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Review– Study of Manganese Metal Toxicity in Water and Methods of Removal

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ABSTRACT

Manganese is a naturally occurring element and an essential nutrient. Comprising approximately 0.1% of the earth's crust, it is the twelfth most abundant element and the fifth most abundant metal. Manganese does not exist in nature as an elemental form, but is found mainly as oxides, carbonates, and silicates in over 100 minerals with pyrolusite (manganese dioxide) as the most common naturally-occurring form. As an essential nutrient, several enzyme systems have been reported to interact with or depend on manganese for their catalytic or regulatory function. As such, manganese is required for the formation of healthy cartilage and bone and the urea cycle; it aids in the maintenance of mitochondria and the production of glucose. It also plays a key role in wound-healing. An alarming situation of exceedingly high Fe and Mn concentrations in both surface water and groundwater has been identified in a tectonically active region located in Assam-Arakan basin of northeast India. Cross plots, Pearson correlation, principal component analysis and flow net methods were applied to elucidate the present state and possible sources of Fe and Mn contamination. Out of 32 water samples collected for the study, all of them found exceeding 28 times more for Fe and 136 times more for Mn than EPA limit. Correlation and cross plots of pH, TDS, EC, Fe, Mn, Cu, Zn suggest the reduction of both Fe-hydroxides and Mn-oxides in redox condition into dissolve states leading to Fe and Mn elevations in groundwater.

Principal component analysis exhibits three PC factors in which PC1 and PC3 reflected oxidized condition and PC2 reflected reducing environment that controlled Fe and Mn concentrations. The study also revealed that source of high Fe and Mn contaminations was controlled by groundwater flows. Water table contour flow net suggests that the Chathe river acts as influent stream and supplies elevated Fe and Mn water into the shallow aquifers. Baseflow from the discharge areas into low lying areas causes accretion of Fe and Mn in pond, oxbow lake, backswamp and shallow aquifers.

I. INTRODUCTION

Although low levels of manganese intake are necessary for human health, exposures to high manganese levels are toxic. Reports of adverse effects resulting from manganese exposure in humans are associated primarily with inhalation in occupational settings. Inhaled manganese is often transported directly to the brain before it is metabolized by the liver. Manganese toxicity can result in a permanent neurological disorder known as manganism with symptoms that include tremors, difficulty walking, and facial muscle spasms. These symptoms are often preceded by other lesser symptoms, including irritability, aggressiveness, and hallucinations. Some studies suggest that manganese inhalation can also result in adverse cognitive effects, including difficulty with concentration and memory problems. Although the workplace is the most common source of excess inhalation of manganese, frequent inhalation of fumes from welding activities in the home can produce a risk of excess manganese exposure leading to neurological symptoms.

Table 1: Adequate Intake (Al) for Manganese

Life Stage	Age	Males (mg/day)	Females (mg/day)
Infants	0-6 Months	0.003	0.003
Infants	7-12 Months	0.6	0.6
Children	1-3 Years	1.2	1.2
Children	4-8 Year	1.5	1.5
Children	9-13 Years	1.9	1.6
Adolescents	14-18 Years	2.2	1.6
Adults	19 years and older	2.3	1.8
Pregnancy	All ages	-	2.0
Lactation	All ages	-	2.6

Environmental exposures to airborne manganese have been associated with similar preclinical neurological effects and mood effects as are seen in occupational studies. Acute or intermediate exposure to excess manganese also affects the respiratory system. Inhalation exposure to high concentrations of manganese dusts (specifically manganese dioxide [MnO_2] and manganese tetroxide [Mn_3O_4]) can cause an inflammatory response in the lung, which, over time, can result in impaired lung function. Lung toxicity is manifested as an increased susceptibility to infections such as bronchitis and can result in manganic pneumonia. Pneumonia has also been observed following acute inhalation exposures to particulates containing other metals. Thus, this effect might be characteristic of inhalable particulate matter and might not depend solely on the manganese content of the particle.

Neurological Effects

There is clear evidence from studies of humans exposed to manganese dusts in mines and factories that inhalation of high levels of manganese can lead to a series of serious and ultimately disabling neurological effects in humans. This disease, termed manganism, typically begins with feelings of weakness and lethargy. As the disease progresses, a number of other neurological signs may become manifest. Although not all individuals develop identical signs, the most common are a slow and clumsy gait, speech disturbances, a masklike face, and tremors. The neurological symptoms may improve when exposure ceases; however, in most cases, the symptoms are found to persist for many years post-exposure. In addition, a syndrome of psychological disturbances (hallucination, psychosis) frequently emerges, although such symptoms are sometimes absent. As the disease progresses, patients develop severe muscle tension and rigidity and may be completely and permanently disabled. Workplace inhalation exposure levels producing overt symptoms of manganism have been on the order of 2–22 mg manganese/m3. While manganese neurotoxicity has clinical similarities to Parkinson’s disease, it can be clinically distinguished from Parkinson’s. Manganism patients present a hypokinesia and tremor that is different from Parkinson’s patients. In addition, manganism patients sometimes have psychiatric disturbances early in the disease, a propensity to fall backward when pushed, less frequent resting tremor, more frequent dystonia, a “cock-walk”, and a failure to respond to dopaminomimetics.

Respiratory Effects

Inhalation exposure to manganese dusts often leads to an inflammatory response in the lungs of both humans and animals. This generally leads to an increased incidence of cough and bronchitis and can lead to mild-to-moderate injury of lung tissue along with minor decreases in lung function. In addition, susceptibility to infectious lung disease may be increased, leading to increased pneumonitis and pneumonia in some manganese-exposed worker populations. These effects have been reported primarily in workers exposed to fairly high concentrations of manganese dusts in the workplace, although there are some data that indicate that, in populations living and attending school near ferromanganese factories, there was an increased prevalence of respiratory effects. The risk of lung injury in people exposed to the levels of manganese typically found in the general environment is expected to be quite low. However, exposure to manganese-containing dusts from factories, mining operations, automobile exhaust, or other sources may be of concern. It should be noted that these effects on the lung are not unique to manganese-containing dusts but are produced by a variety of inhalable particulate matter. On this basis, it seems most appropriate to evaluate the risk of inflammatory effects on the lung in terms of total suspended particulate matter (TSP) or particulate matter

Reproductive Effects

Impotence and loss of libido are common symptoms in male workers afflicted with clinically identifiable signs of manganism. These symptoms could lead to reduced reproductive success in men. Impaired fertility (measured as a decreased number of children/married couple) has been observed in male workers exposed for 1–19 years to manganese dust (0.97 mg/m3) at levels that did not produce frank manganism. This suggests that impaired sexual function in men may be one of the earliest clinical manifestations of manganese toxicity, but no dose-response information is available; therefore, it is not possible to define a threshold for this effect. Evidence obtained in laboratory mammals indicates that exposure to high levels of manganese may adversely effect sperm quality, produce decreased testicular weights, and impair development of the male reproductive tract.

II. RECOMMENDED AND REGULATORY LEVELS FOR ENVIRONMENTAL MN

A variety of agencies have prepared risk assessments for Mn and developed recommended reference concentrations or regulations for chronic oral or inhalation exposure levels for Mn in the environment. This discussion does not include workplace regulations for Mn, which are reviewed in Santamaria et al25 Exposure guidelines for ambient inhalation exposure to Mn include the following: the U.S. Environmental Protection Agency reference concentration (RfC) is 0.05 µg/m3, the Health Canada tolerable daily intake (TDI) is 0.11 µg/m3 ; the World Health Organization (WHO) air quality guideline is 0.15 µg/m3 ; the Agency for Toxic Substances and Disease Registry (ATSDR) minimum risk level is 0.4 µg/m3 ; and the California EPA reference exposure level (REL) is 0.2 µg/m3 - (CalEPA has a current draft REL of 0.09 µg/ m3). In 1994, the US EPA developed a range of possible RfC values of 0.09 – 0.2 µg/m3 using benchmark doses developed from the Roels et al34 cohort116. These recommendations and guidelines apply to respirable dust, which corresponds roughly to PM5 (fraction of airborne particles with an aerodynamic diameter of 5 µm or less).

The oral exposure recommendations and guidelines include EPA’s oral reference concentration of 0.14 mg/kg/day, EPA’s maximum contaminant level (MCL) of 0.05

mg/l in water (based on aesthetic properties), and the WHO drinking water guideline of 0.4 mg/l (health-based)119.

There are significant differences in magnitude between the recommended exposure levels for oral versus inhalation exposure to Mn. The existence of wellknown homeostatic mechanisms has led regulatory authorities to conclude that the body is able to handle substantial variations in dietary Mn on a daily basis without adverse consequences due to hepatic excretion of Mn and the low absorption of Mn through the gastrointestinal tract. However, there have been uncertainties expressed regarding the pharmacokinetics of Mn following inhalation exposure versus oral exposure and concerns expressed about the potential for greater absorption through the respiratory tract than SANTAMARIA: MANGANESE TOXICITY 495 the gastrointestinal tract119,126 In addition, there is a broad range of recommended exposure levels for Mn exposure by inhalation, reflecting the different quantitative approaches taken and different qualitative assumptions used by the Agencies in developing the recommended levels. Although all of these Agencies used the same occupational study34 to derive the inhalation reference values, the values derived from this study were different and included NOAELs, LOAELs, or benchmark doses as the point of departure for establishing the recommended levels. Uncertainty factors were applied to the various point of departure values to account for human variability, sensitive subpopulations, potential differences in the pharmacokinetics or toxicity of different forms of Mn, and less than chronic exposure. These modifying and uncertainty factors ranged from 50 to 1,000. Important and extensive research has been conducted over the last 15 years to address many of these uncertainties and it is anticipated that the development of PBPK models will also permit for the reduction of these uncertainties and permit for the application of chemical-specific adjustment factors (CSAFs), greatly improving risk assessments for Mn.

III. DIFFERENT METHODS FOR REMOVAL OF TOXICITY OF MANGANESE FROM WATER

Chemical Precipitation

Chemical precipitation is the most effective method on removing heavy metal from wastewater. According to Fu & Wang (2011), chemical precipitation method is simple and inexpensive to operate. During precipitation process, the chemical will react with heavy metal ions to form insoluble solid. Then, the precipitates formed can be separated by filtration. However, this method will produce large amount of sludge which can lead to the disposal problem (Iwa Water Wiki, 2010). Ceribasi & Yetis (2010) also mentioned that concentration limits are one of the problems which may cause chemical precipitation process become expensive and ineffective in wastewater treatment. Chemical precipitation will cause serious disposal problem which produce large amount of sludge to be treated. Grandt & Mcdonald (1981) proved that chemical precipitation is not suitable to be used because this method have a major disadvantage to the requirement of large doses of alkaline materials to increase and maintain pH values typically from 4.0 to 6.5 for optimal metal removal.

Ion Exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyuz &

Veli, 2009). The most common cation exchangers are strongly acidic resins with sulfonic acid groups (–SO3H) and weakly acid resins with carboxylic acid groups (–COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Altun and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process.

Membrane Separation

Membrane filtration is a thin layer of material capable of separating substances when a driving force is applied across the membrane. Membrane filtration showed high efficiency of removal of heavy metal, easy operation and also space saving (Fu & Wang, 2011). It also produced less solid waste and chemical consumption. However, Fu & Wang (2011) also found that this method is not suitable to removal heavy metal since it is high cost, complexity process and it will 12 cause membrane fouling. These statements are supported by Chang & Kim (2005) that membrane filtration will cause the membrane fouling which leads to a frequent cleaning and replacement of membranes and will increase the operating cost. Therefore, the removal efficiency of single metal will decrease since there is present of other metals.

Adsorption

process is widely used in wastewater treatment. In adsorption process, one or more components of gas and liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished (Geankoplis, 2008). Application of adsorption process include removal of organic compounds from water, coloured impurities from organics, fructose from glucose using zeolite and fermentation products from fermentor effluents. There are various types of low cost adsorbents which are derived from agricultural waste, industrial by product, natural material, or modified biopolymers (Barakat, 2010). These adsorbents are applied for the removal of heavy metals from metal-contaminated wastewater.

Adsorbent

There are several types of adsorbents used in adsorption process such as activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbent (Geankoplis, 2008). 13 Activated alumina is a synthetic porous crystalline gel, which is available in the form of granules of different sizes having surface area ranging from 200 to 300 m 2 g -1 (Gupta & Suhas, 2009). Bauxite a naturally occurring porous crystalline alumina contaminated with kaolinite and iron oxide normally having surface area ranging from 25 to 250 m2 g -1. According Geankoplis (2008), hydrated aluminium oxide is activated by heating to drive off the water. It is mainly used to dry gases and liquids. Activated carbon is the most common adsorbent used and it is usually prepared from coal, coconut shells, lignite and wood. Normally, activated carbon has a very porous structure with a large surface area ranging from 500 to 2000 m2 g -1 (Gupta & Suhas, 2009). Studies have shown that activated carbons are good adsorbents for the removal of different types of adsorption process but the used of the adsorbent is restricted due to their highest cost (Fu & Wang, 2011). Also, the activated carbons after their use in wastewater treatment become exhausted and are no longer capable of further adsorbing process. It has to be regenerated for further use in purifying water. Furthermore, the regeneration process will result in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with virgin activated carbon. However, Monser & Adhoum (2001) showed in their studies that modified activated carbon enhance the removal capacity for the inorganic pollutants.

IV. CONCLUSIONS

Mn is a neurotoxic substance at certain exposure levels regardless of route of exposure; however, the threshold exposure level for the development of subclinical neurological or neurobehavioural effects has not been clearly established, although benchmark modeling of data from the various studies34,108 derived benchmark dose level [BMDL10] [the 95 % lower bound internal dose corresponding to a 10% increased outcome] ranges of 0.10-0.27 mg/m3 respirable Mn, encompasses a likely threshold for subclinical neurological effects61. With the exception of a few studies, most available epidemiological studies of Mnexposed cohorts are inadequate for determining a doseresponse relationship for subclinical or clinical neurotoxicity and exposure to Mn. There may be other studies that can be used to develop benchmark doses, if there are individual-specific response data and personal respirable Mn exposure data. Regulatory Agencies are recommending the use of benchmark doses when the data are available and the use of PBPK models for conducting dosimetry-based risk assessments127,128. As the understanding of the pharmacokinetics of Mn continues to be developed for the diverse forms of Mn and in different age groups, more refined and robust risk assessments may be developed for Mn. Such data will allow for the application of CSAFs in the dose response evaluation as recommended by WHO129. The use of CSAFs and PBPK models can reduce the need for the application of various uncertainty factors when developing reasonable and appropriate reference values, guidelines, and regulations for this essential element.

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