilitation, Sustainable Minerals Institute.

Dark skies—expressions like "Phytoextraction: Where's the action?" (Robinson *et al.*, 2015).

Inspite of expression of some reservations, promising bioeconomic potential exists for metallophytes in the following areas:

1. Biofortified nutraceuticals for human health.
2. Biofortified animal feed/poultry feed.
3. Ecocatalysts for green chemistry (Grison, 2015).
4. Bioremediation based bioeconomy (Prasad, 2015).

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