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Heavy Metals: An Ambiguous Category of Inorganic Contaminants, Nutrients and Toxins

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ABSTRACT
The term heavy metals has been vaguely applied to a group of physically miscellaneous and chemically heterogeneous elements, at times being biologically essential or environmentally significant inorganic contaminants, in most of the published literature without any established authoritative or coherent scientific basis or reference. Although Potentially Toxic Elements (PTEs) as an alternative for popularly known heavy metals, describes their toxic nature in terms of concentration fluctuations, exposure limits and speciation varieties for a given exposed organism, yet it is poorly explicative in potential hazard classification qualitatively from species to species on an ecosystem-scale. This has led to a controversy in the categorization of large range of unrelated metal (loid)s with specific mode of action relevant to their speciation and the organism concerned. The aim of describing a comprehensive element-specific identification, characterisation and quantification exposure-toxicity model in context of key factors like geo-chemical speciation, bio-availability, or fate and effect is unrealistic unless a proper and scientifically recommended categorization of differently behaving divergent class of elements is achieved. Hence, an appropriate nomenclatural prospect is required to rectify the inconsistency for which I suggest the term Biologically Labile Elements (BLEs), or simply Bio-labile elements for its biological, chemical, environmental and toxicological relevance as discussed in this paper.

Key words: Heavy metals, trace elements, micronutrients, potentially toxic elements (PTEs), biologically labile elements (or bio-labile elements, BLEs)

INTRODUCTION
Inorganic contaminants have pervaded the environment in all its compartments and comprise much of the contamination at sites throughout the world. The term heavy metals has been widely adopted for a group of metals and metalloids and their compounds probably because it evokes the concepts of recalcitrance and toxicity in biological systems besides contamination and persistence in the environment. However, the term being uncertain easily leads to misunderstanding as there is no single authoritative description (Duffus, 2002; Ansari *et al*., 2004; Goyer *et al*., 2004; Hodson, 2004; Pizzol *et al*., 2011). Saxena and Misra (2010) deem approximately 65 elements as heavy metals. Some authors define heavy metal as a metal with an atomic mass greater than that of sodium, whereas others define it inconsistently as a metal within a density range of 3.5-6 g cm^{-3}. According to Srivastava and Majumder (2008) heavy metals are elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0. In Engineering high density alloys

are included in the term heavy metals. A heavy metal is a member of an imprecise subset of transition metals, some metalloids, lanthanides and actinides that exhibit metallic properties (Babula *et al.*, 2009). Appenroth (2010) introduced three sub-groups of heavy metals based on periodic system of elements -(i) all transition elements except La and Ac; (ii) rare earth elements (lanthanide series and actinide series), including La and Ac; and (iii) a heterogenous lead-group comprising of p-block elements of Bi (metal); Al, Ga, In, Tl, Sn, Pb, Po (amphoterous oxide forming elements); and Ge, As, Te (metalloids). The term is also applied to semi-metals (metalloids), such as arsenic and selenium, allegedly because of the hidden assumption that density and toxicity are in some way identical. Normally, metals and metalloids differ in their capacity to form Pearson's Lewis acids and Lewis bases of varying degree of hardness/softness determining their affinity for both abiotic and biological interaction (Duffus, 2002; D'Amore *et al.*, 2005). Besides, International Union of Pure and Applied Chemistry (IUPAC) do not recommend designating elements as heavy metals due to contradictory definitions (Duffus, 2002; Hodson, 2004; Madrid, 2010). Despite the fact that the term heavy metals has no sound terminological or scientific basis, it has been used in much of the scientific literature, mainly to refer to metals, semi-metals or radionuclides like Ag, Al, Am, As, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, La, Mg, Mn, Ni, Pb, Pd, Pt, Ra, Rh, Ru, Sb, Sc, Se, Sn, Tc, Te, Th, Tl, U, W, Y, Zn; and even a miscellaneous toxic material - asbestos for convenience sake (Matlack, 2010). Such a controversial classification of hazardous inorganic pollutants is justified for very weak reasons of convenience or conventional usage and the understanding of heavy metals as environmentally bad elements. Therefore, the tendency of categorization of certain elements and their compounds under the title heavy metals with relevance to eco-toxicity despite being characteristically disparate in density (specific gravity), atomic weight (relative atomic mass), atomic number, or chemical properties sounds obsolete.

COMMON SYNONYMS OF HEAVY METALS

Sometimes, authors choose trace elements (or metals), micronutrients, microelements, minor elements, trace inorganics, etc., synonymous to heavy metals (Kabata-Pendias and Pendias, 2001; Adriano, 2001). Pertinently heavy metals are important from the perspective of not only their toxicity but their essentiality. According to Mertz (1998), "An element is considered essential to an organism when reduction of its exposure below certain limit results consistently in a reduction in a physiologically important function, or when the element is an integral part of an organic structure performing a vital function of the organism". Elements like vanadium, tungsten though toxic are beneficial for certain organisms and under certain conditions. The optimum dietary intake or exposure range, referred to as the Acceptable Range of Oral Intake (AROI), falls between the minimum level required to prevent deficiency and the maximum threshold level of exposure to prevent toxicity and is represented by a trough in the U-shaped dose-response curve (ILO/UNEP/WHO, 2002). Several heavy metals are micronutrients (Feiziasl *et al.*, 2009), others are potent cell toxins and virtually all are detrimental when/if critical thresholds for toxicity is exceeded. Further, the concentration ranges of deficiency, optimal supply and toxicity are very close together. Munoz-Olivas and Camara (2001) classify heavy metals as potentially toxic (arsenic, cadmium, lead, mercury, nickel, etc.), probably essential (vanadium, cobalt) and essential (copper, zinc, iron, manganese, selenium). Trace elements such as B (for plants); Co and Se (for animals); or Cu, Fe, Mn, Mo, Ni and Zn (both) are essential micronutrients that need to be consumed in adequate amounts to maintain normal physiological functions in biological systems (Ibrahim *et al.*, 2009; Rutkiewicz and Namiesnik, 2009; Lombi *et al.*, 2011). In contrast, dietary exposure to other elements such as Hg, Cd and Pb has been associated with toxic and adverse health effects (Peralta-Videa *et al.*, 2009). In medical usage heavy metal toxicity includes excessive amounts of iron; beryllium to the lightest element though it excludes bismuth because of its low toxicity though it is one of the heaviest. The essential elements can also produce toxic effects when their intake is extremely elevated, or even at low concentration when ingested for prolonged period (Kabata-Pendias and Pendias, 2001; Tuzen and Soylak, 2007; Marmiroli and Maestri, 2008; Rahimi *et al.*, 2010; Vali and Naser, 2011) and to paraphrase Paracelsus (1493-1541) “All substances are toxic and there is nothing without toxic properties. It is only the dose which makes something a poison”. A concensus for a trace element being toxic works as long as it is present in a proportion below 0.1% in natural matrix, or below 0.01% in affected organism (Adriano, 2001) but the problem evolves when any element becomes toxic at higher concentrations (>0.1%), or hyper-accumulates in concentrations >0.01% despite being available below 0.1% in ambient media (Mishra and Tripathi, 2008; Ndimele and Jimoh, 2011; Rascio and Navari-Izzo, 2011). Interestingly, heavy metals of antimony, arsenic, bismuth, copper, gallium, gold, iron, rhodium, ruthenium, platinum, vanadium and zinc notorious for their cytotoxic and oncogenic properties tend to be a regular and deliberate constituent of complexation compounds intended for therapeutic purposes in anti-cancer remedies (Desoize, 2004; Dabrowiak, 2009). Thus, the term heavy metal includes both essential and non-essential trace elements (Park *et al.*, 2011) which may be toxic to the organisms depending on their own properties and concentration levels besides the organism’s susceptibility levels.

POTENTIALLY TOXIC ELEMENTS (PTES) AS AN ALTERNATIVE

The title heavy metals or toxic metals or trace elements seem to be unsatisfactory misrepresenting a large and diversified group of elements. A more convenient term of Potentially Toxic Elements (PTEs) in concurrent practice is adopted as an alternative (Wilkinson *et al.*, 2001; Fariasa *et al.*, 2002; Gonzalez-Chavez *et al.*, 2004; Pavlikova *et al.*, 2007; Okorie *et al.*, 2010; Papastergios *et al.*, 2010). In the environmental context, Potentially Toxic Elements (PTEs) may encompass both essential and toxic elements (all elements are toxic beyond a certain threshold value) but still the toxicity varies with the nature and species of element and organism involved (Hsu *et al.*, 2006; Uysal *et al.*, 2008). The bioaccumulation paradigm in a particular organism in relation to toxicity effects is complex, being influenced by biological processes, chemistry of the growth media, multiple routes of exposure and different strategies of organisms to regulate PTEs (Luoma and Rainbow, 2005; Casado-Martinez *et al.*, 2010). The mere presence of PTEs does not confer it to be used with connotations of pollution and toxicity. Ionic speciation is a key factor in controlling mobility (solubility), recalcitrance or persistence and corresponding bioaccumulation of metal(loid)s and their compounds in natural environments since most PTEs in the environment are present as cations, though some semi-metals may occur as oxy-anions (e.g., arsenate, AsO_4^{-3}). The chemical form or valence can determine toxicity (Baranowski *et al.*, 2002; Bhavsar *et al.*, 2008; Paiva *et al.*, 2009; Diamond *et al.*, 2010; Bose *et al.*, 2011), mobility and bioavailability (Espinoza-Quinones *et al.*, 2008; Chen *et al.*, 2010) in living environments. While many PTEs are highly toxic in one form, they may be essential in another. In fact, it is increasingly recognized that the availability and toxicity of a given contaminant or micronutrient varies substantially in relation to the interaction between different chemical species present (Ghosh *et al.*, 2007; Komjarova and Blust, 2009; Scheckel *et al.*, 2009; Yizong *et al.*, 2009; Israr *et al.*, 2011). The pattern of PTE accumulation in organisms also varies qualitatively and quantitatively and from species to species

(Etesin and Benson, 2007). PTEs like Cu, Ni and Zn are essential micronutrients for plants but in excess all these metals are harmful to humans, animals and plants; as are the non-essential metals Pb, Cd and Hg (Reeves and Baker, 2000; Singh *et al.*, 2010). Still other organisms may be tolerant of PTEs and will accumulate to concentrations several orders of magnitude higher than those of ambient growth environment without experiencing any toxic effects (Casas *et al.*, 2008; Agunbiade *et al.*, 2009; Yilmaz and Parlak, 2011). The toxicity of a given concentration of a PTE not only depends on its speciation but also upon physical and chemical attributes of ambient environment for adsorption, complexation, cation exchange capacity and biological affinity (Deheyn *et al.*, 2005; Nobi *et al.*, 2010; Park *et al.*, 2011; Smolyakov *et al.*, 2010). Thus, the toxicity of PTEs is a function of complex interplay and synchronization between chemical properties of the element and its group of compounds in presence of biological properties of the organism at risk, driven by appropriate environmental variables.

BIOLOGICALLY LABILE ELEMENTS (BLES)-A PROSPECT

PTEs as a category could not accommodate diverse inorganic substances with peculiar physico-chemical properties and characteristic environmental chemistry, accounting for their differential ecological fate and effect at species and ecosystem levels. The phrase potentially toxic elements is unable to distinguish between the deficiency, essentiality and toxicity criteria for a biologically significant element in relation to different organisms. The scientific literature amply demonstrates that the effective doses and species-specific toxicity of an element will vary widely depending on its ionic form. Nevertheless, the so-called PTEs have a specific mode of action, influenced by the instant environmental chemistry, depending on its properties (e.g., speciation) and the exposed organism (Fairbrother *et al.*, 2007), it would be unrealistic to generalize their toxic behavior on each and every organism (Pizzol *et al.*, 2011). So, for the purpose of indicating a category of elements with no characteristic or functional similarity in biological and toxicological properties, I would propose to label them as Biologically Labile Elements (BLEs), or in simpler terms Bio-labile Elements. This categorization as BLEs would reflect the biological basis of toxicity (Nieboer and Richardson, 1980) in relation to species specificity. The criteria of BLEs will select a large range of elements conforming to be variable in physico-chemical properties in their diverse chemical forms that differ in their specificity to organisms and environmental changes. BLEs are natural constituents of the dynamic bio-geo domain and become the cause of concern only when accounted for their risk-related characteristic to form pollutants (Shi *et al.*, 2010) that in turn cause toxic consequences to living organisms. The attributes like bio-accumulation, -essentiality, -magnification, - recalcitrance, -remediation, -sorption, -tolerance (-resistance) and -toxicity are predominantly linked with these elements of interest due to their importance from a biological and/or an eco-toxicological point of view. The requirement of classifying them as BLEs enhances when they perform a range of structural and functional biomolecular roles typical to an organism (Fraga, 2005) but still being susceptible to be deleterious subject to altered equilibria (Kori-Siakpere *et al.*, 2006; Chakravarty *et al.*, 2007; Sharma *et al.*, 2008). Further, both the speciation of BLEs and their specificity to an organism lead to a defined outcome on exposure, unique to the duo (Saby *et al.*, 2009). Lastly, a synoptic element-specific Life Cycle Assessment (LCA) and hazard cum risk assessment modelling practice for BLEs is feasible when accounted for their differential distinctiveness over an array of environmental variables (Rosenbaum *et al.*, 2008).

CONCLUSION

A nomenclatural prospect which satiates the characteristic and functional relevance of all of these elements should replace the conventional and scientifically discouraged practice of categorization. Hence, for brevity sake in biological, environmental and toxicological relevance, a single term of Biologically Labile Elements (BLEs) may refer to a large list of elements, yet preserving their discrete character and shall infer:

- Any element with a potential to be toxic when available in elevated concentration beyond background (threshold) range or maximum permissible limit/ maximum contamination level (MCL) due to altered geochemical cycle or biochemical balance, posing potential implications for life
- Any element with a susceptibility to transform into a bioavailable oxidation state to form organic complexes that either perform a normal biochemical or physiological role in an organism, or otherwise disrupt its homeostasis
- Any element with a propensity to be opportunistic enough to modify its latent mobility and toxicity corresponding to fluctuating biotic and abiotic environmental variables
- Any element liable to risk a specific species in definite exposure gradients of both quantity (amount/concentration) and quality (acute and chronic)
- Any element with a tendency to entail profound ecological consequences of bioaccumulation, biomagnification and genetic erosion
- Any element with variability in nature, either being nutritionally essential or non-essential to different organisms
- Any element liable to be bio-accumulated with uncertainty, whether to play a prominent physiological role or just be an environmental adaption

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