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The Influence of Potentially Toxic Elements on Soil Biological and Chemical Properties

Om Prakash Bansal

Abstract

Soil has been a source of wealth for humans for infinite years and it continues so at present. Both mineral and organic amendments have been applied to soil to slow down its progressive impoverishment. Biological activity, mainly microbial activity, plays a key role in the stability and fertility as well as in biogeochemical cycles. Effect of potentially toxic elements on soil microbial activity, the composition of soil microbial community, soil enzyme activities, and soil physicochemical properties have been reviewed in this work.

Keywords: potentially toxic elements, plant growth, soil microbial activity, soil microbial composition, soil enzyme activities, soil physicochemical properties

1. Introduction

The soil is the basic source for the human being living and most fundamental elements of human production and the carrier linking human economic relationship together. Contamination of soils by potentially toxic elements due to different anthropogenic activities is one of the factors which influence the life in soils [1–3]. There are four major pathways [4] by which potentially toxic elements enter in the soils: (i) atmosphere to soils, (ii) sewage to soils, (iii) solid waste to soil, and (iv) agricultural supplies to soils. Potentially toxic elements are the elements with high density and high relative atomic weight, showing metallic properties as ductility, malleability, conductivity, ligand specificity [5]. Some potentially toxic elements such as Co, Cu, Fe, Mn, Mo, Ni, and Zn are beneficial to the biological system when present in permissible amount but damage the biological system if present in excess. Soil potentially toxic elements such as Pb, Cd, Hg and As (a metalloid but generally referred to as a potentially toxic element) are harmful to crops, humans, and animals. Potentially toxic elements are added to the soil naturally and by anthropogenic activities; metals Cd, Pb, Zn and Ni are also originated from heavy traffic on roads and causes soil pollution. Oves et al. [6] reported that the annual estimate of potentially toxic elements release from all sources in worldwide is around 22,000 metric ton of Cd; 939,000 of Cu; 783,000 of Pb and 1,350,000 of Zn. As the soil and potentially toxic elements have rich and diverse binding characteristics, soil acts as a major reservoir media for potentially toxic elements. Depending on several factors such as water content, pH, temperature, particle size, clay content and the nature of potentially toxic element, the soil

matrix may adsorb, exchange, oxidize, reduce, and catalyze the metal ions. The mobility and toxicity of potentially toxic elements in soils depend on the soil-metal composition and metal ion concentration. The availability of potentially toxic elements in soils besides other factors also depends on soil density and type of charge in soil colloids, soil surface area and the power of complexation with ligands [7, 8].

The present study was undertaken to understand the current situation and the impact of potentially toxic elements on human, on soil microbial activity, on soil microbial composition on soil enzyme activities and on soil physicochemical properties.

2. Impact of potentially toxic elements on plant growth

In soils, plants can uptake potentially toxic elements which are water-soluble or get easily solubilized by roots [9]. As potentially toxic elements cannot be degraded, when their concentrations within the plant exceed permissible limit they adversely affect the plant directly and indirectly. Leaf chlorosis, disturbed water balance, and reduced stomatal opening, inhibition of cytoplasmic enzymes and damage to cell structures due to oxidative stress [10], are some direct toxic effects of potentially toxic elements on plants. Replacement of essential nutrients at cation exchange sites of plants by potentially toxic elements is one of the examples of indirect toxic effect [11]. High metal concentration may lead to decrease in organic matter decomposition, the decline in soil nutrients, decrease in enzymatic activities useful for plant metabolism lead to a decline in plant growth which sometimes results in the death of plant [12].

3. Impact of potentially toxic elements on human

The uptake of potentially toxic elements from contaminated soils by plants comprises a major path for these elements to enter the human and animal food chain [13]. Potentially toxic elements' bioaccumulated in the food chain, harmful to human, enters the human body through inhalation and ingestion and ingestion is the main route of accumulation in humans. Besides it, the potentially toxic elements have also been used for a long time by humans for making metal alloys and pigments for paints, cement, paper, rubber, and other materials. These potentially toxic elements enter the body system when these plants are directly or indirectly consumed, also through air and water and may bioaccumulate over a period of time [14, 15]. Potentially toxic elements entered in the human body by any means affect the immune system, basic physiological processes of cell and gene expression and may cause nausea, anorexia, vomiting, gastrointestinal abnormalities, and dermatitis [16, 17]. Women are more susceptible to the adverse effects of Cd and have higher body burdens due to the long half-life of Cd and increased dietary absorption of Cd is long-lived in the body and low-level cumulative exposure has been associated with changes in renal function and bone metabolism [18]. Potentially toxic elements mainly lead (Pb) effects and damages body organs and systems as kidney [19]; liver [20]; and change blood composition, [21]; damage lungs [22]; reproductive system [23]; central nervous system [4]; urinary system [24]; immune system. Chen [25] has reported that workers who are in close contact with nickel powder are more likely to suffer from respiratory cancer and nasopharyngeal carcinoma. At lower concentration copper acts as co-factors for various enzymes of redox cycling [26]; however, the higher concentration of Cu disrupts the human metabolism leading to anemia, liver and kidney damage, stomach and intestinal irritation. Arsenic induces skin, liver, lung, colotral uterine cancers [27].

Physical, muscular, and neurological impairments, the degenerative processes similar to Alzheimer's disease [19], Parkinson's disease [28], muscular dystrophy and multiple sclerosis [29] may occur when the human population is exposed to potentially toxic elements for a long time.

4. Effects of potentially toxic elements on soil microbial activity

Potentially toxic elements are common and important refractory pollutants, affect the number, diversity and microbial activity of soil microorganisms. As soil microorganisms decompose organic matter, affects nutrient cycling, microbes play a major role in soil fertility and primary production. Soil microbial biomass which is useful for studying the harmful effects of toxic metals at the cellular level is mainly made up of bacteria and fungi. The toxic effect of potentially toxic elements depends on the number of metals bioaccumulated by absorption, migration, and transformation. Adverse effects of higher concentration of toxic metals on microorganisms may be due to inactivation of enzyme activity center; electron-donating groups such as mercapto protein, nucleic acid base and phosphate combination, accumulation of toxic metals more than the ability of organisms to bear resulting in biological disease and death; inhibition in the formation of metallothionein or metalloprotein. A number of studies have shown that the higher number of metallothionein in cells induces the anti-apoptotic effects, and a decrease in the number of metallothionein increases the susceptibility to apoptotic cell death.

Soil microbes are the main participant of all the soil biochemical processes. Soil biochemical processes are the tools for maintaining soil quality; formation of soil organic matter; decomposition of harmful substances; formation of soil structure and biochemical cycles. Contamination of soils by toxic metals decreases soil microbial properties such as soil respiration, enzymatic activities. Soil microbial properties depend on soil pH, organic matter and other chemical properties. Severe potentially toxic element pollution can inhibit soil microbial activity and seriously threaten the soil ecosystem function.

A number of workers [30–33] have reported that potentially toxic elements particularly cadmium, copper, and zinc can disrupt the microbiological equilibrium of soil. Disturbances of the biological balance of soil caused by the excess of potentially toxic elements might be attributed to the disruption of physiological functions, denaturation of proteins and destruction of cellular membranes of soil microorganisms [34–36]. Potentially toxic elements immobilize soil bacteria, while microbial metabolites enhanced the mobility of potentially toxic elements [37–39]. Potentially toxic elements in different quantities and forms in soils cause changes in the counts of microorganisms, microbial biomass and microbial activity [33, 40–43] via inhibiting microbial community diversity, particularly that of fungal groups i.e., Ascomycota and Chytridiomycota) in the large-size fractions, which mainly depends on heterogeneous SOC availability across the PSFs. Potentially toxic elements create abiotic stresses [37, 38] by inducing disorders in the metabolism of the microorganism. Damages to the control systems regulated by regulatory and signal proteins, including the cell's development, apoptosis and regulation of the cellular cycle are caused by potentially toxic elements [36], which might be due to the blocking of enzymatic active centers and driving away cations that are important for the functioning of a cell, supplanting their functions, e.g., discontinuation of the cell-to-cell adhesion (cadmium), direct binding with the DNA (chromium), interacting with the binding sites of protein phosphatases (vanadium) [44]. Tolerant species of microbes demonstrate higher resistance to stress factors than sensitive ones [45]. Tolerance of potentially toxic elements is associated with [46–48]: (1) specific

transport of metal ions in the cytoplasmic membrane; (2) synthesis and excretion to the environment chelating compounds, which bind and transport ions dissolved in the environment; (3) sorption of ions onto mucosal surfaces and the binding by biopolymers of the wall and membrane complex; (4) the presence of plasmids in a bacterial cell, which enables it to acquire resistance to toxic elements.

Many researchers [49–51] have reported that when potentially toxic elements are present in the excessive amount in the soil the microbial count and diversity of microorganisms' decreases. Bansal and Mishra [52] reported that there was a significant increase in the bacterial and fungal population and decrease in actinomycetes population in sewage irrigated soils. The population density of bacteria and fungi increased with duration of sewage irrigation up to 14 days of incubation and thereafter decreased. Kouchou [53] during their studies found that potentially toxic elements contamination in alkaline soils has a negative effect on actinomycetes and fungi soil populations, while a positive effect on the total aerobic heterotrophic bacterial population. They also inferred that the effect of potentially toxic elements on microbial population of the soil is dependent on several factors related to soil environment and soil physicochemical characteristics. Fengqiu et al. [54] during their studies on Microbial diversity and community structure in agricultural soils suffering from 4 years of Pb contamination found that the presence of Pb^{2+} in soil showed the weak impact on the diversity of soil bacterial community. Contamination of soil by Pb influences soil chemical properties and number of some genera of bacteria. The number of heavy metal-resistant bacteria at genus level viz. *Bacillus*, *Streptococcus*, and *Arthrobacter* is highly correlated with the amount of Pb. There was a negative correlation between soil organic matter and available Pb and total Pb. The total relative abundance of Gemmatimonadetes, Nitrospirae, and Planctomycetes was negatively correlated with total Pb. Both the microbial community composition and physicochemical properties of soil are influenced by the amount of Pb. Workers [52, 55] found that nitrifying bacteria, symbiotic nitrogen-fixing bacteria, and *Azotobacter* spp. are the microorganisms most susceptible to potentially toxic elements. Potentially toxic elements produce a stronger effect on *Azotobacter* cells than organotrophic bacteria mainly because richer communities of microbes are more resistant to potentially toxic elements than single species and genera [51, 56]. Wyszowska et al. [48] reported that the inhibitory effect of potentially toxic elements on soil microorganisms can be represented as follows: oligotrophic bacteria: (Ni > Pb > Cr(III) > Cu > Zn > Cd), copiotrophic bacteria: (Cd > Ni > Cr(III) > Zn > Cu), ammonifying bacteria: (Ni > Pb > Cr(III) > Cd > Zn > Hg), nitrogen immobilizing bacteria: (Zn > Cr(III) > Hg > Cu), actinomycetes: (Cu > Cr(III) > Ni > Zn > Pb). Few researchers [57] found that crops can moderate the influence of potentially toxic elements on soil microbes, crops improve the microbiological activity of the soil, mainly owing to substances secreted by roots.

5. Effects of potentially toxic elements on soil microbial composition

Potentially toxic elements when accumulated in soil beyond their permissible limit they firstly influence the quality and quantity of soil bacteria, fungi, actinomycetes, and other microbial population. Potentially toxic element contamination in soil not only produces different microbial community patterns but also change the chemical and biological properties of the soil. In the soils which are polluted by potentially toxic elements for a long time, those soil microorganisms which can specifically be adapted exist. The efficiency of microbial populations in organic mineralization is inversely correlated with the soil organic carbon content, an indicator of the impact of potentially toxic element pollution. Microbial communities

in soils are very important as they are helpful in nutrient cycling, plant symbiosis, and the detoxification of noxious chemicals (used to control plant pests and plant growth) [58]. When metal enriched sewage sludge is added to soils microbial biomass leads to a decrease in functional diversity [59] and changes in microbial community structure [60]. However, metal exposure may also lead to the development of metal-tolerant microbial population [61].

Potentially toxic elements affect the microbial activity and microbial community structure. The number of bacteria and actinomycetes significantly decreased as compared to the control, while no significant difference in fungal cells up to 2 weeks of incubation [62] of potentially toxic elements. The negative effect of studied potentially toxic elements on culturable heterotrophic bacteria was more than actinomycetes and fungi. The DGGE profile indicated that the bacterial community structure was changed in the Cd/Pb-amended samples, particularly at high concentrations, but not bacterial taxon richness and community composition [63]. The relative abundance of specific bacterial taxa including, Acidobacteria, Actinobacteria, Bacteroidetes, Chloroflexi, Planctomycetes, and Probacteria is affected by potentially toxic elements pollution. A significant correlation between a group of metal-resistance genes and metal concentration in soil was also reported by Azarbad et al. [63]. Acidobacteria Gp and *Proteobacteria thiobacillus* bacteria had more links between nodes and more positive interactions among microbes in CL- and CH-networks were positively correlated with cadmium concentration while *Longilinea*, Gp2 and Gp4, had fewer network links and more negative interactions in CL and CH-networks where negatively correlated with Cd [63]. There was the only positive correlation in between the members of the phyla Crenarchaeota and Euryarchaeota, class Thermoprotei and order Thermoplasmatales and Cd metal and had more network interactions in CH-networks. Li et al. [64] also reported that (i) the microbial community composition, as well as a network interaction was the shift to strengthen adaptability of microorganisms to potentially toxic element contamination, (ii) archaea was resistant to potentially toxic element contamination and may contribute to the adaption to potentially toxic elements. Pb²⁺ in soil showed a weak impact on the diversity of soil bacteria community, but it influenced the abundance of some genera of bacteria, as well as soil physicochemical properties [54]. At the genus level, there was a significant difference in the relative abundances of heavy-metal-resistant bacteria such as *Bacillus*, *Streptococcus*, and *Arthrobacter*. The abundance of main bacteria phyla was highly correlated with total Pb. The relative abundance of Gemmatimonadetes, Nitrospirae, and Planctomycetes was negatively correlated with total Pb. Lead influences both the microbial community composition and physicochemical properties of soil.

6. Effects of potentially toxic elements on soil enzyme activities

The biological activity of soils is an essential parameter of their ecological status. The potentially toxic elements present in the soil due to anthropogenic activities disturb the normal functioning of soil biota and, hence, the entire soil system. As the concentration of potentially toxic elements increases, the activity of most enzymes is significantly reduced and may be caused directly by the interaction between the enzyme and the potentially toxic elements, which is not associated with a reduction in microbes. Potentially toxic elements influence the enzymatic activity, by destroying the spatial structure of the active groups of the enzyme, by inhibiting the growth and reproduction of microorganisms which reduces the synthesis and metabolism of the microbial enzymes. Soil microbes and soil enzymatic activities are significantly correlated. Some enzymes secreted by microorganisms participate in soil ecosystems and energy together.

Potentially toxic elements in enzymes play a triple function: catalytic, structural and regulatory. Zinc is an integral part of the number of enzymes and number of intracellular enzymes viz., carbon anhydrase, carboxypeptidase, thermolysin, alkaline phosphatase, dehydrogenases (glyceraldehyde-3-phosphate, alcohol, glutamine), fructo-diphosphate aldolases, superoxide dismutase, DNA and RNA polymerase, tRNA transferase need zinc for proper functioning. When potentially toxic elements are present in excess the natural functions of metals are distorted.

Tejada et al. [65]; Yu and Cheng, [66] reported that the enzyme reactions are inhibited by potentially toxic elements in three different ways: (1) complexation of the substrate; (2) combination with protein-active groups on the enzyme, and; (3) reaction with the enzyme-substrate complex, while Vig et al. [67] reported that as potentially toxic elements interact with the enzyme active sites and substrate complexes, denatures the enzyme protein and competes with metal ions those are needed to form enzyme-substrate complexes, inhibit soil enzyme activities. Nuaimi and Maktoom [68] reported that potentially toxic element pollutants found in the soil can cause their deleterious effects by any of four ways: (1) There is oxidative stress in organisms due to the release of the oxy radical which is produced by redox cycling of potentially toxic elements, (2) proteins are deactivated or denatured as metals bind to sulfhydryl groups of proteins, (3) antioxidant ability of cells retards as potentially toxic elements bind an intracellular glutathione and/or antioxidant enzymes, (4) metalloenzymes became inactivated as potentially toxic elements compete for metal cofactor binding of metalloenzymes. Nuaimi and Maktoom [68] also reported that the potentially toxic elements such as Hg^{2+} , Cu^{2+} inhibited alkaline phosphatase enzyme more strongly than Cd^{2+} , and Co^{2+} and also that alkaline phosphatase is readily inactivated with the exposure to potentially toxic elements, uncharged at neutral pH, arsenic can diffuse across the cell membrane, it can inhibit the enzymatic activities even at a low concentrations.

Bhattacharyya et al. [69] reported that arsenic reacts with the sulfhydryl group of the enzyme to form arsenic sulfide resulting in the decrease of enzymatic activities. The decrease in enzymatic activity by arsenic may be due to: (1) by interacting with the enzyme-substrate complex; (2) by denaturing the enzyme protein, or; (3) interacting with the active protein groups.

The influence of potentially toxic elements on soil enzyme activity depends on pH, nutrient form and amount, potentially toxic element concentration and availability, enzyme type, etc.

Ofoegbu et al. [70] during their research found that there was the significant negative correlation with the potentially toxic element contents and the activities of dehydrogenase, polyphenol oxidase, hydrogen peroxidase, alkaline and acid phosphatases and urease. There was a negative but non-significant correlation between Zn content and dehydrogenase activity; Cd content and hydrogen peroxidase and urease activities.

Diana et al. [71] reported that at the brownfield LSP, extracellular soil enzyme activities are notably high at a site with the highest potentially toxic element loads (soil had been unmanaged for over 40 years, left alone to naturally succeed), and there is a strong relationship between these enzyme activities and Cr and V in particular. This study demonstrates the capacity of some potentially toxic element contaminated soils to enzymatically function well under seemingly restrictive conditions.

Wiatrowska et al. [72] found that Dehydrogenases, acid and alkaline phosphatases exhibited the highest sensitivity toward Zn and it decreased in the order of metal concentrations: $Zn > Cd > Cu > Pb$. In contrast, urease was more tolerant to Zn. The sensitivity of urease was as follows: $Cu > Zn > Cd > Pb$. In respect of their sensitivity to concentrations of the bioavailable pool of Cd, Cu,

Pb, and Zn, the enzymes can be arranged as follows: alkaline phosphatase > acid phosphatase > dehydrogenases > urease. Bansal et al. [42] and Bansal [43] during their studies found that potentially toxic elements accumulated in soils due to sewage water irrigation increased the activity of the enzymes dehydrogenase, acid and alkaline phosphatase, urease and catalase up to 14 days of incubation and decreased thereafter.

Derdzyan et al. [73] during their studies found that potentially toxic element pollution affects the activities of beta-glucosidase, chitinase, leucine-aminopeptidase acid, phosphomonoesterase and acetate-esterase enzymes in the soils.

Gromakova et al. [74] during their work reported that the increase of mobile potentially toxic element forms content in soil inhibited the cellulose-degrading and urease activities after 30 days of the input of metal into the soil. The inhibition of biological activity of the studied metals formed the following series:

Cd > Pb > Zn > Cu.

Yu and Cheng [66] during their studies found that addition of Cu, Cd, and Pb firstly enhanced urease activity and thereafter it declines, while with the increased concentration of Zn the activity of urease declines. In addition to Cu the catalase enzymatic activity initially enhanced and thereafter decreases, the catalase activity continuously decreases with the addition of Cd, Pb, and Zn. Addition of Cu, Cd, Pb, and Zn in soil results in a decrease in microbial biological carbon content.

Khan et al. [62] found that in the Cd and Pb treated soils the activity of acid phosphatase and urease was minimum after 2 weeks of incubation.

The enzymatic activities of the acid phosphatase and β -glycosidase were lowest in the soil samples having the maximum concentration of potentially toxic elements [75]. They also reported activity of acid phosphatase and β -glycosidase was significantly influenced by pH and non-significantly with soil organic matter.

A review of the literature shows that sensitivity of: dehydrogenases [76, 77] is: Hg (2 mg) > Cu (35 mg) > Cr⁶⁺ (71 mg) > Cr³⁺ (75 mg) > Cd²⁺ (90 mg) > Ni²⁺ (100 mg) > Zn²⁺ (115 mg) > As³⁺ (168 mg) > Co²⁺ (582 mg) > Pb²⁺ (652 mg kg⁻¹), Cu²⁺ > Zn²⁺ > Cr⁶⁺ > Hg²⁺ > Ni²⁺ > Cd²⁺ > Cr³⁺, : acid phosphatase: Cu²⁺ > Al³⁺ > Cd²⁺ > Zn²⁺ > Fe³⁺ > Ni²⁺ > Pb²⁺ > Sn²⁺ > Fe²⁺ > Co²⁺, and alkaline phosphatase: Cd²⁺ > Al³⁺ > Zn²⁺ > Fe³⁺ > Cu²⁺ > Pb²⁺ > Ni²⁺ > Fe²⁺ > Se²⁺ > Co²⁺.

7. Effects of potentially toxic elements on soil physicochemical properties

Li et al. [78] during their studies found that water holding capacity, soil bulk density, porosity, permeability, infiltration besides other factors also depends on the concentration of potentially toxic elements. Soil chemical properties depend on soil pH which affects the availability of soil nutrients and form of potentially toxic elements. The amount of plant available organic matter is also influenced by the concentration of potentially toxic elements.

Dawaki et al. [79] during their studies on the effects of heavy metals on physicochemical properties found that clay content and soil pH were non-significantly negatively correlated with soil total potentially toxic element's concentration. Organic carbon, cation exchange capacity, total nitrogen, phosphorous, calcium, potassium, sodium were positively significantly correlated with soil chromium, zinc and lead content, while no significant correlation with copper and nickel content. Sharma and Raju [80] reported that soil pH is positively correlated with potentially toxic elements content. Soil moisture content is positively correlated with potentially toxic elements content except for Cu and Cr. They also reported that there was no specific correlation between potentially toxic elements content and soil

water holding capacity. There was a negative correlation among potentially toxic elements. Tripathi and Mishra [81] during their studies found that soil moisture content is positively significantly correlated with soil water holding capacity, soil organic matter, soil cation exchange capacity, amount of iron and lead; chromium content was significantly correlated with lead and nickel content while there was a significant positive correlation between soil copper content and nickel and zinc content. Lead and zinc in soils are significantly positively correlated. Similar results were reported by Singare et al. [82] during their studies on physicochemical properties and heavy metal content of the soil samples from Thane Creek of Maharashtra, India. Nwaogu [83] reported that in presence of Hg, Pb and Cd ($100 \mu\text{g}/\text{dm}^3$) soil physicochemical properties viz., moisture, phosphate, sulfate, chloride, calcium carbonate, total nitrogen and organic carbon were significantly changed.

8. Conclusion

Due to the persistent, toxic and non-biodegradable nature of potentially toxic elements, the problem of potentially toxic elements in the soil is a turning point for soil scientists. Potentially toxic elements contaminated soils, in general, are nutrient deficient and are likely to become barren in future. Soil microbes are very sensitive to potentially toxic elements. Microbial activities reflect changes in soil environment and are considered to be sensitive indicators in the soil. Microorganisms and their enzymes exert a beneficial effect in soil quality, plant growth as the activities of microbes increase nutrient availability and stimulate the degradation of pollutants. The potentially toxic element in soils also affects the soil physicochemical properties and depends on the form and amount of potentially toxic elements.

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Author details

Om Prakash Bansal
Chemistry Department, D.S. College, Aligarh, India

*Address all correspondence to: drop1955@gmail.com

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