Chromium & Lead as Soil Pollutants: Insights on Toxicity Profiles and their Remediation

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Abstract: This is an insight on induced toxicity and remediation of heavy metals chromium and lead as the prominent soil pollutant. Chromium and lead both are used in many industries viz; leather, chemicals, metal finishing, paint, pigment manufacturing, stainless steel production, anti-corrosive, textile, tanning, electroplating, wood-preservation,
photography and process effluents. Low Cr³⁺ level is vital for metabolism, while Cr⁶⁺ is fatal, to mutagenic to many bacteria, plants and animals besides water soluble at all pH. Chromium toxicity causes cardiac troubles, metabolic dysfunction, and diabetic. The heavy metal contaminations due to Cr (VI) and Lead (II) become fatal environment by virtue of toxic and detrimental effects beside accumulation throughout food chain. Cr (VI) and Lead (II) pollutants are toxic and non-biodegradable thus pave health hazardous. Cr (VI) in soil own detrimental effects on all the organisms and imparts serious environmental concerns. Cr (VI) owe +ve redox potential to offer strong oxidizing capacity being unstable in an electron donors groups. Diverse species reacts with Cr (VI) depend on pH and concentration. Most industries discharged wastewater contamination by Lead (II) and deemed utmost hazardous to health and environment. Lead (II) is absorbed in living species and subsequently penetrates food chains. Lead ingested beyond its stringent level results acute health disorders. Thus, its compulsory to treat Pb(II) contaminations prior to its discharge into the environment. This is perspective insights and new ideas on how solid waste, an unused resource available in large quantities from industries, so targeted to boost environmental protection in our environment.

Keywords: Soil, Lead (II), Chromium (III)/ (VI), toxicity, heavy metal, bioremediation.

1. INTRODUCTION

Soil pollution is persistent due to toxics, chemicals, salts, and other materials owing adverse effects on nature [1]. Soil contains lean layer of organics and inorganics in the form of the rocky surfaces of planet. Organics are derived through plants and animals decayed as concentrated in the dark uppermost topsoil while inorganics stay prolong in old rock fragments due to weathering of bedrocks [2]. Assorted soil contaminations includes, landfill leaching, industrial waste discharge, polluted water, underground storage, excessive pesticides/herbicides/fertilizer uses, and improper solid disposal. Urban and industrial aerosols, fuel burning, mining, and agricultural chemicals contribute metal pollution in soil. Heavy metal pollution in soil is very acute and poses varied health hazardous [3]. Heavy metals are absorbed at specific sites in soil through wide distribution and retained firmly onto inorganic and organic colloidals. Yet trace amount heavy metals are essential for growth of plants and animals as stated in Table **1** below:

In agricultural soils, multiple metals get contaminated in some ways, like sewage, sludge, farmslurry, fertilizers, pesticides and agro-chemicals exhaustive use [2] as shown in Table **2** below:

Metal penetrates soil in different rates up taken by plants and organic matter in soil own great affinity for metals which is viable for reduction of nutrient content [2-4]. The range of solid sludge containing heavy metal contamination is shown in Table **3** below:

2. TYPES OF SOIL POLLUTION

Currently, $1/3^{rd}$ of soils are highly degraded via erosion, loss of organic carbon, salinization, compaction, acidification and chemical pollution. It needs span of 1000 years to form 1 cm of top soil, means it's difficult to produce more soil within this lifetime. Earths soils yet face even more stress from heavy metal pollution. The current rate of soil degradation menaces capacity of next generations to rally most basic needs. The food, water and air besides the health of planet depend on fit/pure soil. The nutrient ratio in plant is directly related to the quality and ability of the soil to exchange nutrients and water within its root. In general soil pollution arises typically by industrial activity, agricultural chemicals and improper disposal of wastes/effluents [2]. Assorted forms of soil pollutions are known as revealed below:

• Agricultural soil pollution includes surface soil and underground soil, as resulted due to poor and unsustainable agricultural practices. This pollution also reduces soil organic matter and ultimately affects soils capacity besides quality to degrade organic pollutants.

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Table 1: Assorted Heavy Metal Concentration in the Hithosphere, Soils and Plants [4]

Table 2: Prominent Heavy Metal in Common Fertilizers

Table 3: Range of Heavy Metal Contamination in Solid Sludge

• Industrial effluents and solid wastes induce pollution of surface soil and disturbances in soil profile. Today vast modernization imparts soil contamination due to toxic and hazardous metals through effluents and wastes. Each soil owns individual characteristics for productivity and

such faultily disposed chemicals degrade quality and soil's capacity.

• Advanced urban activity too pollutes surface and underground soil. Varied wastes enrich heavy metal through assorted domestic activities, or

xenobiotic chemicals and other elements augment soil pollution land degradation.

3. SOIL POLLUTION SOURCES

Twofold sources namely agricultural and nonagricultural pollute soil environments [1-2] as mentioned below:

i. Agro-Sources

Soil pollution arises through various sources including agriculture and animal husbandry. Many agricultural practices lead to soil pollution comprising animal wastes, persistent pesticide, herbicide, fungicide, nematocide and fertilizer usages.

ii. Non-Agro-Sources

Soil pollution via non-agro-sources and urban huge population rapidly induce per capita waste outputs. Metallic elements enter in soil system being long persistence and accumulative and thus poses pollution.

4. CAUSES OF SOIL POLLUTION:

Soil pollution is caused through human and industrial or other alteration in the environment. These pollutants worsen the quality, texture and mineral contents and disturb the biological balance in soil and all life forms. Following factors are associated with pollution in soil environment [1-5]:

i. Indiscriminate Agro-Chemicals Use

The random usage of pesticides, insecticides and herbicides in farming and agriculture pose many threatens to health and environmental systems.

ii. Dumping of Solid Wastes

Solid waste from garbage, domestic refuse and discarded solid materials from commercial, domestic and industrial activities through increasing amounts of paper, cardboards, plastics, glass, old constructions, packaging material and toxic or hazardous substances. Since a significant amount of urban solid waste are non-recyclable or biodegradable in landfills. Most agricultural waste gets recycled but mining waste left on sites as such without treatments. The solid waste such as oils, battery metals, heavy metals from smelting industries and organic matters are hazardous in the long run, as it gets deposited in soils of the surrounding area causing pollution by varying chemical and biological properties of nature [2-5].

iii. Deforestation

Soil Erosion occurs if weathered particles from soil gets dislodged and carried by wind/water in the ecosystems. Various factors like deforestation, agrodevelopment, extreme heats, precipitation, acid rain, and domestic activities contribute to soil erosion. Humans speed up this process by construction, mining, vegetation removal, timber cutting, over cropping and overgrazing. It results in floods and cause soil erosion. Forests and grasslands offer binding material to intact healthy soil and support many habitats of ecosystems by providing innumerable feedings/food chains to all life forms. Forest loss menaces the food cycles and survival of living species on this planet. In past few years lots of vast green lands are converted into dry/deserts. Deforestation has annihilated the most productive flora and fauna in the world, also form vast tracts of a very valuable sink for CO2 [6].

iv. Urbanization

Pollution of surface soils materials (like vegetables, animal wastes, papers, wooden pieces, carcasses, plant twigs, leaves, cloth wastes as well as sweepings) and many non-biodegradable materials (plastic bags, plastic bottles, plastic wastes, glass bottles, glass pieces, stone/cement pieces) [2, 7]. On a rough estimate Indian cities are producing solid city wastes to tune of 50,000 - 80,000 metric tons every day and if uncollected and decomposed, then it causes several problems.

v. Underground Soil Pollution

Underground soil in cities is likely to be polluted by chemicals released by industrial wastes and industrial wastes. Decomposed and partially decomposed materials of sanitary wastes: Many dangerous chemicals like cadmium, chromium, lead, arsenic, selenium products are likely to be deposited in underground soil. Similarly underground soils polluted by sanitary wastes generate many harmful chemicals. These can damage the normal activities and ecological balance in the underground soil [6-7].

5. DOMAIN OF SOIL POLLUTION

Soil contaminations through heavy metal and other chemicals impose assorted hazardous and imbalance in varied spears ecosystem as mentioned below [8]:

i. Agricultural

Reduced soil fertility, cut nitrogen fixation, boost erosion, cut soil/nutrients, silt deposition in

tank/reservoir, low crop yield, imbalance in soil fauna and flora.

ii. Industrial

Dangerous chemicals entering underground water, ecological imbalance, release of pollutants, radioactive ray causes health problems, huge salinity, and low vegetation.

iii. Urban

Clogging of drains, Inundation of areas, public health problems, pollution of water sources, foul smell, release of gases, solid/sludge waste management issues.

iv. Environmental

Soil becomes unavailable to grow food on contamination the crop land produce low yields and cause more harm to plants due to soil erosion. Pollutants change soil's and microorganism's makeup and change whole ecosystems.

6. CHROMIUM: AS A TOXIC SOIL POLLUTANT [8-10]

i. Chemistry of Chromium

In 1798 chromium was discovered in crocoites ore of Siberian red lead by the French chemist Louis - Nicholas Vauquelin. Chromium is derived from a Greek word chroma means color. Chromium is a serious pollutant that constitutes 0.1 - 0.3 mg/kg of crust. Chromium occurs as the $17th$ copious element in the Earth's layer in the form of ultramafic and serpentine rocks like chromite (FeCr₂O₄) crocoite (PbCrO₄), bentorite $Ca_6(Cr, Al)_2(SO_4)_3$, tarapacaite (K₂CrO₄) and vauquelinite (CuPb₂CrO₄PO₄OH) [2]. Chromium is used in many industrial applications comprising textile dyes mordant, pigments, alloying, tanning animal hides, water corrosive inhibitor, ceramic glaze, refractory brick, and pressure-treated lumber [8]. Vast anthropogenic chromium utility raised environmental contaminations in past few years [9]. Chromium (0) offer high fusion point for steel and alloys making, and Cr (VI) is used in dye pigment, ink, plastic, anticorrosive paints, primer, surface coats, and metal electroplating.

But Cr (III) is a vital nutrient in many bio-processes like metabolism of certain sugars, proteins and fats. Both chromium Cr (VI) and (III) are used in chromeplating, leather tanning and wood protection. Chromium

compounds like chromate/CrO₄⁻⁻, dichromate/CrO₄⁻⁻ and $CrO₃$ are most lethal due to high oxidation potential, high solubility, and mobility across the membranes of organisms and environment too. Cr(III) oxides, hydroxides and sulphates are less toxic, less mobile, and water insoluble, bound organic matter and aquatic environments. Cr (III) forms hydroxide and also precipitates with iron at usual ground water pH conditions. Cr (III) oxidizes to Cr (VI) in high oxygen atmosphere or in presence of manganese-oxide. Since Cr (VI) and Cr (III) own dissimilar chemical, toxicological, and epidemiological properties are correspondingly regulated by EPA, [8]. Cr(VI) is a potent epithelial irritant and acts as carcinogenic and teratogenic to many plants, aquatic animals and microorganisms including humans. Cr (III) is a vital element for sugar and lipid metabolism in contrast to Cr (VI) being non-harmful/hazardous. Cr (III) at low level endorses growth and yield of plants. Chromium exists in some stable oxidation states like Cr (0), Cr (III) and Cr (VI) and toxicity depends on its valence state. Cr (VI) is very movable and toxic than Cr (III) being less mobile and less noxious. Chromium uptake, translocation, and accumulation by plant depend on speciation to induce toxicity like lower seed germination, fall-growth, low-yield, enzyme inhibition, photosynthetic protest, nutritional /oxidative discrepancy and mutagenesis [9].

ii. Environmental Existence of Chromium

Chromium comes in the natural system of air water and land through assorted sources like weathering of rocks, ores minerals, industrial discharge, and soil leaching. Chromium undergoes varied physic-chemical transformation like reduction, oxidation, sorption, desorption, dissolution, and precipitation in environments as discuss in flowing pattern.

a. In Water

Chromium comes in water system through leaching soils, minerals and rocks beside as industry effluents. In water chromium endure assorted chemical changes like redox reaction, adsorption, dissolution, and precipitation. Aqueous solubility of assorted chromium species depend on pH of the medium, above basic pH >7 Cr(III) precipitates while in acidic conditions pH < 7 it get solubilized. Cr (VI) in the form of chromate and dichromate are extremely soluble at all pH and gets precipitated with many cations. Chromium allowed level in water is 8 *µ*g/L for Cr (III) and 1 *µ*g/L for Cr (VI) besides industry effluents range 2-5 g/L [8-10].

b. In Soil

Chromium amount (both Cr-III and VI) in soils vary as per native conditions like nature of rocks and sediments that creates it. Chromium level in soil rises mostly via anthropogenic and atmospheric deposition, also deposit of chromium-bearing waste, slag, or plating bath. The doil oxidants like dissolved oxygen and $MnO₂$ oxidize Cr (III) to Cr (VI); but Cr (III) oxidation by dissolved $O₂$ is residual. Cr (VI) gets reduced by many elements like iron, vanadium, sulfides and organic matter. On surmount soil reducing power Cr (VI) persist as sediment for many years, especially if its sandy soil or owing little organics. Chromium own high soil mobility, thus it causes higher toxicity on plant seedlings [9].

c. In Plants

Chromium is highly uptake by plants, being an essential for specific mechanism subjected to its speciation. Cr(III) uptake by plants occur without energy loss in a passive manner, while Cr(VI) uptake performs via competing with Fe, S, and P for sulphate binding. Cr(VI) has high dissolubility, so bioavailability is quite toxic at lower level than Cr(III) which form stable complexes in soils. Cr(VI) gets reduced to Cr(III) on the plants root surface and its toxicity depends on speciation as determinant for uptake, translocation and accumulation. Cr is toxic for agronomic plants at 0.5- 5 mg/mL in nutrient and 5-100 mg/g in soil and at normal conditions, plants own Cr with 1 *µ*g/g [10-12]. Chromium accumulation and translocation into roots and shoots of various vegetable crops and plants characterize latent health hazards if present hexavalent form or high amount. Many chromium transporter genes are identified like CDF (cation diffusion facilitator), HMA (heavy metal ATPase), ATP binding cassette (ABC) and ZIP/ZRT-IRT like protein, still role in translocation is vague [11]. Cr (VI) translocation via shoots involves some anionic carriers like phosphate and sulfate besides mediator channels like Fe and S. Chromium accrues in largely in roots and slightly translocation in shoots of plant with order as roots > stem > leaves > seed (0.1% in seeds and 98% primarily in roots). Plants root accumulated 10 times more chromium than leaves and stem. Some seedlings grown in C(III) accumulated in roots of wheat, oat, and sorghum than shoots. Still certain crops like wheat, oat, and sorghum exhibits Cr(III) and Cr(VI) translocation from roots to shoots (100-fold higher than shoots, despite of Cr valence). Cr(VI) rather than Cr(III) gets transported from root to shoot of the plant and at high doses roots accumulated huge Cr beside translocation

happens to cotyledonary leaves with little in hypocotyls. Cr is mainly accumulated in roots, stems and leaves; besides minor amounts is translocated to leaves (despite of Cr species). Cr(III) is an essential micronutrient for organisms owing particular role of maintaining normal carbohydrate metabolism. Cr(III) is engaged in tertiary protein structure by conforming RNA, DNA cell [13].

iii. Role of Chromium in Nature

a. Nutrient Uptake by Plants

Metals interact with vital minerals to form insoluble compounds and change nutrient uptake in plants. In this sense chromium restricts the nutrient uptake in soil thus hinder its growth. Extreme chromium masks sorption sites of many essential minerals like iron magnesium phosphorus and calcium and reduce their uptake by plants. Chromium transports to different parts of plants enhance manganese and phosphrous and reduce micronutrients like sulphur, copper, zinc and iron by disturbing nutrient balance. Thus ed vital element translocation via nutrients dislocation from binding site declines root growth and harm its penetration under chromium toxicity. Chromium undergoes hyper-accumulative bio-transformative chelation with reductant and get compartmentalized in cytoplasm/vacuole of plant root-cells mechanism for detoxification. Plants uptake chromium from the soil by different organs/tissues of like leaves, stems and roots [2, 14]. Chromium compromise several processes in plants like ability of seed germination markedly affected at 500–1000 mg/kg of soil, while. Many seeds showed low germination through inhibit radicals growth to chromium contaminated soil. Cr exposure decrease in α/β amylase metabolism under metal stress as starch hydrolysis is vital for sugar supply in embryo growth and inhibits seed germination. Plants lateral growth and roots hair number is also affected by chromium metals. Root growth is decrease due to Cr(VI) presence through inhibition of cell-cycle division/elongation viable for tissue collapse and make roots unable to absorb water and nutrients from soil [15]. Chromium high amount reduces surface of root surface in plants and cut water stress while low concentration stimulates root growth. Chromium presence reduces length of stem and cutback plant height at exposure to 100 mg/L due to shrinking nutrients and water to the top of the plant. Cr transport to aerial way crashes cellular metabolism of shoots results in drop of plants height. Leaf growth usually reduces with raising chromium amount in plants by lessening cells through stunt salinization cell size.

Extreme Cr (VI) reduces leaf size and turned it yellow, wilted, beside turgor hung defeat from petioles. Continuous Cr supply changes lamina of old leaves to make it necrotic, stable wilted, dry and shed. Overall yield/productivity of plant found to depend on growth, area, and number of leaves, but presence of excess Cr distress many biochemical and physiological process in plants. About 80% significant reduction of grain's weight and yield of paddy seen with 200 mg/L of Cr in soil/land. Cr (VI) has adverse effects on plants and some beneficial soil microorganisms as indicators of soil fertility and quality [16].

b. Chromium and Photosynthesis

Chromium influences photosynthesis process in plants and controls its productivity and yield. Exposure to Cr(VI) reduces chloroplast auto-fluorescence and volume in plants. Both Cr(III) and Cr(VI) alter ultrastructures in chloroplasts and further inhibit chlorophyllase enzymes involved in photosynthesis. Degradation of pigments like chlorophyll-a/-b is observed on exposure to 0.5 mM of Cr (III) and Cr(VI) in leaves and sshoots. Cr(III) in low amount is less toxic than Cr(VI) instead boots many systems like photosynthesis, carotenoids and chlorophylls ratio in plants. Excess Cr changes pigment biosynthesis through degradation of *δ*-aminolaevulinic acid dehydrates enzyme engage in biosynthesis of chlorophyll pigments. Reactive oxygen species typically augments in presence of excess Cr and spoils pigment-protein complexes of thylakoid membranes besides pheophitinization of chlorophylls shifts Mg^{2+} with H^+ viable for thylakoid membrane damage. Cr (VI) exposure decreases rate of photosynthesis, transpiration, and intercellular $CO₂$ in pigment metabolism. Both macro-mineral (N, P, K) and micromineral uptake by plant are influenced by the presence of chromium. Excess Cr shifts these nutrients from physiological binding sites, thus minimize uptake and translocation. Decrease in iron in leaf tissue occurs due to chromium (VI) intrusive destruction of metabolism. Many antioxidant enzymes like, peroxidase, catalase, glucose-6-phosphate dehydrogenase and superoxide dismutase activity gets enhanced in Cr-sensitive exposure in plants [17]. Metabolic responses to Cr(VI) exposure in plants boosts sucrose ratio while cuts glucose contents. Invertase activity gets decreased in leaves due to soils enriched with Cr(VI). Cellular antioxidants are pivotal in protecting plants from chromium induced stress detoxifying ROS species [18].

Root cell growth and division of root tips of plants suffer lowering mitotic index with raising chromium contamination in plants. Cr(VI) affects chromosome morphology through apt boosting like c-mitosis, chromosome bridges, anaphase bridges, and chromosome stickiness. Cr(VI) significantly vary many activities like cell-cycle dynamics and ploidy level in leaves; cell-cycle arrest at G2/M in roots; beside polyploidization at both 2C and 4C levels. Many leaves and roots, of plants suffer DNA damage by hypermethylation and polymorphism enhancement in presence of excess Cr(VI) ions. Chromium imparts genotoxicity in small flowering weeds and plants. Cr(VI) and Cr(III) persuade micronucleus frequencies in many plants and assess genotoxicity. Molecular changes at pollen germination are arised by chromium viable for genotoxicity through protein reduction in mitochondrial oxidative phosphorylation besides rejecting ATPs. Cr(III) uptake by plant occurs in passive way, while Cr(VI) uptake exist via sulphate carriers mainly on roots and translocation to shoots of plant. Although chromium is toxic to plants, several species also hyperaccumulate it from soil/water and display great potential for phytoremediation tactic. Chromium affects several functions in plants like, seed germination, growth, yield, photosynthesis, genotoxicity besides nutrients and oxidative imbalances [16-18].

iv. Chromium Contamination in Environment [18- 19]

Anthropogenic activities are responsible for chromium contaminations including stainless steel plant, alloy-making, metal-plating, tanning, refractory, dyes, water cooling, paper-pulp, petrol-refining, woodpreservation and nuclear-power. Thus, chromium persists in effluents from such activities poses acute pollutant in sediments, soil, and water which impart toxicological risk to life. Cr (VI) is very much dispersed in sediments and waters, due to greater solubility, mobility and bioavailability than Cr(III) and other forms, so facile to disperse from native contamination sites [20]. Raising pH of soil also augments leaching ability of Cr (VI). Cr (III) has low mobility being inert is easily grab by mineral surfaces and solid-phase organic matter/clays ensue low bio-availability. Cr(III) is insoluble at significant pH range and forms insoluble hydroxides and oxides, beside binds iron oxides also reduce its solubility. Least solubility of Cr(III) diminish its bioavailability, mobility and toxicity in salt-waters. Cr(VI) is very soluble and much mobile anionic chromate/CrO₄⁻⁻ and bi-chromate/HCrO₄⁻ states. Cr(VI) quickly adapt Cr(III) state in anaerobic conditions and in presence of reducing agent like sulfides, ferrous and organic matters. Certain bacterial reduction is also

feasible for Cr (VI) degradation biogeochemical cycle [21]. While Cr (III) is stable in water and its oxidation to Cr (VI) is not possible, even in high dissolved oxygen. Cr (III) oxidizes to Cr(VI) in presence and mineralogy of manganese hydroxides, pH and solublizing agents. Cr (III) oxidants exist rarely and less abundant than potential Cr (VI) reductants in natural sediments, thus its oxidation is sluggish. Cr(VI) own strong oxidation potential which quickly reduces organic matter and converts into Cr(III) in acidic soil conditions. But extreme Cr(VI) level defeat reducing capacity of the environment, so persist prolong [22].

v. Chromium Sources [2, 19]

Chromium is mined in different countries around the world (such as South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines) as the naturally occurring form, chromate ore (FeCr₂O₄). Chromium is unstable in an oxygenated environment and, when exposed to air, instantly produces oxide layer as impermeable to further oxygen contamination.

a. Chromium in Agricultural Soils [2]

The mobility and amount of chromium is relied on native concentration and availability in the environment. In soil most chromium appears in 0-VI oxidation states but Cr (0), Cr (III) and Cr (VI) are most stable and usually observed. Chromium effects on health depend on the dose, exposure time and its oxidation state. Cr (VI) is highly soluble; mobile; and toxic but Cr(III) is relatively less toxicity and mobility and acts as micronutrients. Cr (III) forms facile precipitates/ complexes with clay minerals present in soil although it's sparingly water soluble. But Cr(VI) is readily soluble in water and absorbed by plants through bonding with essential anions like sulfate. In soil chromium uptake, accumulation, and translocation varies with speciation or oxidation state. Cr toxicity in plants persuades various problems like germination drop, growth fall, enzymes inhibition, photosynthesis mutilation and oxidative discrepancy.

b. Chromium Transport in Environment [18]

Chromium enters the environment through both natural processes and human activities. Increases in Chromium III are due to leather, textile, and steel manufacturing; Chromium VI enters the environment through some of the same channels such as leather and textile manufacturing, but also due to industrial applications such as electro painting and chemical manufacturing. Groundwater contamination may occur due to seepage from chromate mines or improper disposal of mining tools and supplies, improper disposal of industrial manufacturing equipment.

c. Chromium Bioavailability [17]

Chromium affect quality of air water and land through its uptake accumulation and contamination though anthropogenic and industrial sources which eventually lead to soil pollution. Chromium contamination in water is limited to surface and not affect groundwater due to strong attachments to soil. Chromium restrains within silt layer surrounding or inside groundwater reservoirs. Chromium consumption can include respiratory problem, reduce disease resistivity, birth defects, infertility and tumor formation.

d. Chromium Impacts on Human [2]

Chromium (VI) being carcinogen induces mutagenesis and considered toxic level-3 pollutant which gets concentrated in bone, blood and many organs of our body. But Cr (III) is vital in regular metabolism and vascular activities besides combating diabetes. Chromium (VI) induces allergies, skin-rash, nose-irritations and nose-bleeding, ulsers, weak immunity, genetic change, kidney/liver harm, and death in acute exposure. Individual's consumption of 1000mg Cr/day leads no harmful effects while too much usage causes poisoning. Chromium (VI) chronic inhalation arise assorted health problems like harm nose lining, throat/lungs irritation, damage liver and kidneys, besides gulping upset the gastrointestinal tract. Hexavalent chromium not causes cancer if ingested, most likely as rapidly converted to trivalent state after reaching stomach. Overview of chromium biogeochemistry, bioavailability and risk assessments including physicochemical factors, speciation and toxicity with notable stress on remediation techniques is shown in Figure **1** below.

e. Sediment and Soil [2]

Improper disposal of sludge from coal fly-ash, power plants, agricultural/paper wastes, metal plating and atmospheric fallout attribute soil's chromium contamination, depending on its speciation, redox potential and pH. Chromium exists predominantly in (III) state as a least soluble/ mobility and low reactive/toxic to the life. But chromium (VI) is quite toxic and feasible in aerobic soils/organic matter to carry out redox biochemical reaction at low pH. Oxidation of chromium (III) to chromium (VI) in soil is assisted by many factors like organic-humic acids, % oxygen, MnO2 and % moisture. Soil containing maximum aeration and pH > 7.3 induce more oxidation of

Figure 1: Overview of chromium biogeochemistry, bioavailability and risk assessments.

chromium (III) to chromium (VI). Soluble chromium (III) in soil gets partly oxidized to chromium (VI) by % $MnO₂$, and at pH values >6. Most chromium (III) in soil stable due to adsorption and complexation as ionic materials prohibit oxidative conversion. Soil components including iron, sodium sulfite, sodium hydrosulfite, sodium bisulfite, sodium metabisulfite sulfur dioxide, and certain organics also reduce chromium (VI) to (III) conversion. Chromium content in soils varies with composition of parent rock from which the soils get formed e.g., basalt and serpentine soils, ultramafic rocks, and phosphorites own highest contaminations whereas soils derived from granite or sandstone own less pollution chromium. Certain rock strata enriched with Cr (III) bearing minerals, particularly chromite, birnessite. Cr (III) within ultramafic and serpentinite soils/sediments get oxidized and dissolved through natural processes, leading to hazardous Cr (VI) in soil [2]. These minerals are primary geological source for chromium and are resistant to weathering, diagenesis, and low-grade metamorphic transformation. Chromium concentration in the Earth's crust is >200 mg/kg in ultramafic rocks and serpentinites of ophiolite complexes owing ≈1% of terrestrial landscape. Chromium concentrations in such soils and sediments are further magnified by weathering and diagenetic reactions. Chromium(III) released through weathering quickly adsorbs on clay minerals and precipitates as homogeneous solids. Chromium occurs naturally in rocks, soil, plants, and animals in combination with other elements. While pure metallic form of chromium can't exists naturally. Chromium (III) exists naturally in many vegetables, fruits, meat, grains, and yeast. Cr (VI) exists in oxidizing conditions and move down through soil ranges from 1 to 2,000 ppm.

Chromium ranks at $21st$ among the elements found in crustal abundance at about range of 100 mg/kg. The chromium ratio in soils is dependent on parent

materials which normally range from 10 to 150 mg/kg. Chromium concentration in granitic igneous rock range from 20 to 35 mg/kg, limestone/sandstones contain 220 mg/kg and basaltic rock own 1800 mg/kg in ultramafic rock. Soil mineral chromite (FeCr2O4, spinel) mineral owns nearly 40% chrome (Cr2O3) while clay particles act as hosts for surface sequestering Cr(III) from mineral sources [19]. Cr(III) undergoes complexation and precipitation at $pH > 4$, and $Cr(VI)$ is highly adsorbed by many soils. Cr(VI) suffers ligand exchange with hydroxyl functionality of soil colloids and participates with soil particle surface by attributing -ve charge to the soil surface. Most of the chromium appears in atmosphere due to dust, forest-fires, meteoric dust, sea-salt spray and volcanic eruptions ranging from 0.015 to 0.03 μ g/m³.

vi. Mitigation of Chromium Toxicity from Contaminated Soil [2]

Advance technology aids mitigation of chromium from polluted soils. Mitigation of Cr conditions depends on the soil quality and its decontamination based on soil flushing, electro-kinetics, chelantive extraction and assembly of permeable barriers. Cleanup of the contaminants can be achieved oil is attained by in situ flushing either a physical or chemical manner ensuing the separation, segregation and volume which drops with pH, oxidizing/reducing matter, organic matter and clay content. Methodologies used to mitigate Cr toxicity from soil involved soil flushing, sorption, reduction, EC, phytoremediation and membrane separation are very much cost-effective technique. High amount of free electrons in organics reduces Cr (VI) to Cr (III) in microbial conditions critically decide controlling conditions for chromium decontamination of soil are mentioned below:

• Transformation and dynamics of chromium in soil is affected by biotic and abiotic conditions to develop remediation techniques in different environmentally complex settings.

- The physical, chemical and biological properties of soil along with rainfall and temperature environmental parameters affects retention and mobility of Cr(VI) in soil.
- The ligands present in soil adsorbs Cr(VI) by inner-sphere and outer-sphere complexation and increase its retention in contaminated soil as shown in Figure **2** below:

Modern industrialization and fast urbanization poses heavy metal pollution of in the terrestrial environment. Trace metals like lead, chromium contamination in soil accumulate in crops and plants anyhow threaten our life. Hence many regulatory agencies strictly regulated the maximum permitted concentrations of toxic metals in foodstuffs. Crops/plants soak up metals in dissolved form through soil and exchangeable from organic and inorganic components forms. Amount of metals in soil is concern with many environmental soil factors, including pH, organic matter content, oxidationreduction status, cation exchangers, $CaCO₃$ clays, Fe and Mn oxides. Speciation and dissolution of metal is controlled by soil pH which also decides its phytoavailability. An exchangeable organic matter present in soil also determines phytoavailability of metals can deteriorate soil texture.

vii. Chromium Remediation Techniques [2, 10]

Chromium phyto-remediation is apt for mitigating contaminations from soil as mention below:

a. Bioremediation by Microorganisms

Decontamination of polluted/degraded soils is done by enhancing chemical degradation or through soil organism activity. Organic matter content, soil bioactivity and oxygen grade are the deciding factors. In aerobic conditions organic matter rich systems decrease Cr (VI)/chromate in soil via rising microbe activities. The bacterial populations found resistant to Cr (VI) amount of 500 mg/L in soils. Usual methods for mitigation of chromium include chemical precipitation, oxidation/reduction, ion-exchange, filtration, membranes, electro-dialysis, evaporation and adsorption [23]. But such processes own some drawbacks like high energy input, huge chemical reagent use, and large sludge makes inconvenient in economic view. However, bioremediation using metabolic potential of microorganisms is innovative in mitigation of chromium from soil. Bioremediation techniques are performed in situ or ex situ based on an intrusion of apt bacteria directly on the site, or on portions of environmental matrices like water, sediment or soil [24]. Bioremediation through microorganisms appear safe, inexpensive and eco-friendly option for reducing Cr(VI) to less mobile Cr(III) ensued quick precipitation as vital in treatment of contaminated soil [25]. Amid biotechnological approach, microbial reduction is profitable and green alternative for Cr(VI) polluted soil detoxification. Bio-sorption and bioaccumulation of chromium occurs in such bioremediation mechanisms onto selected microbes, yeasts and fungi. Microorganisms genus like *Lactobacillus* bacteria bind Cr(VI) to carry its detoxification. Bio-remediation/augmentation is sometimes followed by phyto-extraction for better outputs [26]. Microorganisms sometime alter Cr ions into amorphous or crystalline precipitates under biomineralization process as promising strategy for chromium removal. Such bio-mediated transformation, immobilization, and mineralization of Cr signify perspective bioremediation technique.

Figure 2: Inner-sphere and outer-sphere complexation of Cr(VI) by ligand present in soils.

b. Phyto-Remediation

Phytoremediation is also bioremediation uses various plants to eliminate, transfer, stabilize, and/or demolish pollutants from soil/water. Pytoremediation mechanisms occur through rhizosphere biodegradation. Phytoremediation of Cr can be attained by plants like Typha angustifolia and photosynthetic microorganisms as microalgae, macroalgae and cyanobacteria. Multifunctional plant-growth-promoting bacteria (PGPB) showed chromium resistance and reducing traits and acts as bio-inoculants with phytoremediating plants. PGPB advances chromium uptake by modifying plants root architecture, secrete sequestering in rhizosphere and lessen phyto-toxicity. Soil contains varied nutrient-rich resource and apt microbial-activities vitally retain fertility and plant productivity by easing decay, mineralization, fixation

and immobilization of nutrients. Soil microbes appear innate useful in sustaining soil-ecosystem by promoting/opposing or inhibiting diverse biotic and abiotic processes [27]. The most prevailing heavy metals in soils and their regulatory limits are mentioned in Table **4** below:

Amid varied soil microbes, plant-growth-promoting bacteria produces growth regulators, mineral solubilizers, phytohormones and diverse secondary metabolites to expedite plants progress against metal poisoning. PGPB are employed for contaminated soils in phytoremediation of chromium in tandem. The chromiums effective metabolism for plant growth promoting bacteria (PGPB) is shown in Figure **3** below:

Cr(VI) is a toxin which typically originates from anthropogenic activities and also formed naturally by

Table 4: Heavy Metals Prevailing in Soils and their Regulatory Limits

Figure 3: Chromiums effective metabolism for plant growth promoting bacteria (PGPB).

oxidation of Cr(III) within ultramafic- and serpentinite derived soils/sediments [2]. In prokaryotes and eukaryotes including plants, Cr(VI) toxicity is due to easy diffusion across the cell membrane, reduction within cells to produce free radicals and reactive oxygen species which adds more toxicity. Cr(VI) oxyanion pierces cells nonspecific channels in membranes due to morphological similarity with sulfates and phosphates. Within cell Cr(VI) sequentially reduces to Cr(IV) and lastly to Cr(III) along with free radicals. Cr(III) is unable to cross cellular membrane due to weak membrane permeability, so trapped intracellular frames and complexes with protein/nucleic acid, beside ruin DNA via inhibiting replication/transcription [26]. PGPB-aided plant-growth and phytoremediation of chromium-stressed soil is shown in Table **5** below:

PGPB advances plant-growth in tandem, phytoremediation of chromium-contaminated soils

Table 5: PGPB-Aided Plant-Growth vis-à-vis Phytoremediation of Chromium-Stressed Soils

varying as per soil type and environmental conditions like rhizosphere colonization and chromium phytoavailability. PGPB accelerates phyto-remediation vis-àvis plant-growth amelioration as environment own many constraints including biotic (bio-antagonism by native microflora and phyto-pathogens) and abiotic (acidity, salinity, drought, temperature and radiation) factors. Biotechnology and genetic engineering have revolutionized the phyto-remediation as new traits are produced in the organism by inserting specific genetic sequence in host organisms. Many approaches can be genetically modified to increase the phytoextraction or mobilization of chromium from contaminated soil. Plantgrowth promotion with chromium-stress evasion and simultaneously expediting phyto-remediation via designed PGPB is realized with full potential [22].

c. Rhizo-Filtration

Rhizo-filtration is also capable for phyto-remediation as achieved through mass of plant's root to remove metals like chromium from contaminated sample (soil/water). Generally aquatic plants roots like Scirpus lecusteris, Phragmites karka and Bacopa monnieri are very much significant decontamination of assorted metals from soil/water Rhizo-filtration approach uses hydroponically cultivated plant roots to remediate/filter contaminated sample through absorption, concentration, and precipitation of pollutants (take up pollutant dissolved in it). Plant natively uptakes heavy metals due to many reasons like sequestration, drought resistance, leaf abscission disposal, other plants interference and pathogen defense beside herbivore activity. Rhizo-filtration resembles phyto-extraction as both path trap contaminant into harvestable plant biomass. Plants put in contamination contact gets acclimated and absorb metal through roots and store in root biomass and/or transport up to stems and/or leaves until become harvested. Rhizo-filtration aims to concentrate and precipitate heavy metals than organic contaminants, used for treatment in aquatic environments, while phytoextraction deals with soil remediation. The series of aquatic and land plants are used for rhizofiltration with varying hyperaccumulation capacity, like sunflower, mustard, tobacco, rye, spinach, corn, cattail, saltmarsh bulrush, scirpus robustus [21].

d. Phyto-Extraction

Harvestable plant tissues are used in phytoextraction of chromium from polluted soils. Varied plant can accumulate Cr from soil in their tissues like *Sutera fodina, Dicoma niccolifera* and *Leptospermum Scoparium*. Nutrient culture chelates with Cr-DTPA/EDTA/EDDHA and translocate chromium in gram-ve bacterium Proteus vulgaris. All the above mentioned chromium remediation techniques are ecofriendly and are frequently used to clean up contaminated soils [2]. The chromium concentration in various environmental zones is shown in Figure **4** below:

7. LEAD TOXICITY IN THE ENVIRONMENT [23]

Lead in the environment effects health and the surround environment. Certain major environmental sources of lead contamination include leaded paint, gasoline, stationary sources, dust/soil, food, and water. Lead contaminated soil is limited often by a lack of information on human exposure factors and soil conditions. In fact heavy metal lead is soft, malleable, bluish grey colour being picky interested due to innate toxicity and extensive existence in the atmosphere. Lead is the most toxic metal considered as a priority pollutant as an industrial pollutant, enters in an

	Chromium concentrations in the environment
Sample type	Concent r —a.
tion	
Natural soils	10 to 15 mg $kg-1$
Serpentine soils	634-125,000 m g
$\rm kg^{-1}$	World soils
200 mg kg^{-1} (mean)	
100-300 mg $kg-1$	
10-150 mg kg^{-1}	US soils
$25-85$ mg kg^{-1}	
57 mg kg^{-1}	Canadian soils
100-5000 mg kg^{-1}	Japanses soils
87 mg kg ¹	Swedish soils
74 mg kg^{-1}	Sediments
0-31,000 mg $kg-1$	Fresh water
0-117 μ g L ⁻¹	Sea water
0-0.5 μ g L ⁻¹	Air
$1-545,000$ ng m ³	
100 ng m ³	Plants
$0.006 - 18$ mg kg ⁻¹	Animals
$0.03-1.6$ mg kg ⁻¹	

Figure 4: Chromium concentration in various environmental zones.

environment via soil, air and water/wastewater. Lead metal is systemic poison being very toxic in nature which causes anaemia, kidney malfunction, brain tissue damage and death in severe poisoning. Lead pollution as dispersed over earth and ground-water through natural sources and industrial effluents [24]. Certain processing industries, like acid-battery making, metal plating and finishing, ammunition, antiknocking agent-tetraethyl-lead synthesis, ceramic/glass industries and environmental clearout practices deal and disperse lead polluted water being foremost lead pollution sources. High lead concentration in the atmosphere results an enduring health risks to all the elements of ecosystem. As per WHO, the maximum tolerable limit of lead metal in drinking water is 0.05 ppm (parts per million), while Environmental Protection Agency allows permissible limit for Pb (II) in wastewater as 50 ppb (part per billion). However, an industrial wastewaters own lead (II) amount range between 200–500 mg/L; which is huge than that of water quality standards. This needs to reduce/mitigate lead (II) concentration in wastewater to 0.05–0.1 mg/L level before discharge to outlets [23-25].

i. Sources of Lead Exposure [26]

As per EPA-1986 standards natural lead concentration in surface soils is below 50 ppm and ATSDR- 1988 has identified its sources as paint dust, weathering, chalking paint, airborne fallout, solid-waste disposal, glazed pottery, stain-glass, ventilated indoor firings, and vehicle gasoline emissions. The organic matter in atmosphere retains Pb in the upper 2-5 cm of undisturbed soil [27] while lead-smelting and superfund sites infer lead pollution in soil [28]. Soil gets contaminated by lead through many ores/minerals including galena cerusite (lead carbonate), anglesite (lead sulfate) and massicot (lead oxide). Lead forms low soluble compounds with major anions including hydroxide, carbonate, sulfide, and sulfate of raw water. Exterior paint poses critical and major lead contamination besides accumulation in soil as a function of the rate of atmospheric deposition. Mineral interface adsorption and precipitation of sparingly soluble solid organic matter in soil decides the fate of lead in soil. Atmospheric lead enters the soil as lead sulfate which is relatively soluble, so leach easily at pH > 5. Lead immobilizes by organic matter of soil and its exposure is huge at surface than subsurface. The size of lead metal in paint dust/chips ranges from 200 to 300 pm to the visible range are less absorbed, thus less bio-available. Today, advanced road systems and related automobile traffics also induce obvious environmental contamination of lead.

ii. Adversity of Lead

Lead is prime harmful metal contaminant owe major impact on soil quality and growth of plant, based on its form, as well as its transport and accumulation [29].

Lead metal gets absorbed or accumulated and then penetrate in living systems through food chains and beyond severe exposure poses health problems. Lead is soft, malleable, bluish grey metal own native toxicity and extensive existence in the atmosphere via soil, air and water [30-31]. Lead is systemic poison to human that causes anaemia, kidney malfunction, brain tissue harm and death in acute conditions. Lead pollution as dispersed over earth via natural sources and industrial wastes. Industrial processing including like battery making, metal plating, ammunition, anti-knocking agent-tetraethyl-lead, ceramic and glass practices deal and disperse lead pollution [32]. High lead concentration in the soil endures health risks to all the elements of ecosystem. Maximum contamination/limiting concentration some heavy metals to be discharged as directed USEPA norms [27] as mentioned in Table **6** below:

iii. Treatment for Lead Mitigation [27]

The environmental pollution due to the detrimental heavy metal ions must be removed from water so as to protect the human beings and the environment. To accomplish the increased stringent environmental regulations and maximum permissible limit of contaminant in water, a wide range of treatment technologies such as chemical precipitation, coagulation flocculation, flotation, ion exchange, membrane filtration, electrochemical treatment technologies, adsorption [33] and bio-adsorption are most frequently examined for the mitigation of heavy metals from wastewater [34]. Certain merits and demerits of varied physico-chemical methods for Pb^{2+} mitigation is mention in Table **7** below:

iv. Precautionary Measures in Soil Preservation [2, 39]

The preventive measures are to be ascertained in effective mitigation of soil contaminations. Soil pollution occurs through varied activities and experiments done by human ends up with excessive contamination of soil. Industrial wastes such as harmful sludge needs to be properly disposed and use of chemicals, agricultural

Table 6: Maximum Contamination Level of Metals Discharged as Directed by USEPA

Table 7: Various Physico-Chemical Methods for Mitigation of Pb (II) [35]

S N	Treatment Techniques	Merits	Demerits
	Physico-chemical precipitation	Low-cost, easy operation, high efficiency	Huge Sludge/waste formations, addition burden of solid-waste disposal
2	Adsorption	Cheap, simple conditions for operation, wide pH workability, high binding capacity/efficiency	Less selective, create large wastes/secondary pollutants
3	Membrane filtration	Small space requirement, low pressure, high separation selectivity	Highly expensive, membrane fouling
4	Electro-dialysis	Elevated separation selectivity, great efficiency	Costly, membrane fetid, needs more energy/power
5	Photo-catalysis	Remove metals, organics, green process, less by-products	Limited utilities, Prolong time,

pesticides, fertilizers and insecticides are to be minimized. Need to concentrate on soil management systems and harmful irrigation practices, improper disposal, supervision, maintenance of soil erosion besides forestation programs are to be performed on war-level. Urgent approach in ecological risk assessment of contaminated soils is to be taken into consideration. Generic soil screening levels are needed and ecological risk assessment must own site-specific review. It's vital to have framework or decision support from all the parts of society as evidence approach is noticeable in handling such uncertainties. Approach categorizes information in chemistry, toxicology, and ecology TRIAD is an appropriate way for managing intangible suspicions [2, 40]. Advices eco-toxicity testing consent to major development in risk estimates. As to bio-availability in risk estimates, more dated facts of exposure routes, dose and combination effects, besides bio-monitoring are alternatives for augmentation.

CONCLUSION

Pollution of soil causes chain reaction like alters its biodiversity, reduces organic matter and filter capacity. Soil pollution contaminates water and groundwater resources and appears a basis for imbalance in soil nutrimental values. Amid viable soil pollutants the heavy metals are emerging contamination which deteriorates environment and accordingly for all forms of life. Polluted soil contaminants get accumulated in tissues of plants and animals and then pass finally to the humans. Soil pollution disturbs food chain and causes varied diseases, excessive mortality, short-term acute effects like intoxications, and diarrhea to longterm chronicity such as cancer. Beyond the environment deterioration, soil pollution has high economic costs by virtue of reduce crop yields and quality. Thus prevention of soil pollution/contamination must be utmost priority throughout the globe. The majority of soil pollutants are due to domestic activities

means human is straight guilty for making it contaminated, thus need control over pollution to secure our future. Soils must be recognized and valued for its productive ability which contributes to food security by maintaining key ecosystem services. This chapter gives an insight with just a few reasons why soil pollution can't be under-evaluated instead to be focused to live better life on this planet. Such metal pollution deteriorates the soil, which is a fixed resource and once degrades then unrecoverable within human's lifespan. Soil pollution too affects the quality and quantity of water, food, and air which ultimately deteriorate health of our planet. Without healthy and good quality of soils nature is unable to grow food and life. Hence healthy soils are essential to food-chain security and sustainable future of all living creatures on the Earth. Good quality of soil sustains food production, mitigates and adapts climate changes, filter water, recover resilience to floods and droughts. Yet, certain factors like metal contamination, deforestation and erosion are major threats and risks to soils.

Mitigation methodologies are developed for mitigation of Pb^{2+} from water/wastewater including chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation, and adsorption [36]. All such developed treatment techniques are cheaper and more effective with the concern of reducing further/secondary wastes generations besides boost processing quality. Physicochemical adsorption is the preferred treatments seeking for cheap, biocompatible adsorbents get intensified nowadays [37]. Techniques are grown for treating Pb^{2+} and Cr^{6+} contaminated water must focusing on crucial parameters like pH, initial metal concentration, efficiency, overall output, functioning costs and socio-environmental, and economic impacts. Factors including technical applicability; plant simplicity and operational-cost are crucial in picking utmost treatment techniques for protecting ever degrading nature [38]. Lead and chromium metal removal from soil/water are carried out through assorted techniques viz; physic-chemical precipitation, electrochemical reduction, ion-exchangers, reverse-osmosis, cementation, electro-dialysis, electro-winning, electrocoagulation, membrane-separation and adsorption. But, technical applications, plant easiness and economy are critical in choosing appropriate treatments technique [30]. Advanced physico-chemical adsorption is preferred to remove lead and chromium due to unique features economic, facile, and profitable features.

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