“HEAVY METALS”—A MEANINGLESS TERM?

(IUPAC Technical Report)

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“Heavy metals”—a meaningless term?

(IUPAC Technical Report)

Abstract: Over the past two decades, the term “heavy metals” has been widely used. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of “heavy metals” to which they apply. Such lists differ from one set of regulations to another and the term is sometimes used without even specifying which “heavy metals” are covered. However, there is no authoritative definition to be found in the relevant literature. There is a tendency, unsupported by the facts, to assume that all so-called “heavy metals” and their compounds have highly toxic or ecotoxic properties. This has no basis in chemical or toxicological data. Thus, the term “heavy metals” is both meaningless and misleading. Even the term “metal” is commonly misused in both toxicological literature and in legislation to mean the pure metal and all the chemical species in which it may exist. This usage implies that the pure metal and all its compounds have the same physicochemical, biological, and toxicological properties, which is untrue. In order to avoid the use of the term “heavy metal”, a new classification based on the periodic table is needed. Such a classification should reflect our understanding of the chemical basis of toxicity and allow toxic effects to be predicted.

1. INTRODUCTION

Over the past two decades, the term “heavy metals” has been used increasingly in various publications and in legislation related to chemical hazards and the safe use of chemicals. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of “heavy metals” to which they apply. Such lists may differ from one set of regulations to the other, or the term may be used without specifying which “heavy metals” are covered. In other words, the term “heavy metals” has been used inconsistently. This has led to general confusion regarding the significance of the term. There is also a tendency to assume that all so-called “heavy metals” have highly toxic or ecotoxic properties. This immediately prejudices any discussion of the use of such metals, often without any real foundation.

The inconsistent use of the term “heavy metals” reflects inconsistency in the scientific literature. It is, therefore, necessary to review the usage that has developed for the term, paying particular attention to its relationship to fundamental chemistry. Without care for the scientific fundamentals, confused thought is likely to prevent advance in scientific knowledge and to lead to bad legislation and to generally bad decision-making.

2. METALS AND THEIR CHEMICAL CLASSIFICATION

2.1 Introduction

A thorough understanding of chemical principles is an essential prerequisite for the safe use of metals and thus any proposed system of classification must be referenced to the periodic table of the elements. Metals are defined chemically as “elements which conduct electricity, have a metallic luster, are malleable and ductile, form cations, and have basic oxides” [1]. From this definition, most elements can be
described as metals. Thus, there is a need to subdivide the metals into different chemical classes if we are to consider carefully their individual properties and safe use.

2.2 Terms commonly used to specify groups of metals

Terms that have been commonly used in specifying groups of metals in biological and in environmental studies are listed with comments in Table 1. The limitations of these terms are clear. They are arbitrary and imprecise. Several categories overlap, making them inexact. The term “heavy metal”, because it is often used with connotations of pollution and toxicity, is probably the least satisfactory of all the terms quoted as it leads to the greatest confusion. “Heavy” in conventional usage implies high density. “Metal” in conventional usage refers to the pure element or an alloy of metallic elements. Knowledge of density contributes little to prediction of biological effects of metals, especially since the elemental metals or their alloys are, in most cases, not the reactive species with which living organisms have to deal.

Table 1 Terms often used to classify metals in biological and environmental studies (after [3]).

<table>
<thead>
<tr>
<th>Term</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Metals may be defined by the physical properties of the elemental state as elements with metallic luster, the capacity to lose electrons to form positive ions and the ability to conduct heat and electricity, but they are better identified by consideration of their chemical properties (see accompanying text). The term is used indiscriminately by nonchemists to refer to both the element and compounds (for example, reference by biologists to “the uptake of copper by...” does not distinguish the form in which the metal is absorbed).</td>
</tr>
<tr>
<td>Metalloid</td>
<td>See “semimetal”.</td>
</tr>
<tr>
<td>Semimetal</td>
<td>An element that has the physical appearance and properties of a metal but behaves chemically like a nonmetal [1]</td>
</tr>
<tr>
<td>Light metal</td>
<td>A very imprecise term used loosely to refer to both the element and its compounds. It has rarely been defined, but the originator of the term, Bjerrum [6], applied it to metals of density less than 4 g/cm–3.</td>
</tr>
<tr>
<td>Heavy metal</td>
<td>A very imprecise term (see Table 2 for definitions), used loosely to refer to both the element and its compounds. It is based on categorization by density, which is rarely a biologically significant property.</td>
</tr>
<tr>
<td>Essential metal</td>
<td>Broadly, one which is required for the complete life cycle of an organism, whose absence produces specific deficiency symptoms relieved only by that metal, and whose effect should be referred to a dose–response curve. The term is often used misleadingly since it should be accompanied by a statement of which organisms show a requirement for the element. Again, it is used loosely to refer to both the element and its compounds.</td>
</tr>
<tr>
<td>Beneficial metal</td>
<td>An old term, now largely disused, which implied that a nonessential metal could improve health. Another term that has been used loosely to refer to both the element and its compounds.</td>
</tr>
</tbody>
</table>

(continues on next page)
Toxic metal An imprecise term. The fundamental rule of toxicology (Paracelsus, 1493–1541) is that all substances, including carbon and all other elements and their derivatives, are toxic given a high enough dose. The degree of toxicity of metals varies greatly from metal to metal and from organism to organism. Pure metals are rarely, if ever, very toxic (except as very fine powders, which may be harmful to the lungs from whatever substance they may originate). Toxicity, like essentiality, should be defined by reference to a dose–response curve for the species under consideration. This is another term that has been used loosely to refer to both the element and its compounds.

Abundant metal Usually refers to the proportion of the element in the earth’s crust, though it may be defined in terms of other regions, e.g., oceans, “fresh water”, etc.

Available metal One that is found in a form which is easily assimilated by living organisms (or by a specified organism).

Trace metal A metal found in low concentration, in mass fractions of ppm or less, in some specified source, e.g., soil, plant, tissue, ground water, etc. Sometimes this term has confusing overtones of low nutritional requirement (by a specified organism).

Micronutrient More recent term to describe more accurately the second of the meanings of trace metal, above.

The term “heavy metal” has been queried over many years, for example by Heuman [2], by Phipps [3], and by VanLoon and Duffy [4], but efforts to replace it by chemically sound terminology [5] have so far failed. As will be shown below, the term “heavy metals”, however defined, always covers an extremely disparate group of elements, and an even more disparate group of compounds of the elements. Thus, any assumption of underlying functional similarity in biological or toxicological properties is bound to be wrong.

2.3 A review of current usage of the term “heavy metal”

Table 2 lists all the current definitions of the term “heavy metal” that the author has been able to trace in scientific dictionaries or in other relevant literature. It must be noted that frequently the term has been used without an associated definition, presumably by authors who thought that there was agreement about the meaning of the term. The table shows how wrong this is and explains some of the confusion in the literature and in related policy and regulations. It should also be noted before going further that the term “heavy metal” has even been applied to semimetals (metalloids) such as arsenic, presumably because of the hidden assumption that “heaviness” and “toxicity” are in some way identical. This illustrates further the confusion that surrounds the term.

Before 1936, the term was used with the meanings “guns or shot of large size” or “great ability” [7,8]. The oldest scientific use of the term to be found in the English literature, according to the Oxford English Dictionary, is in Bjerrum’s Inorganic Chemistry, 3rd Danish edition, as translated by Bell in collaboration with Bjerrum, published in London in 1936 [6]. It is worth noting that no comparable inorganic chemistry textbook published since seems to have used Bjerrum’s classification, and it has not been included in the IUPAC Compendium of Chemical Terminology [9], which is the gold standard in terminology for chemists.
Bjerrum’s definition of “heavy metals” is based upon the density of the elemental form of the metal, and he classifies “heavy metals” as those metals with elemental densities above 7 g/cm\(^3\). Over the years, this definition has been modified by various authors, and there is no consistency. In 1964, the editors of Van Nostrand’s *International Encyclopaedia of Chemical Science* [10] and in 1987, the editors of Grant and Hack’s *Chemical Dictionary* [11] included metals with a density greater than 4 g/cm\(^3\). A little later, in 1989, 1991, and 1992, Parker [12], Lozet and Mathieu [13], and Morris [14] chose a defining density “greater than 5 g/cm\(^3\)”. However, Streit [15] used a density of 4.5 g/cm\(^3\) as his reference point, and Thornton [16] chose 6 g/cm\(^3\). The *Roemp Chemical Dictionary* [17] gives 3.5 g/cm\(^3\) as a possible defining density. However you work with these definitions, it is impossible to come up with a consensus. Accordingly, any idea of defining “heavy metals” on the basis of density must be abandoned as yielding nothing but confusion.

At some point in the history of the term, it has been realized that density is not of great significance in relation to the reactivity of a metal. Accordingly, definitions have been formulated in terms of atomic weight or mass, which brings us a step closer to the periodic table, traditionally the most sound and scientifically informative chemical classification of the elements. However, the mass criterion is still unclear. Bennet [18] and Lewis [19] opt for atomic weights greater than that of sodium (i.e., greater than 23), thus starting with magnesium, while Rand et al. [20] prefer metals of atomic weights greater than 40, thus starting with scandium. Lewis [19] suggested that forming soaps with fatty acids is an important criterion of “heaviness”. This, together with the absurdity of classifying magnesium as a “heavy metal”, when there has developed a conventional association of “heaviness” with toxicity, makes the Bennet and Lewis definition untenable. As for starting with scandium, it has a density of just under 3 and so would not be a “heavy metal” under any of the definitions based on density. Thus, again we have no consistent basis for defining the term.

Another group of definitions is based on atomic number. Here there is more internal consistency since three of the definitions cite “heavy metals” as having atomic numbers above 20, that of sodium. Interestingly, one of them comes from the chapter by Lyman in Rand (1995) [21] and contradicts the definition favoured by Rand himself cited in the previous paragraph. The problem with citing metals of atomic number greater than sodium as being “heavy” is that it includes essential metals such as magnesium and potassium and flatly opposes the historic basis of definition based on density, since it includes elements of density lower than any that has been used as a defining property by other authors. Burrell’s definition [22] even includes the semimetals, arsenic and tellurium and the nonmetal selenium.

A fourth group of definitions is based on other chemical properties, with little in common, density for radiation screening, density of crystals, and reaction with dithizone. This brings us to the definitions based vaguely on toxicity. One of these definitions [23] even refers to “heavy metals” as an “outdated term”. The same authors also point out, as we have already noted in Table 1, that the term has been applied to compounds of the so-called “heavy metals”, including organic derivatives where the biological and toxic properties may reflect more on the organic moiety than on the metal itself, thus making the term even more misleading than usual in the literature.

With the above in mind, it is not surprising that the most widely used textbook in toxicology, *Casarett and Doull’s Toxicology* [24] never uses the term “heavy metal”, although it does include both arsenic and arsine as “Major Toxic Metals”! It is not surprising either that Phipps, one of the authors whose definitions are cited in the table, calls the term “hopelessly imprecise and thoroughly objectionable” [3] or that recently VanLoon and Duffy conclude that “there is no chemical basis for deciding which metals should be included in this category (heavy metals)” [4]. What is surprising is the persistence of the term and its continuing use in literature, policy, and regulations, with widely varying definitions leading to confusion of thought, failure in communication, and considerable waste of time and money in fruitless debate.
Table 2 Definitions of “heavy metal”: A survey of current usage (April 2001).

1. Definitions in terms of density (specific gravity)
   - Metals fall naturally into two groups—the light metals with densities below 4 and the heavy metals with densities above 7 [6].
   - Metal having a density greater than 4 [10]
   - Metal of high density, especially a metal having a density of 5.0 or over [25]
   - Metal with a density greater than 5 [26]
   - Metal with a density greater than 6 g/cm³ [27]
   - Metal of density greater than 4 [11]
   - Metal with a density of 5.0 or greater [28]
   - Metal whose density is approximately 5.0 or higher [12]
   - Metal with a density greater than 5 [13]
   - (In metallurgy) any metal or alloy of high density, especially one that has a density greater than 5 g/cm³ [14]
   - Metal with a density higher than 4.5 g/cm³ [15]
   - Metal with a density above 3.5–5 g/cm³ [17]
   - Element with a density exceeding 6 g/cm³ [16]

2. Definitions in terms of atomic weight (relative atomic mass)
   - Metal with a high atomic weight [29]
   - Metal of atomic weight greater than sodium [18]
   - Metal of atomic weight greater than sodium (23) that forms soaps on reaction with fatty acids [19]
   - Metallic element with high atomic weight; (e.g., mercury, chromium, cadmium, arsenic, and lead); can damage living things at low concentrations and tends to accumulate in the food chain [30]
   - Metallic element with an atomic weight greater than 40 (JHD note—starting with scandium Atomic Number 21). Excluded are alkaline earth metals, alkali metals, lanthanides and actinides [20]
   - Metal with a high atomic mass [31]
   - “Heavy metals” is a collective term for metals of high atomic mass, particularly those transition metals that are toxic and cannot be processed by living organisms, such as lead, mercury, and cadmium [32]
   - Metal such as mercury, lead, tin, and cadmium that has a relatively high atomic weight [33]
   - Rather vague term for any metal (in whatever chemical form) with a fairly high relative atomic mass, especially those that are significantly toxic (e.g., lead, cadmium, mercury). They persist in the environment and can accumulate in plant and animal tissues. Mining and industrial wastes and sewage sludge are potential sources of heavy metal pollution [34].
   - A metal such as cadmium, mercury, and lead that has a relatively high relative atomic mass. The term does not have a precise chemical meaning [35].
   - Metal with a high relative atomic mass. The term is usually applied to common transition metals such as copper, lead or zinc [36].

3. Definitions in terms of atomic number
   - In electron microscopy, metal of high atomic number used to introduce electron density into a biological specimen by staining, negative staining, or shadowing [37].
   - In plant nutrition, a metal of moderate to high atomic number e.g., Cu, Zn, Ni, Pb, present in soils due to an outcrop or mine spoil, preventing growth except for a few tolerant species and ecotypes [37].
   - The rectangular block of elements in the periodic table flanked by titanium, hafnium, arsenic, and bismuth at its corners but including also selenium and tellurium. The densities range from 4.5 to 22.5 g/cm³ [22]
   - Any metal with an atomic number beyond calcium [38]
   - Any element with an atomic number greater than 20 [39]
   - Metal with an atomic number between 21 (scandium) and 92 (uranium) [21]
   - Term now often used to mean any metal with atomic number >20, but there is no general concurrence [3]
4. Definitions based on other chemical properties

• “Heavy metals” is the name of a range of very dense alloys used for radiation screening or balancing purpose. Densities range from 14.5 g/cm\(^{-3}\) for 76 % W, 20 % Cu, 4 % Ni to 16.6 g/cm\(^{-3}\) for 90 % W, 7 % Ni, 3 % Cu [40].
• Intermetallic compound of iron and tin (FeSn\(_2\)) formed in tinning pots which have become badly contaminated with iron. The compound tends to settle to the bottom of the pot as solid crystals and can be removed with a perforated ladle [41].
• Lead, zinc, and alkaline earth metals that react with fatty acids to form soaps. “Heavy metal soaps” are used in lubricating greases, paint dryers, and fungicides [42].
• Any of the metals that react readily with dithizone (C\(_6\)H\(_5\)N), e.g., zinc, copper, lead, etc. [43]
• Metallic elements of relatively high molecular weight [44].

5. Definitions without a clear basis other than toxicity

• Element commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but not every one is dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn [45].
• Outdated generic term referring to lead, cadmium, mercury, and some other elements which generally are relatively toxic in nature; recently, the term toxic elements has been used. The term also sometimes refers to compounds containing these elements [23].

6. Nonchemical definitions used before 1936

• Guns or shot of large size [7]
• Great ability [8]

3. FACTORS TO BE CONSIDERED IN CLASSIFYING METALS FOR TOXICITY OR ECOTOXICITY

Categorization of substances can be very useful in permitting quicker and simpler assessment of those substances that have properties in common. For example, aliphatic alcohols are a coherent group of compounds with sufficient common properties to be grouped legitimately for both scientific and regulatory consideration. The same is not true for metallic elements. Although they have certain properties in common, each is a distinct element with its own physicochemical characteristics which determine its biological and toxicological properties and how it may move through the environment. Not only this, but each can exist as part of a wide range of compounds with properties at least as diverse as those of carbon compounds. For example, there is no similarity in properties between pure tin, which has low toxicity, and tributyltin oxide, which is highly toxic to oysters and dogwhelks. Nor is there any similarity in properties between chromium in stainless steel, which is essentially nontoxic, and in the chromate ion which has been associated with causing lung cancer. Thus, the tendency to group certain metals and their compounds together for toxicity assessment under the title “heavy metals” must lead to fuzzy thinking and is another reason to abandon the term.

With regard to toxicity, differentiation between metals depends upon the chemical properties of the metals and their compounds and upon the biological properties of the organisms at risk. Thus, classification of metals for relevance to toxicity must be based on one or the other, or ideally both. At present, our knowledge of the relationship of biological speciation to toxicity is still at a very early stage, and we have none of the fundamental understanding needed to compile a periodic table of organisms from which their properties can be readily predicted by analogy with the chemical periodic table. Scientific classification must for the present be based on the chemical periodic table, and the main possibilities for this will be discussed in the next section.

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4. POSSIBILITIES FOR A CHEMICAL CLASSIFICATION OF METALLIC ELEMENTS AS A BASIS FOR TOXICITY ASSESSMENT WITHOUT ANY REFERENCE TO “HEAVINESS”

4.1 Introduction

In order to replace current terminology with something better for toxicity assessment or for the consideration of potential biological effects, it is desirable to establish an appropriate chemical classification of metals. Any such classification may have some weaknesses in practice depending upon the use envisaged [5,46], but at least its scientific basis will be sound because chemical properties determine what biological functions are possible [47].

A functional chemical classification of metals for use by scientists (including toxicologists), policy makers, and regulators must be related to relevant biological and environmental processes and must provide a scientific basis for the consideration of chemical speciation and biological uptake selectivity [48], functional role [46,49–51], and toxicity [52]. With this in mind, there are various possibilities that will be considered below.

Table 3 Biological significance of classification of metals based on the last electron subshell in the atom to be occupied (after [3]).

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Biologically significant chemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-block</td>
<td>The alkali metal ions are highly mobile, normally forming only weak complexes. Biologically, they act chiefly as bulk electrolytes. The alkaline earths form more stable complexes and have more specialized functional roles as structure promoters and enzyme activators. Neither group has any significant redox chemistry in vivo.</td>
</tr>
<tr>
<td>p-block</td>
<td>Some limited redox chemistry, e.g., Pb(^{4+}/\text{Pb}^{2+}) complicates the action of these metals. They generally form more stable complexes than the s block. The higher atomic number elements tend to bind strongly to sulfur; this is a major cause of their toxicity (see Section 4.3 on Class B metal ions).</td>
</tr>
<tr>
<td>d-block</td>
<td>Shows an extremely wide range of both redox behavior and complex formation. These properties underlie their catalytic role in enzyme action.</td>
</tr>
<tr>
<td>f-block</td>
<td>The lanthanide and actinide elements show a wide range of redox behavior and complex formation. Usually biologically unimportant, but some (the actinide group) may be significant pollutants.</td>
</tr>
</tbody>
</table>

4.2 Chemical classification of metallic elements based on the periodic table

The most complete and chemically sound classification of the metallic elements is their separation into 14 groups within the 18 groups of the conventional periodic table. In each of the groups, the members are related by (valence) electron configuration and hence by similarities in chemical reactivity. This group classification has guided the development of inorganic chemistry [53]. It has also guided the development of bioinorganic chemistry since it illustrates trends in behavior and similarities and differences between elements, both within groups and also between groups [47].

Using the periodic table (Fig. 1), one may divide metallic elements into four broad categories: s-block, p-block, d-block transition, and f-block (lanthanides and actinides). Table 3 relates these categories to their biologically significant properties. This scheme is based on a consideration of general reactivity, and it can be argued that it fails to emphasize sufficiently the broad differences between the metal ions in each of the different sections. However, together with the scheme outlined below, it can...
provide a basis for a useful classification scheme for rational consideration of the chemical and biological behavior of metallic elements and their compounds.

4.3 Chemical classification based on Lewis acid behavior

The interaction of metallic elements with living systems is dominated by the properties of metal ions as Lewis acids [54]. Lewis acids are defined as elemental species with a reactive vacant orbital or an available lowest unoccupied molecular orbital (LUMO). In other words, any elemental species with a net positive charge behaves as a Lewis acid because it can act as an electron acceptor. Any practical classification of metals should include assessment of the behavior of metal ions as electron acceptors since this determines the possibilities of complex formation. The currently preferred categorization of metal ions in terms of differential Lewis acidity is over 40 years old [55]. In the original scheme, metal ions were described as Class A, Class B, or borderline, depending on their observed affinity for different ligands (Fig. 2).

Table 4 lists metal ions according to the Lewis acid classification, and Fig. 2 shows the position of Classes A, B, and borderline in the periodic table. In general, there is a relatively sharp separation between Class A and borderline metal ions, but the difference between borderline and Class B is less clearly defined. Although alternative descriptions have evolved, notably the use of the term “hard acids” for Class A ions and “soft acids” for Class B ions [56–58], the basic concept of the scheme remains unaltered from the original.

The classification of metals by their Lewis acidity indicates the form of bonding in their complexes. Class A metal ions, which are hard, or nonpolarizable, preferentially form complexes with similar nonpolarizable ligands, particularly oxygen donors, and the bonding in these complexes is mainly ionic. Class B or soft metal ions preferentially bind to polarizable, soft ligands to give rather more cova-
lent bonding. In general, it is noticeable that hard–hard or soft–soft combinations are preferred wherever possible.

Classification of metals by their Lewis acidity permits us to predict both the preferred ligands and the general trend in the properties of metal complexes. The ultrahard, s-block metals bind only poorly to soft ligands and form mainly ionically bound complexes with hard (oxygen) donor ligands. As the bonding is mainly ionic, the metal ions are easily displaced and mobile. The p-block metal ions, in contrast, are generally softer, though Al\(^{3+}\) is much more like members of the s-block than others in the p-block. The higher atomic number p-block metals show strong affinity for soft ligands, such as sulfide or sulfur donors, and form highly covalent complexes from which they are difficult to displace. Thus, they are relatively immobile in the environment. In living organisms, they are not readily excreted and tend to accumulate with resultant toxicity. The two categories, a and b, have much in common with the older geochemical classification of metals (or rather their ions) as lithophile or chalcophile [59] (Fig. 3). The borderline metal ions are much more difficult to assess. Such metal ions generally form relatively stable complexes with both hard and soft donor ligands, but the exact order of stability is not easily determined. First-row d-block transition metal ions fall mainly into this group and show widely variable coordination chemistry.

Certain caveats must be applied to the Class A, Class B, and borderline classification. It must be recognized that the classification refers in each case to a specific ion, so that in cases where the metal may exist in more than one oxidation state, each ionic form must be treated separately (see Fig. 2). In such cases, the ion with the higher charge, which is therefore smaller and less polarizable, normally has considerable Class A character (or at least fewer Class B properties), whereas in the lower oxidation state the reverse is true. Thus, Fe\(^{3+}\) is generally described as hard or Class A, and, in keeping with this,

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**Fig. 2** The periodic table showing those metals classified as: Class A: hard metals (darkest gray); Class B: soft metals (lightest gray); and borderline: intermediate metals (intermediate gray). N.B.: Copper may be either Class B or borderline depending upon whether it is Cu(I) or Cu(II), respectively; lead may be either Class B or borderline depending upon whether it is Pb(II) or Pb(IV), respectively; and iron may be either Class A or borderline depending upon it is Fe(III) or Fe(II), respectively.

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binds preferentially to oxygen donor ligands such as phenolate or carboxylate groups in humic and fulvic acids, whereas Fe$^{2+}$ is considered borderline and has a higher affinity for softer ligands, including the unsaturated nitrogen donors of the tetrapyrroles in haem, and the sulfide and thiolate groups in the ferredoxins. A complication occurs in mixed ligand complexes, where the influence of one ligand affects the binding of the next, so that the Class B character is increased by binding a soft ligand, and mixed complexes with both hard and soft ligands are generally less stable.

It must be noted that the Class A (hard)/Class B (soft) classification scheme is not absolute (hence the borderline classification) and different authors may place the same metal ion into different classes, but, in general, agreements outweigh disagreements [5,60]. It should also be noted that this classification is empirical, based on observed chemical behavior. However, a theoretical basis has been suggested by Klopman [61,62]. This depends on the calculated orbital electronegativity of cations or anions. Metals with calculated orbital electronegativities above 1.45 all belong to Class A, while those with calculated orbital electronegativities below −1.88 are all Class B.

4.4 Conclusion

It is clear that we should abandon classification of metals using terms such as “heavy metals”, which have no sound terminological or scientific basis. A classification of metals and their compounds firmly based on their chemical properties is needed. Such a classification would permit interpretation of the biochemical basis for toxicity. It would also provide a rational basis for determining which metal ionic species or compounds are likely to be most toxic. For example, Nieboer and Richardson, on the basis of known Lewis acid properties, pointed out that, because of their affinity for phosphate groups and nonoxygen centers in membranes, borderline and Class B ions similar in size to calcium (II) ions are likely to cause harmful membrane structural changes [5]. This points the way forward to the day when...
toxicity testing can be minimized for metals and their compounds because our chemical and biological knowledge permits many toxic effects to be predicted.

Table 4 Class A and Class B metals [63].

Class A (hard) metals
Lewis acids (electron acceptors) of small size and low polarizability (deformability of the electron sheath or hardness)
Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, Fe(III), Rb, Sr, Y, Zr, Cs, Ba, La, Hf, Fr, Ra, Ac, Th.

Class B (soft) metals
Lewis acids (electron acceptors) of large size and high polarizability (softness)
Cu(I), Pd, Ag, Cd, Ir, Pt, Au, Hg, Ti, Pb(II).

Borderline (intermediate) metals
V, Cr, Mn, Fe(II), Co, Ni, Cu(II), Zn, Rh, Pb(IV), Sn.

5. GENERAL CONCLUSIONS

The term “heavy metal” has never been defined by any authoritative body such as IUPAC. Over the 60 years or so in which it has been used in chemistry, it has been given such a wide range of meanings by different authors that it is effectively meaningless. No relationship can be found between density (specific gravity) and any of the various physicochemical concepts that have been used to define “heavy metals” and the toxicity or ecotoxicity attributed to “heavy metals”.

Understanding bioavailability is the key to assessment of the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters and on the physicochemical properties of metallic elements, their ions, and their compounds. These in turn depend upon the atomic structure of the metallic elements, which is systematically described by the periodic table. Thus, any classification of the metallic elements to be used in scientifically based legislation must itself be based on the periodic table or some subdivision of it. Some possibilities for this have been discussed in this document.

Even if the term “heavy metal” should become obsolete because it has no coherent scientific basis, there will still be a problem with the common use of the term “metal” to refer to a metal and all its compounds. This usage implies that the pure metal and all its compounds have the same physicochemical, biological, and toxicological properties. Thus, sodium metal and sodium chloride are assumed by this usage to be equivalent. However, no one can swallow sodium metal without suffering serious, life-threatening damage, while we all need sodium chloride in our diet. As another example, epidemiological studies show that chromium and its alloys can be used safely in medical and dental prostheses even though chromate is identified as a carcinogen.

Finally, it should be emphasized that no one uses the term “carbon” to refer to all carbon compounds. If they did, then “carbon” would have to be labeled as a human carcinogen since so many carbon compounds fall into this category. If metallic elements are to be classified sensibly in relation to toxicity, the classification must relate logically to the model adopted for carbon and each metal species and compound should be treated separately in accordance with their individual chemical, biological, and toxicological properties.
ACKNOWLEDGMENT

This paper is based on a review of the usage of the term “heavy metal” carried out for Eurometaux by the author. The full review is available from Eurometaux, together with other relevant publications relating to the toxicity, ecotoxicity, and risk assessment of metals and their compounds.

REFERENCES


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