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Introductory Chapter: Introducing Heavy Metals

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1. Introduction

“Heavy metals” are natural elements characterized by their rather high atomic mass and their high density. Although typically occurring in rather low concentration, they can be found all through the crust of our planet. Commonly, a density of at least 5 g cm^{-3} is used to define a heavy metal and to differentiate it from other, “light” metals. Other, broader definitions for “heavy metals” require an atomic mass higher than 23 or an atomic number exceeding 20; these definitions are highly error prone and confusing. Both alternative definitions cause the inclusion even of nonmetals; resorting to the atomic mass criterion, the maximum number of elements classified as “heavy metals” rockets high to 99 out of the in total 118 building blocks of our universe. Looking at the periodic table of elements, we learn that heavy metals *sensu stricto* (according to the density criterion) occupy the lion’s share, namely, columns 3–16, of the periods 4 to 6, encompassing the transition metals, post-transition metals, and lanthanides [1].

Some heavy metals like copper, selenium, or zinc are essential trace elements, with functions indispensable for various biological processes also driving the entire human metabolism [2]. The heavy metal cobalt, acting as the central atom in the vitamin B₁₂ complex, is a key player in the reductive branch of the propionic acid fermentation pathway [3]; without this special heavy metal compound, the gourmet would have to do without the unique flavor of Emmentaler cheese. Many heavy metals are of outstanding technological significance, e.g., iron, zinc, tin, lead, copper, tungsten, etc. Recently, different heavy metals act as the central atom of artificially designed “bioinorganic” catalysts for special chemical transformations [4]. Moreover, among them we find precious noble elements like gold, silver, iridium, rhodium, or platinum [5]. On the other hand, many of them, e.g., mercury, cadmium, arsenic, chromium, thallium, lead, and others, classically represent the “dark side of chemistry”; they exert toxic effects already at low concentration [6]. In this context, some heavy metals have gained dubious popularity by being the materials major crimes can be made of [7].

Heavy metals were literally heaven's sent by originating from asteroid impacts. Typically, heavy metals occur in the earth's crust in rather low concentrations between the low ppb ranges (noble metals) and up to 5% (iron); here, heavy metals are mainly found chemically bound in carbonate, sulfate, oxide, or silicate rocks or also occur in their metallic, elemental form. Weathering and erosion resulted in their leaching and mitigation into soil, rivers, and groundwater. About 4–5 billions of years ago, when Earth's mantle was still liquid, heavy metals sank to Earth's center and formed Earth's core, which today predominately consists of the heavy metals iron and nickel [1].

2. Heavy metals and the eco- and biosphere

It is important to emphasize that there are some trace elements among the heavy metal family, which are essential for many biological processes; they are predominantly found in period 4 of the periodic table of elements. For strict aerobic beings as we are, it would not be possible to survive without having cytochromes, which make aerobic life forms breathe since the very beginning [8]. Iron also plays a major role in our respiration system as central, oxygen-affine, atom of the blood pigment heme. Copper plays a similar role in the transport of electrons and oxygen, especially as central atom in hemocyanin in mollusks and arthropods [9]. Zinc in turn is pivotal as constituent of zinc finger enzymes [10]. Selenium is described as an antioxidant; further, it is involved in hormone biosynthesis [11]. Cobalt was found to be significant in biosynthesis of complex compounds and different steps in cellular metabolism, especially as central atom in vitamin B₁₂, which is needed for cell division, blood formation, the nervous system, and in propionic acid biosynthesis (*vide supra*) [12]. Moreover, vanadium and manganese are important for regulation and functioning of several enzymes [13], whereas some metabolic functions are also assigned to the typically known-as-toxic elements chromium, arsenic, and nickel. Regarding arsenic, this element was only recently revealed as a natural constituent in herring caviar, where it was shown to substitute phosphorus in phosphatidylcholine-like lipids, the so-called arsenolipids [14]. Further, we should mention the role of molybdenum in some redox reactions [15], in addition to the function of cadmium in the metabolism of some microalgae from the Diatomophyceae class [16]. Moreover, the role of the heavy metal tungsten in the metabolism of prokaryotes is scientifically confirmed [17].

To give an impression on the quantities of heavy metals present in our human body, hence, the “heavy metal load” we are steadily carrying along with us, we can estimate that only about 0.01% of our mass originates from the presence of heavy metals, with iron (about 5 g in a person weighing 70 kg), zinc (2 g), lead, and copper (0.1–0.2 g each) being the top four heavy metals in our body; the rest, from the mass-related perspective, can be considered negligible [18].

Besides the abovementioned leaching and mitigation of heavy metals by erosion and weathering, these elements are mainly mobilized by the action of humans during their physical (extraction, smelting) or chemical (reductive) release from ores and the subsequent processing for diverse applications. Other processes releasing heavy metals into the ecosphere involve their (agro)industrial, domestic, automotive, medical, electrical, and other technological use, resulting in their extensive distribution in both aquatic and terrestrial environments.

Currently, we witness increasing global worries regarding their possible adverse health effect and their negative enduring impacts on biosystems. Some heavy metals are reported or at least suspected to be carcinogenic (hexavalent chromium, arsenic, cobalt, nickel, antimony, vanadium, mercury), mutagenic (arsenic, vanadium), teratogenic (arsenic), allergenic (nickel), or endocrine-disrupting (silver, copper, zinc, selenium). Others (e.g., thallium) lead to neurological and behavioral alterations, particularly in the case of children, central nervous system damage (mercury, lead, thallium, manganese, and tin), bone marrow damage, and osteoporosis (cadmium); are hepatotoxic and/or nephrotoxic (cadmium, cadmium, mercury, heptavalent manganese); cause heart rhythm disturbances (thallium); or negatively affect the immune system (lead) [19].

3. Determining heavy metals

Classically, quantification of heavy metals involves well-established techniques, such as wet chemical methods (gravimetric, titrimetric, colorimetric, etc.), coupled plasma/atomic emission spectrometry (ICP/AES), inductively coupled plasma with mass spectrometric detection (ICP/MS), or atomic absorption spectroscopy (AAS) [20–22]. Moreover, diverse ion selective electrodes are frequently reported for heavy metal determination [22, 23]. Currently, new, robust, sensitive, selective, inexpensive, and fast optical [24–26], chemical [27, 28], and biological [29–33] sensory systems are currently in status of development. Such advances in analytical chemistry are currently tightly connected to nanotechnology [26, 28, 34]. Moreover, so-called lab-on-paper sensors were also developed for heavy metal determination, as demonstrated for quantification of mercury, silver, copper, cadmium, lead, chromium, and nickel [29]. This sensor, operated by an immobilized enzyme, is an example for so-called biosensors, which synergistically combine the scientific fields of biotechnology and microelectronics; such “biosensors” consist of an immobilized biological component in combination with a transducer [30]. As a very recent technology, so-called genetically encoded fluorescent sensors can be used for monitoring heavy metals inside biological cells and were already assessed for determination of heavy metals like zinc, copper, lead, cadmium, mercury, or arsenic [35].

4. Mitigating heavy metals

To elevate the negative impacts of heavy metals, remediation techniques are increasingly improved in order to address the growing public pressure to reduce prevailing environmental hazards and to bequeath the subsequent generations a future worth living.

Traditional physical, thermal, chelating, and other chemical techniques often display serious shortcomings such as too high cost, excessive expenditure of work, and invasive change of soil properties and microflora [36]. Traditionally, remediation of soils contaminated by heavy metals resorts to simply digging the contaminated soil and subsequently disposing it at landfills. Of course, this disposal strategy merely postpones the eco-problem by shifting it from one location to the next and, moreover, generates hazards connected with transportation

of precarious soil and leaching of heavy metals at the ultimate disposal site. In the case of water polluted by heavy metals, alkaline lime precipitation is known as a better advanced and maybe the most efficient traditional technique for treating heavily polluted effluents. Lime precipitation can effectively be used to treat wastewater with metal loads exceeding 1 g L^{-1} . However, the remaining heavy metal-alkali-sludge stills need ultimate disposal [37].

Modern physical and chemical approaches for remediation of heavy metal pollution involve the use of adsorption on new adsorbents such as nano-carriers, ion exchange techniques, removal via advanced membrane filtration techniques, electrodialysis, or photocatalysis. Among these novel physicochemical techniques, new adsorption- and membrane filtration-based methods are most thoroughly investigated and are most commonly applied to treat contaminated wastewater [37, 38]. Among new adsorbents, both inorganic (kaolinite, montmorillonite) [39] and organic materials (e.g., agricultural waste or bio-char) [40–43] were studied for heavy metal recovery. In this context, the application of carbon-, metal-, or metal oxide-based nanoparticles as adsorbents benefits from high surfaces susceptible toward metal adsorption and expedient reactivity. Here, the mechanisms of interactions of nanomaterials with, on the one hand, heavy metals and, on the other hand, heavy metal with additional wastewater constituents with metal-binding groups need to be understood in order to optimize the recovery processes [44].

Photocatalysis uses photons from the UV-near vis region of light's electromagnetic spectrum and, when operated in a smart way, is able to degrade toxic organic pollutants in parallel to metal recovery in just one single process step. This technique resorts to photocatalytic semiconductors, e.g., TiO_2 , which, when illuminated with UV light, generate highly reductive electrons that in turn reduce heavy metal ions in contaminated wastewater. As an example, photocatalysis was successfully implemented for reduction of the dramatically precarious hexavalent chromium to its about 500 times less toxic trivalent form. In the case of precious noble metals like gold, this process does not only mitigate an environmental pollutant but also mines value-added materials for further use ("photorecovery") [45].

Phytoremediation is an emerging technology to overcome shortcomings of above-discussed methods. During phytoremediation, plants act synergistically with diverse soil microbes, which convert the heavy metals in a form bioavailable for the plants, finally decreasing the concentrations of contaminants in affected environments. Phytoremediation resorts to the ability of many plants for specific and efficient uptake, translocation, and storage of hazardous elements with chemical properties mimicking those of elements essential for plant growth [46]. Being a relatively recent technology, phytoremediation is supposed to be efficient, cost-effective, and ecologically benign; is driven by sunlight as the sole energy source; and enjoys an excellent public acceptance [47]. In the context of heavy metals, new powerful "heavy metal hyperaccumulator" plants are currently assessed for both phytoremediation (getting rid of the unwanted heavy metal) and phytomining (accumulating the precious heavy metals for further use). Such "hyperaccumulators" are characterized by their capacity to take up toxic metal ions at levels of thousands of ppm. In the optimum scenario, the toxic metals are transported from the plant's rhizosphere up to the shoots in the plant's periphery; now, the shoots, enriched with the target contaminants, can easily be harvested and burned for energy generation and,

if economically reasonable, recycling the metal from remaining ash [48]. Using aquatic plants, phytoremediation can also be used to cure polluted water bodies. Various plant species have successfully performed in absorbing heavy metals such as arsenic, cadmium, chromium, lead, and even radionuclides from contaminated soil. Among the different phytoremediation categories, phytoextraction can be used to mitigate heavy metals from soil by profiting from its ability to uptake and accumulate those heavy metals, which constitute elements essential for plant development, such as iron, copper, manganese, molybdenum, or nickel. In addition to these essential elements, some chemically similar heavy metals with unknown or not yet confirmed biological function can also be phytoextracted, such as cadmium, chromium, silver, lead, cobalt, selenium, or mercury [49]. Excellent results for phytoremediation of arsenic were reported for the fern *Pteris vittata* L. species [50]; here, the uptake capacity of the plant yielded more than 4 g heavy metal per kg plant material [51]. In the case of lead, several plants, most of all different mustards (*Brassica* spp.), are described to be able to accumulate between 50 and 100 mg of this heavy metal per gram plant dry mass [46].

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