The chemistry of Lead and its toxicity profile

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Abstract

Environmental pollution is the unfavorable alteration of our surrounding due to some of the toxic heavy metals, organic pollutants, radioactive materials and minerals poses an imperative societal issue. The indiscriminate usage of industrial and anthropological activities makes some polluted water/water resources unsuitable for human consumption. Further due to organic/ inorganic pollutants as percolating in water, causes detrimental effects on flora and fauna and are consequently responsible for numerous diseases and health problems some are even epidemic e.g. amoebiasis, minamata, blue baby syndrome, fluorosis, etc. Hence, the environmental decontamination of water/wastewater becomes a major challenge to the developed scientific world. The advanced technological options should not only get restricted to remediation but should also focus on mitigation strategies either by substitution of heavy metals by alternatives or by refining the existing technologies to monitor the environmental pollution.

Heavy metals are those which possessed high density at least 5 times greater than water and are highly detrimental to the humans and animals even at low concentration. Heavy metals are natural constituents but indiscriminate human activities have severely altered biogeochemical balance. There are 35 metals that are bothered because of occupational or residential exposure. Out of these, the 23 metals are the heavy elements or heavy metals viz. mercury, nickel, platinum, antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, silver, tellurium, thallium, tin, uranium, vanadium and zinc that are responsible for adverse effects when their concentrations exceeds than the permissible limits (Makoha *et al*., 2008).
Heavy metals interrupt the human physiological system in two ways:

- They accumulated and thus disrupt functions of various vital organs and glands such as the heart, brain etc. (Jang *et al*., 2008).
- They can shift the essential nutritional minerals from their original site and thus, obstructing their biological roles in human physiological system.

Among all the heavy metal ions, special attention has been given to lead (II) ions contamination in water. During the Roman era, lead was considered to be the father of all metals. Much of its gratitude was due to its huge availability, consequently used in daily life by people across all classes. Lead was ranked second on the CERCLA Priority List of Hazardous Substances in 1999 and 2001 (after arsenic #1, and before mercury - #3). The priority list is prepared by the Agency for Toxic Substances and Disease Registry and EPA and is based on the frequency of occurrence of particular contaminants at National Priorities List (NPL) sites and their potential threat to human health. Lead (II) ions can be found in effluents from battery recycling plants, lead mining and electronic assembly plants. Lead metal elucidates destructive effects almost on every organ systems viz. Nervous, blood circulation, reproductive, digestive, kidneys as become highly toxic and carcinogenic even at low concentration. WHO prescribed the maximum permissible limit (MPL) of lead metal in drinking water as 50 ppb initially during 1995 that was further decreased to 10 ppb in 2010. UNICEF Handbook on water quality, summarizes guideline values for inorganic contaminants, along with Maximum Allowable Concentrations (MACs) fixed by the European Union and Maximum

Contaminant Levels (MCLs) set by the US Environmental Protection Agency and is depicted as **Table 1.1.**

Table 1.: Inorganic contaminants in drinking water with guideline values in mg/L.

Chemical	WHO GV	EU MAC	USEPA MCL
Aluminium	0.1-0.2 (A)	0.2 (A)	0.05-0.2 (A)
Antimony	0.02	0.005	0.006
Arsenic	0.01 (P)	0.01	0.01
Asbestos	-- (X)	--	7MFL
Barium	0.7	--	2
Beryllium	-- (X)	--	0.004
Boron	0.5 (T)	1	--
Bromate	0.01 (Q, T)	0.01	0.01
Cadmium	0.003	0.005	0.005
Chlorine (as Cl_2)	5 (C)	--	4
Chloramines (as Cl_2)	3 (1)	--	4
Chlorine dioxide (as Cl_2)	-- (X)	--	0.8
Chromium	0.05 (P)	0.05	0.1
Copper	2	2	1.3 (TT)
Cyanide	0.07	0.05	0.2
Fluoride	1.5	1.5	4
Iron	0.3 (A)	0.2 (A)	0.3 (A)
Lead	0.01	0.01	0.015 (TT)
Manganese	0.4 (C)	0.05 (A)	0.05 (A)
Mercury	0.006 (M)	0.001	0.002

(Source: UNICEF Handbook on Water Quality)

Abbreviations

A : Based on aesthetic concerns, not health impacts. WHO does not set GVs based on aesthetic concerns, but does note concentrations which may cause complaints.
1 : For monochloramine alone.
C : Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odor of the water.
L : for long-term exposure
M : for inorganic mercury

P : Provisional guideline: evidence of a potential hazard.
Q : Calculated guideline value is below the practical quantification level.
S : For short-term exposure
T : Guideline value is set at the practical treatment limit.
X : Excluded from guideline value due to lack of evidence of adverse health effects.
TT : Lead and copper are regulated by a treatment technique that requires systems to control the corrosiveness of their water.

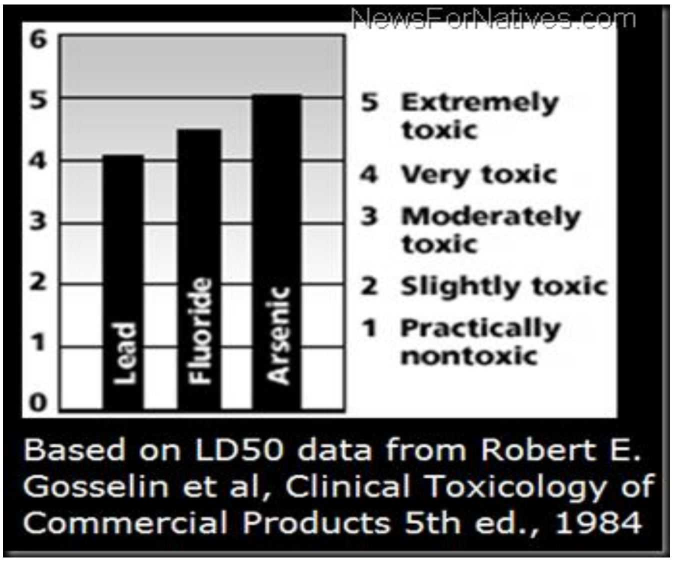

Fig.1.: Relative Toxicity

(Source: http://www.localterror.com/flouride-poisoning/)

Lead is a stable element, bio-accumulative, stored in soft (e.g., kidney) and hard tissues (e.g., bone) and deriving its safe limits is very difficult (Acharya *et al*., 2009). Lead has found major uses in pipes and plumbing, pigments and paints, gasoline, additives, construction materials and lead acid batteries (Kamal *et al*., 2010). Lead poisoning is one of the commonest occupational diseases but now it has shifted from an industrial to an environmental hazard. Lead compounds are divided into two classes viz. Inorganic and organic.

a) **Inorganic lead compounds**: The compounds such as lead oxide and lead chloride are combinations of lead with other elements. The lead found in soil, old paint and leaded gasoline exhaust contributed to inorganic lead contamination. Inorganic lead is absorbed in small amounts from the gastrointestinal tract e.g. ingestion of paint – pica in children or drinking of lead containing water. Inorganic lead is distributed in blood, soft tissue, bones and teeth. Inorganic lead compounds are applied for battery and paint production.

b) **Organic lead compounds**: The compounds where lead is combined primarily with carbon and hydrogen. The lead compounds that were used to make leaded gasoline, tetraethyl lead and tetramethyl lead are examples of organic lead compounds. Organic lead compounds penetrate body and cell membranes through skin easily. Organic lead compounds are fat soluble, and therefore have a particular tendency to distribute into the brain (Haloi *et al*., 2013). Organic lead is applied in petroleum production. Organic lead compounds are quickly converted to inorganic lead, and ends up in water, sometimes even in drinking water. However, organic lead can be more toxic than inorganic lead because the body more readily absorbs it.

Human exposure to lead occurs primarily through air, drinking water, dust, soil and lead-based paints. People are exposed to lead mainly by inhalation or ingestion. On a molecular level, proposed mechanisms for toxicity involve fundamental biochemical processes. These include lead's ability to inhibit or substitute for calcium in the bones and thus delay or possibly prevent osteoporosis. It also interferes with ion channels during nerve conduction consequently interferes with Cognition. However, calcium is the preferred element and lead causes other metabolic problems when it replaces calcium and to interact with proteins (including those with -SH, amine, phosphate and carboxyl groups) (ATSDR, 1999). Lead absorption increases with the deficiency of calcium and iron and its toxicity built the compound $PbCO_3$ instead of $CaCO_3$ in bones.

Many conventional methods are known for lead removal from water namely chemical precipitation, membrane separation, ion exchange, coagulation, reverse osmosis, evaporation and adsorption (Xu et al., 2008). The adsorption process is found to be effective and economic for wide variety of water pollutant adsorption (Sawalha *et al*., 2009).

1. LEAD CHEMISTRY

Lead is a soft, malleable heavy metal belongs to the carbon group with symbol Pb (from Latin: *Plumbum*). It is found in the earth's crust and proportion gets increased with time due to radioactive uranium disintegration. Atomic number of lead metal is 82, atomic weight: 207.2, Melting point 327.5 °C, density is 11.34 g/cm^3 and its electronic configuration [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead metal exists as the natural abundance in four stable isotopic forms viz; Pb^{204}, Pb^{206}, Pb^{207}, and Pb^{208}. Metallic lead Pb^0 rarely occurs in nature, nevertheless, exists in two main oxidation states Pb (II) and Pb (IV) with more stable divalent form in the aquatic environment. Three lead oxides are known i.e. lead monoxide (PbO), lead dioxide (PbO_2) and lead tetroxide (Pb_3O_4) also called as minium. Lead is found in ore with other heavy metals such as zinc, silver and copper etc. and is extracted together with these metals. The main lead mineral is galena (PbS) contains 86.6% lead by weight), However, as a result of human activity in the atmosphere nowadays lead is found mainly as cerussite ($PbCO_3$) and anglesite ($PbSO_4$) (Holleman *et al*., 1985).

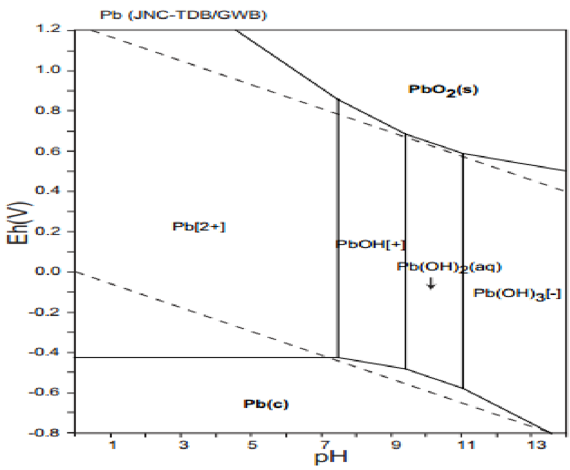

Fig. 2: Eh-pH Diagram for Lead Metal (Brookins, 1988)

Fig. 2. shows the Eh-pH diagram for lead metal (Brookins, 1988). The diagram illustrates the dominant aqueous species and stable solid phases of lead on a plane defined by the Eh and pH axes. The upper and the bottom dotted lines represent the oxidation and reduction boundaries of water respectively. The pH of drinking water is in range of 6-8 where lead mainly exists as Pb^{2+} ion under weakly acidic conditions. At pH 6, Pb^{2+} and $Pb(OH)^+$ are in equal concentration. At increasing alkaline conditions viz. pH range of 7-9 lead forms lead hydroxides $Pb(OH)^+$ that ultimately precipitates as $Pb(OH)_2$ and $Pb(OH)_3^-$.

2. SOURCES OF LEAD IN THE ENVIRONMENT

The presence of lead in water, air and soil environment even in traces has detrimental effects on plants and animals. The natural sources of lead are soil erosion, volcanic eruptions, sea sprays and bush fires. The anthropogenic activities dispersed the lead compounds throughout the environment. Lead is transferred continuously between air, water, and soil by natural chemical and physical processes such as weathering, runoff, precipitation, dry deposition of dust, and stream/river flow etc.

2.1. AIR

The ingestion of lead through food and water is much greater than that of urban air. Inhaled lead of about 20-40 percent which is derived from the air is much more readily absorbed (Carroll, 1970). The air released from the combustion of fossil fuels especially leaded gasoline and several industrial processes dealing with storage batteries, mining and ore smelting operations are of major concern regarding lead pollution in atmosphere (Djuric *et al*., l971). Children are more susceptible to air borne lead poisoning and lead absorbed in the gut of infants and young children is estimated to be 5 to 10 times greater than in adults (Gloag, 1980; ATSDR, 2007). Faulty removal of lead-based paint, street dirt and household dust absorbed through the lungs, skin and intestinal tract also responsible for airborne lead contamination (Mahaffey, 1981). Cigarette smoke is also a significant source of lead exposure due to lead arsenate insecticides sprayed on tobacco. Although most of the lead remains in the ash, an intake of cigarette smoke about 20 nanogram per pack has been estimated for toxic effects of lead (Horton, 1966).

2.2. FOOD

Food sources can be contaminated with lead due to spraying of lead arsenate insecticides or lead accumulations during food processing. Exclusively imported pottery such as ceramic cookware possess lead-containing glaze is a common source of lead toxicity. Lead solder used for sealing of food cans especially the acidic foods such as tomatoes, okra and orange, grapefruit or cranberry juices are also key sources of lead intake. Canned juices and canned baby foods such as evaporated milk may contain up to100 and 200 micrograms of lead per liter respectively (Mahaffey, 1981), thus conferred to as high as 300 micrograms per day total lead uptake through food. The ingestion of peeled lead based paint – pica in children is also an additional cause of lead poisoning in children (Johnson and Tenuta, 1979).

2.3. SOIL

The toxic lead compounds are strongly adsorbed onto the upper layers of soil and does not leach into the subsoil. The average residence time of lead in the atmosphere is about 10 days. The presence of high concentration of lead in the soils results in lead contaminated fruits and vegetables. Particulate pollutants emit through leaded paints, leaded gasoline and lead in pipes can also contaminate the soil with heavy metal lead.

2.4. WATER

The solubility of lead compounds is highest in soft and acidic water and it is a function of pH, hardness and salinity of water sample. The several industries engaged in releasing of industrial wastewater effluents, lead acid batteries, fertilizers, pesticides, mining waste, metallurgical, chemical and petrochemical industries are prominent sources of releasing toxic lead in the water stream (Singh *et al*., 2008).

Lead rarely occurs in natural water bodies but the major source of lead in drinking water is from lead-based plumbing materials. The corrosion of such leaded pipes and fixtures are responsible for enhanced lead concentrations in community drinking water. The old homes constructed before 1986 are probably have lead pipes,

Fixtures and solder is the main contributor to lead in tap water. Other water delivery system such as lead solder used to join copper pipes, brass in faucets, coolers, and valves are liable for lead content in water. Older submerged pumps used in well water can also contain leaded-brass works. Seawater and river water contains 2-30 ppt and 3-30 ppb of lead content respectively. Phytoplankton contains 5-10 ppm, freshwater fish 0.5-1000 ppb and oyster 500 ppb of lead concentration.

3. LEAD & OTHER HEAVY METAL CONTAMINATION STATUS IN INDIA

The Central Pollution Control Board (**CPCB**) carried out a major groundwater quality survey and the report recognized about 20 critical sites of ground water pollution in various states of India. CPCB found that industrial effluents are the primary and major cause for ground water pollution. The major heavy metals contamination sites including lead metal in Indian scenario are given in **Table 2.**

Table 2: Major heavy metal contaminated sites in India

Sr. No.	Area	Industrial activities	Ground water quality problems
1	Digboi (Assam)	Oil refinery	Fe and Mn ions were more than permissible limit. Ni, Zn, Cd, Cr, Pb were also reported.
2	Howrah (West Bengal)	Foundries and Electroplating	Heavy metals viz. Pb, Cd, Cr were very high and Zn, Cu, were within limit. Hg, Fe, Mn and pesticides were also very high, CN & Phenolic compounds in traces.
3	Botharam Patncheru (AP)	Pesticides, Pharmaceuticals	Phosphates, Hg, As, Cd, Fe, Mn & Pb were beyond limit, Pesticides, coliform, TDS, were also exceeded the desirable limit.
4	North Arcot (TN)	Tanneries and dyeing units	Hg, Cd, Pb & As were in traces. Zn, Cu, Cr, Fe & Mn beyond limit at several locations. Total Coli form and fecal Coli form were also on higher side.
5	Ratlam, Nagda (MP)	Distillery Dye, Pharmaceuticals	TDS, Hg, Pb were on higher side. Pesticides and fecal Coli forms were also present.
6	Mandi Gobindgarh (Punjab)	Wooden, chemicals, electro-plating and other steel metals units.	Pb, Cu, Cd exceeded the desirable limit of drinking water, Phenol compounds & Cyanide was also present on higher side
7	Parwanoo (HP)	Ancillary, fruit proceeding plant, air pesticides.	Presence of Cd, Pb, Fe, Mn were observed on higher side. Pesticides and Phenol were above the toxic limit.
8	Kala Amb (HP)	Paper mills	Heavy metals like Cd, Pb & Mn and Phenol compound were higher than the toxic limit. Pesticides, Coli forms were also present.
9	Pali (Rajasthan)	Textile, dyes	Pb and Zn, F, TDS and Cl found higher.

10	Jodhpur (Rajasthan)	Textile, steel, engineering foundry, chemicals, minerals dye plastic, oil, pulses and rubber.	Heavy metals such as Fe, Cr, Mn, Pb were also on higher side. Na, TDS exceeded the limit.
11	Angul Talcher	Thermal power station, fertilizers, chemicals, mining activities.	Cr, Fe, Cd, Pb & F, NO_3 all were found in concentration level exceeding standards limits.

(Source: Central Pollution Control Board)

4. PRODUCTION AND USAGE OF LEAD METAL

Throughout the world the production and usage of lead metal is increasing daily and reached up to 8 million tons of annual lead production. As of 2008, Australia, China, USA, Peru, Canada, Mexico, Sweden, Morocco, South Africa and North Korea are some of the top lead metal producing countries. In 2010, about 9.6 million tons of lead was produced, of which 4.1 million tons came from mining. The various industries engaged in lead-acid batteries, pigments and paints, oil refining, metal plating, phosphate fertilizer, electronic, wood production, combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater, sea spray, etc. releases lead in wastewater (Singh *et al*., 2008). Lead compounds have wide utilities, such as in match box, alloys, solder, ceramics, plastics, building materials (as copper, zinc, magnesium, manganese and silicon alloy), in photography and as catalysts in reactions. It is also used in insulated cables and wiring, household utensils, laboratory equipment, packaging materials, reflectors, paper industry, printing inks, glass industry and waterproofing in the textile industry.

5. REGULATORY ASPECTS OF LEAD (II) IONS IN WATER

According to Indian Standard Institution (ISI) the tolerance limit for discharge of lead into drinking water is 0.05 mg/L and in land surface waters is 0.1mg/L (Gupta *et al*., 2001). The World Health Organization (WHO) in 1995 had proposed the safe total lead limit of 50 ppb in drinking water which was further decreased to 10 ppb in 2010. The permissible limit of lead ions in drinking water as set by European Union (EU), United States Environmental Protection Agency (USEPA) (Li and Wang, 2009) and Guidelines for Canadian Drinking Water Quality in 2012 is 10 ppb, 15 ppb and 10 ppb respectively. However, more recently an EPA document recommends a zero lead value in national primary drinking water standard (EPA, 2002).

6. SYMPTOMS AND HEALTH ASPECTS OF LEAD TOXICITY

The human body contains around 120 mg of lead and 10-20% of lead is absorbed by the intestines. The doorway of poisonous lead in human system mainly through contaminated air, food and water sources manifest an overt and detrimental health problems. Lead is a cumulative poison and it elucidates destructive effects on almost every physiological systems viz; Musculo-Skeletal, Nervous, Cardiovascular, Digestive, Reproductive, excretory, Endocrine and metabolic system etc. Lead is highly toxic and carcinogenic even at low concentration (Liu *et al*., 2008). The International Agency for Research on Cancer (IARC) classifies inorganic lead compounds as probably carcinogenic to humans (Group 2A). The National Toxicology Program (NTP) of the U.S. Department of Health and Human Services concluded that "lead and lead compounds are reasonably anticipated to be human carcinogens" (NTP 2005).

6.1. EFFECTS OF LEAD ON CHILDREN

- Children are usually more vulnerable for toxicity of lead due to immature blood brain barrier and as lead can easily cross blood brain and placental barrier, they readily absorbs large amount of lead per unit body weight than adults.

- The serious effects of lead (II) on health of children include encephalopathy, peripheral neuropathy, cognitive impairment, and personality disorders (US EPA 1986a). If the neuropathy is severe the lesion gets permanent. Lead toxicity shown a dark blue lead sulphide line at the gingival margin of the person.
- The fatal effects of lead (II) marked by seizure, coma and death if not treated immediately (U.S. EPA, 1986b).
- Evidence suggests that lead may cause fatigue, irritability, information processing difficulties, memory problems and a reduction in sensory and motor reaction times, decision making impairment, and lapses in concentration (Ehle and McKee, 1990).
- Lead interferes with heme biosynthesis by changing the activity of three enzymes δ-aminolevulinic acid synthetase (δ-ALAS), δ-aminolevulinic acid dehydratase (δ-ALAD) and ferrochelatase and thus affects the hematological system.
- The lead (II) concentrations above 70 mcg/dL in human blood exhibited microcytic and hypochromic anemia which is characterized by hemoglobin reduction and basophilic stippling of erythrocytes along with a shortened life span of red blood cells i.e., erythropoiesis (Papanikoulou, 2005).
- Increase blood lead level shows decreased intellectual capacity and IQ level of children by four to seven points for every 10 µg/dL(Winneke *et al.* 1990).
- Attention deficit hyperactivity disorder (ADHD) and hearing impairment in children that may disrupt the peripheral nerve function (ATSDR 2007).

6.2. EFFECTS OF LEAD ON ADULTS

- The lead toxicity affects the renal system causing aminoaciduria, glycosuria, and hyperphosphaturia i.e., Fanconi-like syndrome (Al-Saleh, 1994).
- Kidney disease, both acute and chronic nephropathy, is a characteristic of lead toxicity (Goyer, 1988).
- Lead poisoning inhibits excretion of the waste product urate that causes a tendency for gout i.e., saturnine gout (Shadick *et al*., 2000).
- Occupationally lead exposed individual tends to have hypertension than normal people and augmented risk for cardiovascular diseases, myocardial infarction and strokes (Korrick *et al.,* 1999).
- Lead toxicity include gastrointestinal disturbances-abdominal pain, cramps, constipation, anorexia and weight loss-immune suppression, and slight liver impairment (ATSDR, 1993)
- In adults, high levels of lead can cause headaches and disorders of mood, thinking, and memory, irritability, lethargy, malaise, paresthesia.
- There is also some evidence that lead exposure may affect adult's postural balance and peripheral nerve function which can cause tremors or weakness in fingers, wrists, or ankles. (Arnvig *et al.*, 1980).
- Lead poisoning affects the human male reproductive system to decrease sperm count and also increase abnormal sperm frequencies (Telisman *et al*., 2000).
- Women are more susceptible to lead poisoning than men and lead toxicity causes menstrual disorder, infertility miscarriages and stillbirths (Baghurst *et al.,* 1987).
- Lead inhibits several enzymes required for the synthesis of heme, causing a decrease in blood hemoglobin.
- Lead interferes with a hormonal form of vitamin D, which affects multiple processes in the body, including cell maturation and skeletal growth.
- Lead poisoning is also known to cause psychotic behavior such as hyperactivity or schizophrenia.

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