CHAPTER 5
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Mines are the pool of a particular metal under the earth surface. Mining is a process of extraction of metals from reservoirs. The peripheral area of a particular metal mine also contain metal deposits in soil and water. The depositions are results of natural or mining activities. Mining processes leads to metal contamination in nearby area. Sulfide oars and their acid drainage occurred in dumping area and water and soil in land surrounded the mine (Fernandes and Henriques 1991).

The plant species successfully survive in metal rich soil has always been an interesting aspect of researchers working in the field of stress management in plants. The key objective of the study was to focus on tolerant vegetation against metal stress related metabolic disorders.

Analysis of water and soil samples from wild zone shows a number ofdissimilar results than studies conducted on well water, drinking water or crop soil near khetri copper complex (Raju et al., 2013).The concentration of copper and cadmium is much higher in wild zone than previously reported by researchers. Huge storage of copper is present in earth crust in a ratio of about 50 ppm. Major sulfide base oars of copper are chalcopyrite, chalcocite, and carbonate containing oars are azurite and malachite whereas oxide copper is cuprite.

Copper mining generally related to extraction of sulfide oars specially chalcopyrite (CuFeS$_2$). After extractions the oars are moved towards purification process but small fine partials or tailing are remain in contaminate water and soil reside near mining plant. The mine tailing are huge masses of rocks causing metal contamination in water, soil and plants of surroundings. Mine tilling may be dispersed by air but a layer of fine metal dust on soil and plant has been reported by many researchers from diverse metal mines (Davies & Rice, 2001). A thick layer of white dust on surface of vegetation is also observed in present study. The powder is different than normal
grime seen on the surface of plants located in plunk areas and wild spaces. The reason behind should be a major symptom of air pollution or metal dust spreads in area near mining industries. The metal dust covers soil of surrounding area that can alter the physicochemical properties of soil. The soil is a harsh or abiotic stress condition for residing plants over there. Soil contamination is vice versa related to water contamination as reported by previous reports.

**WATER CONTAMINATION IN WILD LAND NEAR COPPER MINE**

Water is a natural resource directly related to topographic and edaphic nature of environment. Metal mine and their surrounding water samples showed higher to lower pH level. The acidic nature of water samples collected from closest vicinity of mine area is slightly in agreement with other reports (Khichar 2014, Mathivanan et al., 2014). Metal ions dissolved through rain fall or mining process may be the root cause to provide acidic nature to water samples. Copper is extracted with sulfide ores and always considered as main cause of acid mine drainage. Similarly acid rock drainage can also direct to acidity of water present near copper mine. The oxidation of metal sulfides varied within water or soil in nearby area also enhanced acidic character of soil and water samples. Sometimes decomposition of metal by means of microbes and archaebacteria may result in increased water acidic level (Mielke et al., 2003).

Electrical conductivity of water or soil solution is an estimation of total dissolved solids in water, salinity and ion component of water. In the other words it is a measurement of conduction of electrical current through salts present in water. The electrical conductivity of distilled water is zero. It has been stated that metal rich water or soil sample has a high value of electrical conduction as metals are good conductors of ions. Therefore, elevated values of electrical conductivity are directly correlated with dissolved matter or ions in water and soil samples. Similarly, electrical conductance is reduced with increasing acidic nature of water which may be a result of metal complexes at a specific pH. The relation of reduced electrical conductance is further associated with calcium and magnesium mediated hardness of water. Hardness in water and soil is also reported near mine that indicates presence of calcium and magnesium bicarbonate and sulphate. The high hardness value is
associated with low pH is also an indication of iron sulphate or calcium iron magnesium sulphate complex (Singh et al., 1988). Present study also shows that water is acidic in vicinity of mine area. Total hardness of water is decreased due to unavailability of calcium and magnesium salts.

High amount of metals viz. Cu, Zn and Cd is reported in water sample collected from ten study points near copper mine. Although, high alkalinity is observed in outer region but soil is acidic near mine area. Metal accumulation is very high in soils of almost all study points near mine. Occurrence and distribution of plant species is significantly correlated with chemical properties and metal contamination of nearby water and soil. A group of metal tolerant and a metal sensitive plant species is prepared on the basis of morphological and distribution analysis.

METAL CONTAMINATION IN SOIL AND PLANTS

High copper, cadmium and zinc concentration with reduced distance from copper mine is also in agreement with previous studies conducted in metal mines. Maharia et al., 2010 also analyzed bioaccumulation of manganese, iron, cobalt, cobalt, zinc, selenium, chromium, nickel, cadmium, arsenic and lead in plants grown in khetri copper mine. The researchers found three to four fold higher copper level, chromium, cadmium, and lead in soil near vegetation of khetri copper mine. High level of metal bioaccumulation was reported in Withania somnifera (Ashwagandha).

Although high deposits of metal were observed in soil samples but pattern of pH, electrical conductance, hardness and metal concentration was almost similar to water samples. These metal deposits may badly influence soil ecosystem, plant physiology, and underground water table which ultimately determine the nature of vegetation near mine area. So many plant species had been reported in previous literature but plants distribution and frequency pattern is studied to identify the most tolerant plant which can survive with huge deposits of metal mixture.

The maximum acceptable amount of copper in plants is 10 mg/kg of plant dry weight. The high levels of heavy metals adversely affect mineral uptake, DNA structure, and reduction of biomolecules, oxidation-reduction reactions and metabolic cycles of
plants. High levels of heavy metals adversely affect mineral uptake, DNA structure, oxidation-reduction reactions and metabolic cycles of plants. Impaired photosynthesis, respiration, transpiration and translation leads to develop various toxicity symptoms. Plant survive in metal rich soil have tendency to accumulate metal for minimizing the toxic effects of metallic disorders. The toxic symptoms of heavy metal accumulation in abody of organism are considered know as higher toxic effect syndrome (HTES) (Singh and Singh, 1981). The toxic effect of major heavy metals on plant growth is classified as cadmium, copper, nickel, zinc, lead, and chromium in high to low order (Athar and Masood, 2002). Munzuroglu and Geckil, 2002 reported the order in decreasing severity as mercury, copper, cadmium, cobalt, lead and zinc during study of germination and growth with Triticumaeastivum and Cucumissativus. Reduction of growth is already reported in Chlorella vulgaris treated with Cu, Hg and Cd (Rosko and Rachlin, 1977).

Raju et al., 2012 also tried to find out metal hyperaccumulators from khetri copper mine and reported Prosopis juliflora and Ailanthus excels as hyper accumulator for copper and zinc, respectively.Rashed (2010) also reported Acia raddiena and Aerva javonica can survive on mercury, cadmium, lead, arsenic, chromium, silver, nickel, gold, molybdenum, zinc, manganese and copper rich mine tailing of Egypt.Ha et al., 2011 also screen out ten plant species prominently survive near near Pb-Zn copper mine in Vietnam.Metal tolerant plants Corrigidiola teletiifolia, Jason montana, Digitalis thaspi are grown in vicinity of metal mine in Spain (Garcia-salgade et al., 2012).

Studies near copper mine also reported other metal tolerant plants such as Silene armeria, Salix viminolis, Typha latifolia and juncus conglomeralis from Italy, Pennsylvania and Portugal respectively (Dinelli and lombini 1996, Rosseli et al., 2003, Ye at al., 2001, Freitas et al., 2004).

Zn is another micro nutrient for organisms but high level of Zn is a of source growth inhibition due to impaired chlorophyll synthesis and aerobic respiration (Kupper et al., 1996). Reduced growth is reported in all plants survive under metal stress is similar to other researches (Rahman et al., 2010, Mathivanan et al., 2014). High
Concentration of copper and zinc can cause metabolic disorders such as enzymatic activity, damage to membranes, hindrance in cellular division and translation has been reported in various plant species (Shen et al., 1998).

Hardening and depositions of substances on plant parts are in agreement with previous reports that metal friendly plants have thick cuticle and trichomes to store heavy metals (Lee et al., 2002, Hauser 2014). Other tolerance mechanism might also working in plants successfully survive in metal rich environment. Plants have a well organized resistance arrangement to struggle metal stress. A distinguished means of trade with excess metal in plant body is binding of metal ions with phytochelatins (PCs). PCs are metal-binding peptides originated from glutathione (GSH) with the common structure (-Glu- Cys)ₙ where-Gly (n = 2–11). Various reports suggested that acidic pH (about 5.5) assist to phytochelatin mediated vacuolar sequestration of metal ions from cellular environment which leads to reduce the metal toxicity and successful survival of plant species(Zhao et al. 2009, Liu et al. 2010). Advance researches show that overexpression of phytochelatine genes is responsible for metal tolerance in plant species occur near mine area(Wojas et al. 2010). Metallothioneins (MTs) are additional cysteine rich proteins present in plants. Similarly, other enzymatic and non enzymatic mechanisms are also reported to compensate excessive metal mediated oxidative damage to plants survive under metal rich soil and water. Enzymatic defense machinery includes superoxide dismutase, ascorbate peroxidase, Guaiacol Peroxidases, catalase, glutathione S-transferase, glutathione reductase and non enzymatic line of protection is consisting of a large pool of non peptide sulphur (glutathione), ascorbate or ascorbic acid, α- tocopherol and a fat soluble pigment carotenoids are reported in stroma of chloroplast, mitochondria, cytoplasm and tonoplast surrounded vacuoles of metal tolerant plant species (Sharma et al. 2007). These tools are associated with several protective cycles running in cellular environment for example ascorbate peroxidase and monodehydroascorbate reductase and dehydroascorbate reductase mediated ascorbate oxidation and reduction cycle, guaiacol peroxidases and glutathione reductase mediated redox cycle of glutathione. Finally all defense mechanisms are moving to achieve the balance in NADP-NADPH redox cycle of plants.
Above said protective trail leads to protect photosynthetic apparatus, cellular membranes, respiratory system and redox status of plants under metal stress. Most promising metal tolerant plant showed following morphological features:

Contrary, to above findings members of family Solanaceae (Solanum nigrum and Datura metel) are observed in only outer most study area. Both plants shows morphological differences with plant grow in garden soil. The height of Datura metel is smaller and width is larger than control plant. Metal stress is clearly evidenced by decreased leaf area, thick cuticle and bush like modifications in plant body.

Another sensitive member is Cassia angustifoli, is a member of family Fabaceae reported in outer most zone of study plant.

Moreover, Vernonia cinereaof family Asteraceae and Pentatropis spiralusof family Asclepiadaceae are two more prominent metal sensitive plant species observed near khetri copper mine. The significant correlation between metal concentration in soil and abundance of plant species also indicate towards metal stress and tolerance in plant species. The amount of metal viz. copper, cadmium and zinc in every plant species present in inner most quadrate reveals a detailed correlation between metal concentration and response of plant system. Highest amount of copper in Cressa cretica indicates metal hyper accumulator nature of plants, whereas Pulicaria crispa is present in almost all study points with lowest metal concentration specifies internal mechanism behind escaping metal accumulation during survival under metal rich environment. High amount of copper may be responsible for sensitivity of Datura metel whereas comparatively small amount of copper may restrict expansion of species Cassia angustifolia up to outer most quadrate. Our results also elaborate cadmium concentration and occurrence of plant species near copper mine. Although cadmium is a toxic metal to plants but Pulicaria crispa is mange to survive with a high amount of cadmium in plant body. Another plant species Aerva persica is present in outer to inner most quadrate but lowest amount of cadmium in plant carcass indicate some strategies to overcome the accumulation of cadmium in aerial parts of plants. Strategies may be sequestration or restricted transport from root to shoot in particular plant species. On
the other hand high amount of cadmium absorption in *Solanum nigrum* leads to limit survival of plant species. Although, *Pentatropis spiralus* is manage a lower amount of cadmium inside body but it is also limited to a definite range of study area. The *Pulicaria crispa* can be identified as zinc hyper accumulator whereas *Aerva persica* has mechanism to restrict excess zinc to shoot of the plant. Plants in outer most area *Vernonia cinerea* are sensitive due to high absorption of zinc and *Pentatropis spiralus* has lowest Zn absorption in plant system.

Study suggested that only a limited number of plants survive in metal rich soil. Some plant may be edaphic ecotypes of sensitive plant species living near mines for a long period of time. The deposits noticed on the outer surface of plants may be metal exudates as it is a common phenomenon of metal toxicity in many plants. About 0.2% plants of total taxa has been reported as hyperaccumulators of Cu, Zn, Ni, Cd, Pb, and Al.

**CONCLUSION**

Industrialization is a foundation for human advancement. It is closely related to Mining and metals. Mining activity has always been considered as health hazards.

Present study dealt with evaluation of metal contamination in wild vegetation rich zone. Water and soil properties were evaluated especially from vicinity of area rich in vegetation. Concentration of metals such as Cu, Zn, Cd and physicochemical properties viz. pH, EC and total hardness were observed above limit in water and soil samples.

Excess copper, zinc and cadmium were noticed in soil and water samples. The concentration of metals has been considered as highly lethel for living organism specially plants. Metal concentration increased with increasing vicinity to core mine area.

Relative study with standard permissible concentration of metals shows that cadmium is three hundred folds, copper is eighty folds and zinc is about five folds higher than the value acceptable for normal growth of a plant.
It was surprising that some plants are able to endure in above metal rich soil and water.

The toxic effect of metal might suppressed by internal mechanisms but morphologically small, bushy appearance, pale green leaf, succulent stem and thick cuticle were perceptible features observed in tolerant plants.

Although amount of metal was above acceptable limit but metal sensitive plants are referred for plants survived only with comparatively low concentration of metal. The sensitive plants also exhibit morphological modifications but they cannot survive in core area or close to mine and limit up to outer most zone only.

Vegetation grown in above unfavorable and harsh conditions is also a matter of interest for researchers. A survey has been conducted to prepare a list of plant species found in mine area. It was observed that five plant species were tolerant to highest level of metal concentration. Three plant species viz. *Adhatoda vasica, Aerva persica,* *Chenopodium album,* *Cressa cretica* and *pulicaria crispa* were maintained constant appearance with changing soil properties. The collected information will developed a solid background for biochemical and molecular analysis of tolerant plants.

Correlation between diverse plant species and metal concentration is highly specific. It was noticed that core sample area near mine has high metal concentration in soil and water which directly related to reduction in number of plant species.

Morphological analysis of prominent plant species also suggests that tolerant plants show more healthy appearance than sensitive.

It may be concluded that wild plant species have specific tolerance means to survive in metal stress. Moreover, there is a strong requirement to unwrap those mechanisms to elucidate an important part of stress plant physiology.