Chapter 2

Literature Review

Removal of contaminants using plants: A review
Current trends in Biotechnology and chemical research, 1-11 (2012)
Global development raises new challenges, especially in the field of environmental protection. The demand for a country’s economic agricultural and industrial development outweighs the demand for a safe, pure & natural environment; therefore, it is the industrial, economic & agricultural developments that are often linked to polluting environment. It has been found that human activities lead to substantial accumulation of heavy metals and other pollutants in soils. These are produced from industrial activities like mining, smelting, refining & manufacturing process. The industries discharge their effluents into coastal water bodies and contribute to a variety of toxic substances on living organisms in food chain by bioaccumulation and biomagnification.

All industries release different types of pollutants but they discharge one or two types of substances which cause major harm. Waste water treatment is essential for health, aesthetic, ecological and other purposes which has become a serious problem and hence there is urgent need for water treatment.

Pulp and paper mill categorized as one of the twelve most polluting industries in India, releases environmentally hazardous liquid effluents containing several toxic and non-biodegradable organic materials and heavy metals. The heavy metals are of great ecological significance due to their toxicity and accumulative behavior. The manufacture of paper consumes 340-425 cubic metric water per tonne and bulk of it comes out as waste water. This industry releases about 80% of the used water back into the streams.

There are several methods employed for the treatment of waste water like reverse osmosis, ground injection, land application, constructed wetlands etc. The traditional physico-chemical processes for treatment involve high energy and large capital investment, whereas aquatic plant based cost effective technologies can be adopted by developing countries for treatment of waste water, especially contaminated by heavy metals.
The important aspects of phytoremediation have been summarized in several comprehensive reviews\textsuperscript{25-30}. The word phytoremediation comes from Greek word phyto which means plant and Latin word remediation which means to remove, which refers to a diverse collection of plants based technologies that use either naturally occurring, or genetically engineered plant to clean contaminants\textsuperscript{31-32}. It is a clean, efficient, inexpensive and environment friendly technology. It is a non-invasive alternative technology for engineering-based remediation methods\textsuperscript{33}. The primary motivation behind the development of phytoremediation technologies is the potential for low-cost remediation\textsuperscript{34-35}. Phytoremediation\textsuperscript{31} is the use of green plant-based systems to remediate contaminated soils, sediments and water. Such plants are known as pollution mitigators.

**2.1 Phytoremediation of wastewater**

According to ecological classification\textsuperscript{36} on the basis of vegetative organs to air, water and ground all non-terrestrial macrophytes are subdivided into five groups:

1. Amphibious plants
2. Plants rooted to the bottom of a water body with leaves emerging at the water surface
3. Rooted plants with vegetative organs submerged in water
4. Plants floating at the water surface without connection to the bottom
5. Completely submerged uprooted plants.

The peculiarities of accumulation of contaminants in the plant organs are of importance for the screening of these macrophyte groups to identify the plants effectively accumulating contaminants.

Plant species with potential for phytoremediation should possess the following properties:

1. These plants should accumulate, extract, transform, degrade or volatilize contaminants at the levels that are toxic to ordinary plants.
2. The plants must have fast growth and high yield and should have ability to remediate multiple pollutant simultaneously\textsuperscript{37-38}.

33
Phytoremediation targets currently include contaminated metals, metalloids, petroleum hydrocarbons, pesticides, explosives, chlorinated solvents and industrial by-products. The use of aquatic plants to reduce pollutant levels from sewage and industrial effluents has been suggested by many researchers\textsuperscript{39-40}.

The aquatic plant species utilized for phytoremediation showed a large range of heavy metal tolerance, and secondary treated wastewater did not affect these species adversely; to the contrary, growth was prompted\textsuperscript{41-44}. One or more trace elements may affect uptake and metabolism of macro and other elements in the plants. There is reduction in heavy metals to below toxic levels\textsuperscript{45}. There is interaction between elements in plants and growth medium\textsuperscript{33}. Excess of macronutrients may interfere with trace elements\textsuperscript{46}.

The change in pH, EC and colour unit could be due to changes in BOD, COD, TS, TDS, TSS and lignin through total phytoremediation. However, a moderate reduction in all the parameters in the non-phytoremediated effluents might be due to the presence of microorganisms and their activities\textsuperscript{29}. In phytoremediated effluents the probability of microbial degradation and its further enhancement is due to the availability of more niches in response to rhizosperic effect.

\textbf{2.2 Plant-based technologies of phytoremediation}

\textbf{2.2.1 Rhizofiltration}

Metal pollutants in industrial-process water and in groundwater are most commonly removed by precipitation or flocculation, followed by sedimentation and disposal of the resulting sludge\textsuperscript{34}. A promising alternative to this conventional clean-up method is rhizofiltration. Rhizofiltration removes contaminants from water and aqueous waste streams, such as agricultural run-off, industrial discharges, and nuclear material processing wastes\textsuperscript{29,47}. Absorption and adsorption by plant roots play a key role in this technique, and consequently large root surface areas are usually required. In research associated with Epcot Centre, closed systems with recirculating nutrients have exhibited
the benefits of Rhizofiltration and biofiltration using a variety of species (such as mosses and scented geraniums)\textsuperscript{48}.

2.2.2 Phytostabilisation
It also known as phytoremediation, is a plant based remediation technique that stabilizes wastes and prevents exposure pathway via wind and water erosion; provides hydraulic control, which suppresses the vertical migration of contaminants into groundwater; and physically and chemically immobilizes contaminants by root sorption and by chemical fixation with various soil amendments\textsuperscript{25,32,49-51}.

Erosion and leaching can mobilize soil contaminants resulting in aerial or waterborne pollution of additional sites. In phytostabilization, accumulation by plant roots or precipitation in the soil by root exudates immobilizes and reduces the availability of soil contaminants. Plants growing on polluted sites also stabilize the soil and can serve as a groundcover thereby reducing wind and water erosion and direct contact of the contaminants with animals. Significant phytostabilization projects have been employed in France and the Netherlands\textsuperscript{52-54}.

The goal of phytostabilization is not to remove metal contaminants from a site, but rather to stabilize them and reduce the risk to human health and the environment.

2.2.3 Phytoextraction
Phytoextraction involves the removal of toxins, especially heavy metals and metalloids, by the roots of the plants with subsequent transport to aerial plant organs\textsuperscript{29,55}. Pollutants accumulated in stems and leaves are harvested with accumulating plants and removed from the site. Phytoextraction can be divided into two categories: continuous and induced\textsuperscript{29}. Continuous phytoextraction requires the use of plants that accumulate particularly high levels of the toxic contaminants throughout their lifetime. The roots of the established plants absorb metal elements from the soil and translocate them to the above-ground shoots where they accumulate (hyperaccumulators), while induced phytoextraction take place if metal availability in the soil is not adequate for sufficient plant uptake, chelates or acidifying agents may be used to liberate them into the soil solution\textsuperscript{56-58}.
2.2.4 Phytovolatization

Some metal contaminants such as As, Hg, and Se may exist as gaseous species in the environment. There are some naturally occurring or genetically modified plants that are capable of absorbing elemental forms of these metals from the soil, biologically converting them to gaseous species within the plant and volatized into the atmosphere through the stomata\textsuperscript{59-61}.

There are certain members of Brassicaceae are capable of releasing up to 40 g Se ha\(^{-1}\) day\(^{-1}\) as various gaseous compounds. Some aquatic plants such as cattail (\textit{Typha latifolia} L.) are also good for Se phytoremediation. \textit{Arabidopsis thaliana} L. and tobacco (\textit{Nicotiana tabacum} L.) have been genetically modified with bacterial organomecurial lyase and mercuric reductase genes. These plants absorb elemental Hg (II) and methyl mercury from the soil and release volatile Hg (0) from the leaves into the atmosphere\textsuperscript{62-65}.

This remediation method has the added benefits of minimal site disturbance, less erosion, and no need to dispose of contaminated plant material\textsuperscript{66}.

2.2.5 Phytodegradation

In phytodegradation, organic pollutants are converted by internal or secreted enzymes into compounds with reduced toxicity\textsuperscript{29,49,59}. For instance, the major water and soil contaminant trichloroethylene (TCE) was found to be taken up by hybrid poplar trees, \textit{Populus deltoides x nigra}, which breaks down the contaminant into its metabolic components\textsuperscript{57}. TCE and other chlorinated solvents can be degraded to form carbon dioxide, chloride ion and water\textsuperscript{60}. 
2.3 Biodiversity prospects for phytoremediation of metals in the environment

Many hazardous waste sites contain a mixture of contaminant like salts, organics, heavy metals, trace elements, and radioactive compounds\textsuperscript{67-69}. The simultaneous clean-up of multiple, mixed contaminants using conventional chemical and thermal methods are both technically difficult and expensive; these methods also destroy the biotic component of soils. Biodiversity prospects offer a several opportunities of which the most important is to save as much as possible of the world’s immense variety of ecosystems. It would lead to the discovery of wild plants that could clean polluted environments of the world. The desire to capitalize on this new ideas need to provide strong incentives for conserving nature. Aquatic plants in fresh water, marine and estuarine systems act as receptacle for several metals\textsuperscript{70-75}.

Examples of simpler phytoremediation systems that have been used for years are constructed or engineered wetlands, often using cattails to treat acid mine drainage or
municipal sewage. Our work extends to more complicated remediation cases: the phytoremediation of a site contaminated with heavy metals and/or radionuclides involves "farming" the soil with selected plants to "biomine" the inorganic contaminants, which are concentrated in the plant biomass\textsuperscript{25,76}. For soils contaminated with toxic organics, the approach is similar, but the plant may take up or assist in the degradation of the organic compounds\textsuperscript{68}. Several sequential crops of hyper accumulating plants could possibly reduce soil concentrations of toxic inorganics or organics to the extent that residual concentrations would be environmentally acceptable and no longer considered hazardous. The potential also exists for degrading the hazardous organic component of mixed contamination, thus reducing the waste (which may be sequestered in plant biomass) to a more manageable radioactive one.

For treating contaminated wastewater, the phytoremediation plants are grown in a bed of inert granular substrate, such as sand or pea gravel, using hydroponic or aeroponic techniques. The wastewater, supplemented with nutrients if necessary, trickles through this bed, which is ramified with plant roots that function as a biological filter and a contaminant uptake system. An added advantage of phytoremediation of wastewater is the considerable volume reduction attained through evapotranspiration\textsuperscript{77}.

Phytoremediation is well suited for applications in low-permeability soils, where most currently used technologies have a low degree of feasibility or success, as well as in combination with more conventional clean up technologies (electromigration, foam migration, etc.). In appropriate situations, phytoremediation can be an alternative to the much harsher remediation technologies of incineration, thermal vaporization, solvent washing, or other soil washing techniques, which essentially destroy the biological component of the soil and can drastically alter its chemical and physical characteristics as well, creating a relatively nonviable solid waste. Phytoremediation actually benefits the soil, leaving an improved, functional, soil ecosystem at costs estimated at approximately one-tenth of those currently adopted technologies. Phytoremediation is actually a generic term for several ways in which plants can be used to clean up contaminated soils and water. Plants may break down or degrade
organic pollutants, or remove and stabilize metal contaminants. This may be done through one of or a combination of the methods. The methods used to phytoremediate metal contaminants are slightly different to those used to remediate sites polluted with organic contaminants.

The various type of phytoremediation process like, Phytoextraction, Rhizofiltration, Phytostabilization, Phytovolatization, phytodegradation has been reported. The key factor for the success of remediation process depends on characteristics to mine waste, geo climatic conditions, types of amendment used and selection of plants species. Evaluation of the different fraction of bioavailable metals, their mobility in plant parts and growth of the plant species on contaminated side could be helpful for phytoremediation of metallic waste. Data is given in Table 2.1.

Table 2.1: Phytoremediation process

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Process</th>
<th>Media</th>
<th>Contaminants</th>
<th>Plants</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoextraction</td>
<td>Hyper-accumulation</td>
<td>Soil, sediment, brown fields</td>
<td>Metals: Cd,Cu, Ni, Pb, Zn with EDTA addition of Pb, selenium</td>
<td>Indian mustard, sunflowers, pennycress, Crusifers, Rape seed plants, barley, alyssum</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) with EDTA addition</td>
<td>Brassica juncea (Indian mustard) and Helianthus annuus (sunflower)</td>
<td>63,64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soil, sediment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soil, sediment</td>
<td>Zn, Co, Cu Se, Pb and Cd</td>
<td>Brassicaceae, Fabaceae, Euphorbiaceae, Asteraceae, Lamiaceae</td>
<td>50</td>
</tr>
<tr>
<td>Contaminant extraction and capture</td>
<td>Soil, sediment, sludges</td>
<td>Metals: Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn; Radionuclides: $^{90}$Sr, $^{137}$Cs, $^{239}$Pu, $^{234}$U, $^{238}$U</td>
<td>Indian mustard, sunflowers, hybrid</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------------------------</td>
<td>-----------------------------------------------------------------</td>
<td>-------------------------------------</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>Contaminant extraction</td>
<td>Soil</td>
<td>Metals: Ag, Cd, Pb</td>
<td>Perennial ryegrass (Lolium perenne)</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Rhizofiltration</td>
<td>Ground water, waste water, lagoons or created wetland</td>
<td>Metals: Cd, Cu, Ni, Pb, Zn; Radionuclides: $^{90}$Sr, $^{137}$Cs, $^{238}$U</td>
<td>Aquatic plants-emergents (Bullrush, cattail, pondweed, arrow root, duckweed) Sebmergents (algae, hydrilla, stonewort, parrotfeather)</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Contaminant extraction and capture</td>
<td>Ground water and surface water</td>
<td>Metals, radionuclides</td>
<td>Sunflowers, Indian mustard, water hyacinth</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Phytostabilization</td>
<td>Soil, sediment sludges</td>
<td>As, Cd, Cr, Cu, Hs, Pb, Zn</td>
<td>Indian mustard, hybrid poplars, grasses</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Complexation</td>
<td>Soil, sediment</td>
<td>Metals: Cd, Cu, Ni, Pb, Zn, Cr, As, Se, U; Hydrophobic</td>
<td>Grasses with fibrous root</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Organism</td>
<td>Phytodegradation</td>
<td>Contaminant destruction</td>
<td>Soil, sediment sludges</td>
<td>Organic compounds, chlorinated solvents, phenols, herbicides, munitions</td>
<td>Algae, stonewort, hybrid poplar, black willow, bald cypress</td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>------------------------</td>
<td>-----------------------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>Degradation in plants</td>
<td>Soil, ground water, land fill leachate land application of waste water</td>
<td>Herbisides ( atrazine, alachlor) Aromatics (BTEX) Choriated alipatics (TCE), Nutrients ( NO₃⁻, NH₄⁺,PO₃⁻), Ammunition waste TNT, RDX</td>
<td>Phreatophyte trees (Popular willow, cotton wood, grasses rye, Bermuda sorghum fescue) Legumes clover alfalfa, cowpeas</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Phytovolatilization</td>
<td>Contaminant extraction from media and release to air</td>
<td>Soil, sediment sludges</td>
<td>Chlorinated solvents, some inorganics (Se, Hg, and As)</td>
<td>Poplars, alfalfa black locust, Indian mustard</td>
<td>35</td>
</tr>
<tr>
<td>Volatilization by leaves</td>
<td>Soil, sediment, ground water</td>
<td>Se, Hg, and Ti</td>
<td>Poplars, Indian mustard, Canola, Tobacco plant</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>volatilization to the atmosphere</td>
<td>Soil</td>
<td>Inorganic pollutant Ni,Zn, Cd, As, Se, Cu,Co,Pb,Hg, and Radionuclides</td>
<td>Soil plants</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>
A comparison of the performance of process phytoextraction has been reported by several scientists\textsuperscript{78-80}. They used the various processes to extract the contaminants from the various plants.

Phytoextraction involves the removal of toxins, especially heavy metals and metalloids, by the roots of the plants with subsequent transport to aerial plant organs\textsuperscript{29,50}. Pollutants accumulated in stems and leaves are harvested with accumulating plants and removed from the site. In the case of heavy metals, chelators like EDTA assist in mobilization and subsequent accumulation of soil contaminants such as lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) in \textit{Brassica juncea} (Indian mustard) and \textit{Helianthus anuus} (sunflower)\textsuperscript{80-81}. The ability of other metal chelators such as CDTA, DTPA, EGTA, EDDHA, and NTA to enhance metal accumulation has also been assessed in various plant species\textsuperscript{82-83}. However, there may be risks associated with using certain chelators considering the high water solubility of some chelator-toxin complexes which could result in movement of the complexes to deeper soil layers\textsuperscript{50,84} and potential ground water and estuarian contamination. There data is also given in Table no. 1

G. M Pierzynski\textsuperscript{85} explain the Applicable Contaminants/Constituents amenable to phytoextraction include Metals, (Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn.), Metalloids (As, Se), Radionuclides, (\textsuperscript{90}Sr, \textsuperscript{137}Cs, \textsuperscript{239}Pu, \textsuperscript{238}U, \textsuperscript{234}U). The accumulation of organics and subsequent removal of biomass generally has not been examined as a remedial strategy.

The relative degree of uptake of different metals will vary. Experimentally-determined phytoextraction coefficients [ratio of g metal/g dry weight (DW) of shoot to g metal/g DW of soil] for \textit{B. junce} \textsuperscript{85} indicate, for example, that lead was much more difficult to take up than cadmium: (Table 2.2).
Table 2.2: Determined phytoextraction coefficients

<table>
<thead>
<tr>
<th>Metal</th>
<th>Phytoextraction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{5+}$</td>
<td>58</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>52</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>31</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>7.0</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>1.7</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 2.3: Contaminated soil concentrations

<table>
<thead>
<tr>
<th>Metal</th>
<th>Soil Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1,250 mg/kg</td>
<td>71</td>
</tr>
<tr>
<td>Cd</td>
<td>9.4 mg/kg</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>11 mg/kg</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>13.6 mg/kg</td>
<td>73</td>
</tr>
<tr>
<td>Cd uptake in vegetables</td>
<td>2000 mg/kg</td>
<td>74</td>
</tr>
<tr>
<td>Pb</td>
<td>110 mg/kg</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>625 mg/kg</td>
<td>70</td>
</tr>
<tr>
<td>Zn</td>
<td>444 mg/kg</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>1,165 mg/kg</td>
<td>72</td>
</tr>
<tr>
<td>Se</td>
<td>40 mg/kg</td>
<td>75</td>
</tr>
</tbody>
</table>
Contaminated soil concentrations used in research studies or found in field investigations are given below in Table 2.3. These are total metal concentrations; the mobile or available concentrations would be less.

The study on assessment of heavy metal accumulation in certain aquatic macrophytes used as biomonitors, in comparison with water and sediments (abiotic monitors) for phytoremediation carried out by some workers. Roots, stems and leaves of native aquatic plants (biomonitors) represented by seven species: *Ipomoea aquatica* Forsk, *Eichhornia crassipes*, (Mart.) Solms, *Typha angustata* Bory & Chaub, *Echinochloa colonum* (L.) Link *Hydrilla verticillata* (L.f.) Royle, *Nelumbo nucifera* Gaerth. And *Vallisneria spiralis* L. along with surface sediments and water were analyzed for Cd, Co, Cu, Ni, Pb and Zn contamination.

The greater accumulation of heavy metals was observed in *Nelumbo nucifera* and the poor content in *Echinochloa colonum*. Based on the concentration and toxicity status observed in the lake's vegetation, the six heavy metals are arranged in the following descending order: Zn > Cu > Pb > Ni > Co > Cd compared with the standard, normal and critical toxicity range in plants. The detected values of Cd and Pb fall within normal range, while that of Co and Ni were within the critical range. However, Zn and Cu showed the highest accumulation with alarming toxicity levels, which are considered as one of the most hazardous pollutants in Pariyej reservoir. Species like *Typha angustata* and *Ipomoea aquatica* are also proposed as bioremediants, which are the two most useful plant species in phytoremediation studies due to their ability to accumulate heavy metals in high concentration in the roots. The results showed the significant differences in accumulation of metals like Zn, Cu and Pb in different plant organs, in roots than that of stems and leaves. Data is given in Table no.2.4.
Table 2.4: Heavy metal concentration in sediments and water and ratios between the concentration in the sediments and that in the water

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sediment (ppm)</th>
<th>Water (ppm)</th>
<th>Sediment / Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.27</td>
<td>0.74</td>
<td>1.70</td>
</tr>
<tr>
<td>Co</td>
<td>34.88</td>
<td>1.76</td>
<td>19.81</td>
</tr>
<tr>
<td>Cu</td>
<td>105.78</td>
<td>19.67</td>
<td>5.38</td>
</tr>
<tr>
<td>Ni</td>
<td>58.08</td>
<td>10.13</td>
<td>5.73</td>
</tr>
<tr>
<td>Pb</td>
<td>9.47</td>
<td>6.11</td>
<td>1.55</td>
</tr>
<tr>
<td>Zn</td>
<td>2114.82</td>
<td>160.70</td>
<td>13.16</td>
</tr>
</tbody>
</table>

There are three main strategies currently exist to phytoextraction inorganic substances from soils using plants\(^{81}\): (1) use of natural hyperaccumulators; (2) enhancement of element uptake of high biomass species by chemical additions to soil and plants; and (3) phytovolatization of elements, which often involves alteration of their chemical form within the plant prior to volatilization to the atmosphere. Concentrating on the techniques that potentially remove inorganic pollutants such as Ni, Zn, Cd, Cu, Co, Pb, Hg, As, Se, and radionuclides, we review the progress in the understanding of the processes involved and the development of the technology.(Table 2.1)

The best example of volatilization is the volatilization of mercury (Hg) by conversion to the elemental form in transgenic *Arabidopsis* and yellow poplars containing bacterial mercuric reductase\(^{91-93}\) (fig 2.2). In a study where the movement of volatile organics was monitored by Fourier transform infrared spectrometry (FT-IR) in hybrid poplars (*Populus deltoides x nigra*), *Tamarix parviflora* (saltcedar), and *Medicago sativa* (alfalfa), chlorinated hydrocarbons were found to move readily through the plants, but less polar compounds like gasoline constituents did not\(^{53}\). However, amounts of the contaminant transpired are in proportion to water flow and are relatively low, especially in the field\(^{94}\).
Found that poplar saplings can concentrate (100 ppb) and transpire methyl tertiary-butyl ether (MTBE), a compound added to gasoline which is commonly found as a groundwater pollutant. In a one week time period, they observed a 30% reduction in MTBE mass in hydroponic solution by saplings at both high (1600 ppb) and low (300 ppb) MTBE concentrations, which suggested that these plants could be successful in the phytoremediation of this toxin from groundwater. Selenium (Se) is a special case of a metal that is taken up by plants and volatilized. Se can also be volatilized following conversion to dimethylselenide by microbes and algae.

Fig 2.2: Volatilization Process
Applicable Contaminants to the phytovolatization include the organic contaminants such as Chlorinated solvents include TCE, 1,1,1-trichloroethane (TCA) and carbon tetrachloride\textsuperscript{95-96} and the inorganic contaminants Se and Hg, along with As, can form volatile methylated species\textsuperscript{85}.

Poplars have also been shown to take up the ammunition wastes 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX) and partially transform them\textsuperscript{97-98}. Root exudates from \textit{Datura innoxia} and \textit{Lycopersicon peruvianum} containing peroxidase, laccase, and nitrilase have been shown to degrade soil pollutants\textsuperscript{49,99} and nitroreductase and laccase together can break down TNT, RDX, and HMX\textsuperscript{50}. The plants are then able to incorporate the broken ring structures into new plant material or organic soil components that are thought to be non-hazardous.

Organic compounds are the main category of contaminants subject to phytodegradation. In general, organic compounds with a \( \log k_{\text{ow}} \) between 0.5 and 3.0 can be subject to Phytodegradation within the plant. Inorganic nutrients are also remediated through plant uptake and metabolism. Phytodegradation outside the plant does not depend on \( \log k_{\text{ow}} \) and plant uptake.

The applicable contaminants amenable to Phytodegradation\textsuperscript{100} include Organic contaminants Phenols, Munitions. The example of Organic contaminants is Chlorinated solvents. TCE was metabolized to trichloroethanol, trichloroacetic acid, and dichloroacetic acid within hybrid poplar trees. In a similar study, hybrid poplar trees were exposed to water containing about 50 ppm TCE and metabolized the TCE within the tree. L. A Licht et al\textsuperscript{101} explain the inorganics contaminants, nutrients: Nitrate will be taken up by plants and transformed to proteins and nitrogen gas.

A multi-process phyto remediation system (MPPS) developed by certain workers\textsuperscript{102} that utilizes plant/PGPR (plant growth promoting rhizobacteria) interactions to mitigate stress ethylene effects, thereby greatly increasing plant biomass, particularly in the
rhizosphere. The MPPS degrades a variety of organic contaminants in soils with accelerated remediation kinetics. Over the last two years at a petroleum impacted site in Sarnia, ON, a decrease of ~ 50% in CCME fractions 3 and 4 was observed. At a site in Turner Valley, AB, 30% remediation of total petroleum hydrocarbons was achieved in 3.5 months. Recently, we tested the MPPS in salt-impacted soils in greenhouse experiments, with promising preliminary results.

Dushenkov S. et al.\textsuperscript{103} have been developed the subsets - phytoextraction, which is based on using high biomass crop plants in combination with a system of soil amendments to extract heavy metals from soil, and rhizofiltration, a technology which employs plants to remove contaminants from aqueous streams.

Rhizofiltration was also shown to be useful in the San Francisco Bay study directed by Norman Terry (University of California, Berkely) and supported by Chevron\textsuperscript{104}. A wetland constructed next to the bay was shown to remove 89% of the Se from selenite contaminated wastewater released from various oil refineries. The water flowing into the wetland was measured to have 20–30 μg L\textsuperscript{-1}selenite, while the outflow from the wetland had less than 5 μg L\textsuperscript{-1} selenite\textsuperscript{104}. In a study of Se removal from agricultural subsoil drainage in the San Joaquin Valley\textsuperscript{105}, a flow-through wetland system was constructed with cells containing either a single species, or a combination of species [e.g. Schoenoplectus robustus (sturdy bulrush), Juncus balticus (baltic rush), Spartina alterniflora (smooth cordgrass), Polypogon monspeliensis (rabbit’s foot grass), Distichlis spicata (saltgrass), Typha latifolia (cattail), Schoenoplectus acutus (Tule grass), and Ruppia maritima (widgeon grass)]. Four years after planting, comprehensive analysis showed that 59% of the Se remained in the wetland, mostly in the organic detrital layer and surface sediment, 35% in the outflow, 4% in seepage and 2% to volatilization. Wetland plant uptake of Se varies with species type, and parrot’s feather (Myriophyllum aquaticum), iris-leaved rush (Juncus xiphioides), cattail, and sturdy bulrush were particularly noted for high Se uptake potential\textsuperscript{105}.
The applicable Contaminants/Concentrations Constituents amenable to phytoremediation\textsuperscript{106-108} include the Metals such as Lead (Pb\textsuperscript{2+}), Cadmium (Cd\textsuperscript{2+}), Chromium (Cr\textsuperscript{6+}), Copper (Cu\textsuperscript{2+}), Nickel (Ni\textsuperscript{2+}), Zinc (Zn\textsuperscript{2+}) and Radionuclides such as Uranium (U), Cesium (Ce), Strontium (Sr).

Contaminated water concentrations used in research studies or found in field investigations are given below in Table 2.5.

**Table 2.5: Contaminated water concentrations found in field investigations**

<table>
<thead>
<tr>
<th>Plant</th>
<th>Metal (water concentration)</th>
<th>Ref-No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb\textsuperscript{2+}</td>
<td>Cd\textsuperscript{2+}</td>
</tr>
<tr>
<td><strong>Indian mustard roots</strong></td>
<td>2mg/L</td>
<td>2mg/L</td>
</tr>
<tr>
<td><strong>Brassica juncea</strong></td>
<td>20 to 2000 g/L</td>
<td>20 to 2000 g/L</td>
</tr>
<tr>
<td><strong>Myriophyllum spicatum</strong></td>
<td>1 to 16 mg/L</td>
<td>1 to 16 mg/L</td>
</tr>
</tbody>
</table>

The different plants contain different metals in varying concentration. Sometimes these metals are useful for environment and some time these are very hazardous. So by using Rhizofiltration techniques\textsuperscript{106-108} the metals can be extracted from various plants. Rhizofiltration is the recent using technique, which is gaining popularity in the field of phytoremediation. Many scientists have work over this, with different concentration of water we are able to extract these metals and then processed these for future use.
A basic research program for developing a phytostabilization revegetation strategy to remediate mine tailings in arid and semi-arid ecosystems was carried out. The researchers will monitor the bioavailability of metals for the native metal- and droughttolerant plant species used, and determine the permanence of expected toxicity reductions. Plants with high transpiration rates, such as grasses, sedges, forage plants, and reeds are useful for phytostabilization by decreasing the amount of ground water migrating away from the site carrying contaminants. Combining these plants with hardy, perennial, dense rooted or deep rooting trees (poplar, cottonwoods) can be an effective combination.

Phytostabilization has not generally been examined in terms of organic contaminants. The following is a discussion of metals and metal concentrations, with implications:

- Arsenic: As (as arsenate)
- Cadmium: Cd
- Chromium: Cr
- Copper: Cu
- Mercury: Hg

Researchers have different views about the potential for use of phytoremediation to clean up contaminated soils and water using plants comprised of two components, one by the roots colonizing microbes and the other by plants themselves, which accumulate the toxic compounds to further non toxic compounds. Plant assays are highly sensitive to many environmental pollutants, including heavy metals and have been used for monitoring the potential synergistic effects of mixtures of pollutants. It is green technology and most important because it’s by products can find a range of other uses. Various Compounds viz. organic synthetic compounds, xenobiotics, pesticides, hydrocarbon and heavy metals are among the contaminants that can be effectively remediated by plants.

Aquatic plants absorb elements through roots and shoots. Much of the metal uptake by plant tissue occurs by absorption to anionic sites in the cell wall and metals do not actually enter the living plants. In aquatic systems, where pollutants inputs are discontinuous and pollutants are quickly diluted, analysis of plant components provide time-integrated information about the quality of the system. Biomonitoring of pollutants using some plants as accumulator species, accumulate relatively large...
amounts of certain pollutants, even from much diluted solutions without obvious noxious effects\textsuperscript{117}.

Various macrophytes have been tested as phytoremediators to purify water by removing nitrogen and phosphorus, elements that cause eutrophication\textsuperscript{118-119}. Aquatic macrophytes can also remove sulphadimethoxine (drug)\textsuperscript{120} and metals like Sr, Cu, Cd, Zn, Cr, Fe, Ni, Pb, Au, Pt and even radioactive elements\textsuperscript{121-125}. According to the component systems of aquatic macrophytes the order based on their accumulation capacity of heavy metals as: Sediment> Root system> Stem system>Leaf system\textsuperscript{126}.

It has been found that heavy metal accumulation in phytoremediators is responsible for the decrease in total chlorophyll concentration and negatively affects the Chl a/Chl b ratio\textsuperscript{127-128}. However, the capacity to accumulate heavy metals in aboveground plant tissues represents the suitability of the plants for metal phytoextraction\textsuperscript{129}.

Some researchers have examined the naturally occurring hyper accumulators, plants which can accumulate 10-500 times higher levels of elements than crops. Plants act as hyper accumulators in following ways:

(1) The plants must be able to tolerate high levels of the element in root and shoot cells.

(2) Hyper tolerance is the key property which makes hyper accumulation possible. Hypertolerance is believed to result from vacuolar compartmentalization and chelation\textsuperscript{130-131}.

The plant must have the ability to translocate an element from roots to shoots at high rates. In hyperaccumulators, shoot element concentration can exceed root levels\textsuperscript{132-134}. There must be a rapid uptake rate for the element at levels which occur in soil solution. Different patterns have been observed in different groups of hyperaccumulators\textsuperscript{132,135}.  

51
The water hyacinth was chosen because it is well-known for its adaptability, alkalescence resistance, fertilizer resistance and tolerance to diseases. Water hyacinth sustains a natural growth in water with a pH of 9. Apart from improving water quality and pollution control, chemical analysis has shown that water hyacinth is rich in nutrition; with organic matter particularly protein content, vitamins, minerals, fertilizer, chemicals and energy (in the form of biogas) which reduced its nuisance value\textsuperscript{136}. Investigations on bioaccumulation and toxicity of Cu, and Cd and uptake of Pb by \textit{Vallisneria spirallis} has been performed under the laboratory conditions\textsuperscript{137-138}, which indicates \textit{V.spirallis} as potential as a phytoremediator. Duckweed is an aquatic, floating plant. It is widely distributed in the world from tropical to the temperate zones, from fresh water to brackish estuaries. Duckweed possess physiological properties like small size, high multiplication rates and vegetative propagation and can be used in a wide range of pH (3.5-10) which make them an ideal test system. It can accumulate certain chemicals and may serve as biological monitors\textsuperscript{139}.

2.4 Phytoremediators

2.4.1 \textit{Eichhornia crassipes} (Water hyacinth)

\textit{Eichhornia crassipes} is a floating plant and has an astonishing reproductive rate and its roots can directly absorb the suspended particulate. Research over the past decades has proved that some floating plants, such as water hyacinth (\textit{E.crassipes}), water lettuce (\textit{Pistia stratiotes}), pennywort (\textit{Hydrocotyle umbellate}), duckweed (\textit{Lemna minor}), water peanut (\textit{Alternanthera philoxeroides}) and lidded cleistocalyx (\textit{Cleistocalyx operculatus}), have the greatest effects on purifying eutrophic water\textsuperscript{140-142}. Therefore, water hyacinth and duckweed were applied in the treatment of wastewater\textsuperscript{143-144}.

The potential of Water hyacinth on the nutrient regime of a lake ecosystem for sewage treatment has been found out by many researchers\textsuperscript{145-146}. Water hyacinth is a prolific aquatic weed of cosmopolitan distribution with a huge potential for the removal of vast range of pollutants from waste water\textsuperscript{147-151}. All these models show logistic growth in the plant, and are dependent on environmental factors.
The ability of *E.crassipes* to take up and translocate As (V), Cd (VI), Cr (VI), Cu (II), Ni (II) and Sc (VI) under controlled conditions has been studied by some workers. According to Jain et al. the water hyacinth has ideal characteristics for water purification and pollution control. The production of high quality vegetable protein, vitamins, minerals, fertilizers, chemicals and energy in the form of biogas from water hyacinth had reduced its nuisance value and made it potential provider. *Eichhornia crassipes* has a high capacity for the uptake of heavy metals, including Cd, Cr, Ni, Co, Pb, and Hg which could make it suitable for the biocleaning of industrial water.

Although water hyacinth is an invasive plant in most countries all over the world, it is also used as a resource in agricultural production and waste water treatment. Water hyacinth is also observed to accumulate Cr (III) in root and shoot tissues in nutrient culture supplied with Cr (VI). Reduction in nontoxic form appeared to occur in the fine lateral roots. In addition to heavy metals, *Eichhornia crassipes* can also remove other toxins, such as cyanide which is environmentally beneficial in areas that have endured gold mining operations.

*Eichhornia crassipes* reduce COD and BOD from paper mill effluent. The percentage of removal was doubled with a detention time of two days and argued that such reduction is related to both physical setting and plant absorption and the removal of nitrogen and phosphorus by biomass production was correlated with factor favoring this production. Among floating aquatic plants, water hyacinth has been extensively studied at the laboratory and pilot levels and evaluated on a large scale for removing organic matter from wastewater.

*E.crassipes, P.stratiotes, L.minor, A. pinnata* and *S. polyrhiza* have wide spread availability and have capability to remove pollutants. *E.crassipes* was the most efficient accumulator among these aquatic macrophytes. *E.crassipes* effectively removes appreciable quantities of heavy metals from wastewater, especially at low concentrations. A plant with relatively high biomass
may have a greater metal uptake capacity, due to lower metal concentration in its tissues because of a growth rate that exceeds its uptake rate. There is higher accumulation of heavy metals in broad-leaved plant *E. crassipes*.

### 2.4.2 *Vallisneria spiralis* (Channel grass)

The elemental composition of certain aquatic plants by X-rays and found high level of heavy metals such as Al, Si, Mn and Fe being found accumulated in *Vallisneria spiralis*, *Hydrida verticillata* and *Azolla pinnata*. Phytoaccumulation of heavy metals by selected fresh water macrophytes viz. *Eichhonia crassipes*, Ipomoea aquatic, *Typha angustata*, *Hydrida verticillata* and *Vallisneria spiralis* was studied to assess the phytoremediation of six heavy metals in Nal Sarovar Bird Sanctuary and Pariyej Community Reserve, Gujarat, India and found that it is necessary to carry out phytoremediation of heavy metal contamination and sediments.

Aquatic macrophytes *Hydrida verticillata* and *Vallisneria spiralis* were studied to see the change in protein profile by the effect of lead and mercury. The accumulation of metals increased with the increasing treatment concentrations, although the amount of Hg accumulated was less than that of Pb in both plants.

Phytoremediated potential of *Vallisneria spiralis* was observed on the industrial effluents. They observed that reduction in BOD, COD, TS, TDS, TSS and lignin due to phytodegradation, phytoextraction and phytovolatilization and reduction in Na and K content in the effluents due to phytoextraction, rhizofiltration and phytostabilization. The change in pH, EC and colour unit could be due to changes in above mentioned parameters through total phytoremediation.

Three water weeds, water hyacinth, pseudo water hyacinth and Lemna species were tested for the removal of chromium from tannery effluent. Water hyacinth accumulated the most chromium (38ppm) followed by Lemna and pseudo water
hyacinth. In all three species the root accumulated higher amounts of chromium than the foliage.

A freshwater submerged, rooted wetland species plants of *Vallisneria spiralis* were tested for Cr accumulation and found that these plants can effectively remove Cr by adsorption and absorption into plant tissues.\textsuperscript{170} and its harvested wetland plant biomass used in biogas production\textsuperscript{171,172}.

### 2.4.3 *Lemna minor* (Duckweed)

Duckweed is a small, free floating aquatic plant belonging to Lemnaceae family\textsuperscript{173} It has been found that *lemna* species have many unique properties ideal for phytoremediation plant species: they have fast growth and primary production; high bioaccumulation capacity; ability to transform or degrade contaminant; ability to regulate chemical speciation and bioavailability of some contaminant in their milieu; resilient to extreme contaminant concentration; and can be applied on multiple pollutants simultaneously. In addition, they have properties significant for public health livestock production and aquaculture and ecological function. Duckweed wastewater treatment systems have been studied for a wide range of wastewater types. Most of the studies have focused on nutrient removal efficiencies and removal rates between 50-95% have been reported for duckweed covered systems\textsuperscript{174-176}.

The duckweed mat, which fully covers the water surface, results in three zones i.e. aerobic, anoxic and anaerobic zone\textsuperscript{177}. In the aerobic zone, organic materials are oxidized by aerobic bacteria using atmospheric oxygen transferred by duckweed roots \textsuperscript{178}.Nitrification and denitrification takes place in anoxic bacteria into ammonium and ortho-phosphate, which are intermediate products used as nutrients by the duckweed\textsuperscript{179}. Duckweed is used in water quality studies to monitor heavy metals and other aquatic pollutants, because it may selectively accumulate certain chemicals and may serve as biological monitors\textsuperscript{140}. 
Aquatic weed-based wastewater treatment plants revealed maximum reduction in suspended solids, BOD and COD, nitrogen, phosphorus, oil and grease\textsuperscript{180-181}. Similar report has been made by Rose et al.,\textsuperscript{182} who inferred that \textit{Lemna minor} is efficient in removing BOD, solids and nutrient from the wastewater.

Higher concentration of nutrients in wastewater resulted in growth and further accumulation of heavy metals \textit{E.crassipes} and \textit{L.minor} showed the high accumulation of Cd among broad-leaved and small-leaved plants. Higher removal of heavy metals by \textit{E.crassipes} and \textit{Lemna minor} may be due to their luxuriant growth in nutrient and heavy metal rich media. Physicochemical analysis shows secondary treated wastewater has high concentrations of nutrients as well as heavy metals\textsuperscript{45}.

The elimination of organic material in terms of BOD and COD is lower in \textit{Lemna} sp. In comparison to other vascular plants and rich in cellulose but the nitrogen removal is same or higher\textsuperscript{183}. Under experimental conditions, \textit{L.minor} is a good accumulator of Cd, Se and Cu but a moderate accumulator of Cr and poor accumulator of Ni and Pb\textsuperscript{184}. Lemna spp. have potential of accumulation of U as well as As in surface waters of decommissioned uranium mining\textsuperscript{185-186}.

\textit{Lemna minor} found suitable for surface water quality assessment as selected endpoints showed consistency among each other with respect to different water samples. The consistency among observed endpoints might lie in the highly homogeneous plant material; due to predominantly vegetation reproduction of duckweed, new fronds are formed by clonal propagation thus producing a population of genetically homogeneous plants. Moreover, water and substances to be tested are taken up directly through the leafy fronds\textsuperscript{187}. Most Lemna plants are capable of withstanding an extreme concentration of contaminants by sequestrating and compartmentalizing them into cell organelles\textsuperscript{188-189}. The immature cells of the enclosed daughter fronds contained large deposits with Cd and S as C-Phytochelatin. Excess Ca\textsuperscript{2+} in \textit{L.minor} and \textit{L.gibba} is deposited in the cells As Ca oxalate\textsuperscript{190-191}.
2.5 Phytoremediated plant biomass as a source of energy

Water hyacinth due to its rapid growth\textsuperscript{192} has been widely employed for the treatment of a variety of wastewaters\textsuperscript{193-195} and has also been a good biogas producer\textsuperscript{196-197}.

The high growth rate of water hyacinth makes it an attractive feed for energy recovery through biogas\textsuperscript{198}. However, water hyacinth has a low solids content (in the range of 7% TS) and needs to be concentrated for efficient use in biogas production\textsuperscript{199}. As \textit{Eichhornia crassipes} has abundant nitrogen content, it can be used as a substrate for biogas production and the sludge obtained for the biogas. The application of sewage sludge to fermenting organic residues enhanced biogas generation\textsuperscript{200}. The animal dung served as a good seeding material for the biogas fermentation process\textsuperscript{201}.

In phytoremediation the plants absorb metals and other toxic materials from wastewaters for metabolic use and sequestering in their body which could make them suitable for the biocleaning of industrial effluent\textsuperscript{31,153}. The rate of biogas production depends on the status, type and constituents of organic materials undergoing fermentation\textsuperscript{202-205} as well as on the digester operating conditions\textsuperscript{206}. In addition to these factors anaerobic digestion and biogas production was influenced by pH, nutrient addition\textsuperscript{207-208} C/N ratio\textsuperscript{209-210}, C/P ratio\textsuperscript{205}, trace elements like iron, vitamins\textsuperscript{211}, and natural inhabitants\textsuperscript{205} which are present in the biomass. Generally the C/N ratio is used as an index for the suitability of organic feed\textsuperscript{212}. The proposed ideal range of C/N ratio varies from 12 to 72\textsuperscript{205,213}.

Anaerobic digestion is proven as a relatively efficient conversion process for producing a collectable biogas mixture with average 60% methane content\textsuperscript{196,205,214}. The biogas used as a substitute of fuel in boilers and the resultant slurry left over as end product used for agricultural application as it has high N, P and K content, for agricultural application\textsuperscript{215}.

Bioenergy potential of eight aquatic weeds \textit{Salvinia molesta}, \textit{Hydrilla verticillata}, \textit{Nymphaea stellata}, \textit{Ceratopteris sp.}, \textit{Azolla pinnata}, \textit{Scirpus sp.}, \textit{Cyperus sp.} and
*Utricularia reticulate* was assessed by Abbasi et al.\textsuperscript{216}. Natural stands of *Salvinia* such as the one employed in study, would yield methane of the order of 10.8 Kcal ha\textsuperscript{-1} year\textsuperscript{-1}, while *Azolla, scirpus, Hydrilla* and *Nymphaea* had energy potentials of the order of 10 Kcal ha\textsuperscript{-1} year\textsuperscript{-1}. In order to digest a mixture of harvested aquatic plant biomass and primary sludge for biogas generation by anaerobic digestion was used by Chynoweth et al.\textsuperscript{217}

Potential productivity of water hyacinth and water chestnut in nutrient enriched waste water has lead to its selection for phytoremediation of various industrial effluents\textsuperscript{151,218}. Since these plants have high nitrogen content therefore, produced biomass used as a feed stock for biogas production to achieve economic success in energy produced from them. In 1971 it was pointed out by Widyanto et al.\textsuperscript{219} that utilization of *Eichhornia* for biogas production was advantageous because of its high water content, soft organic matter and a favourable C/N ratio i.e.20:1-30:1.

Biogas generation in certain aquatic weeds is relatively more and quicker due to their high water content\textsuperscript{220}. The greater biogas production from *Vallisneria spirallis* (Channel grass) could be accounted for their submerged natures which have resulted in fine slurry and finer particles resulted in greater biogas production\textsuperscript{197}.

### 2.6 Air pollution

Suspended particulate matter (SPM), a complex mixture of organic and inorganic substances, arising from both natural and anthropogenic sources, is a ubiquitous air pollutant. These are the particles present in air having particle size ranging from 10\textsuperscript{-3} μm to100μm. These particles have serious impacts on climate\textsuperscript{221-222}, visibility\textsuperscript{223}, biogeochemical cycling in ecosystems\textsuperscript{224} and health\textsuperscript{225-226}. Epidemiologic studies have shown that these particles are responsible for the various problems of the respiratory tract\textsuperscript{227}. Recent studies have shown that elevated fine PM is associated with increased mortality and morbidity\textsuperscript{228-230}. 

58
Particulate matter having size 10µm or less in diameter are called as respirable suspended particulate matter (RSPM), since it penetrates the respiratory system. RSPM is grouped into three types depending upon their size i.e. ultra fine (less than 0.1µm), fine (0.7-1 µm) and course (1-10µm) \(^{231-232}\). Major constituents of fine particles often consist of sulphates, carbonaceous materials, nitrates and trace elements\(^{233-234}\). Organic substances are the second major constituents of fine PM, constituting approx. 26-47\%.\(^{235}\) The coarse fraction mostly consists of aluminium, silicon, sulphur, calcium, potassium and iron (40-50\%) while sulphates, nitrates, ammonium ions, elemental and organic carbon consist of approx. 10-20\%.

The level of total suspended particulate is one of the basic and useful indicators for judging the degree of air pollution\(^{236}\). In order to monitor aerosol quantity and quality the national air quality standards are being reviewed in many countries so as to maintain healthy environment. In India air pollution studies around Delhi revealed that TSPM exceeds the air standards prescribed by Central Pollution Control Board, New Delhi\(^{237}\)

The physical and chemical characteristics of suspended particulate matter depend upon the source from which they are emitted. In a study on particle size distribution of SPM, carried out in ambient air of Nagpur\(^{238}\) and trace metals such as Fe, Mn, Cr, Pb, and Zn were determined. These particle size ranges such as less than 2.1 µm and 2.1µm. The analysis showed that Fe and Mn are associated with coarse fraction of particulates whereas Cr, Pb and Zn having anthropogenic origin are associated with fine fraction.

Level of air pollution in the ambient air of Amritsar was studied\(^{239}\). The study reveals that the average values of combustible matter at 600±10ºC to SPM ranged from 32.6-51.3% which may be due to the partially burnt fuel particles in the SPM. The average values of ratios of benzene soluble particulate matter (BSPM) to SPM at various sites ranged from 3.4-8.3% and overall average for the entire city is 6.4±5.2%. The mean value of BSPM content appears to be affiliated only to industrial activity and the attached vehicular traffic. It was observed that industrial emissions and automobile exhaust may be causal agents of lead\(^{240}\). The average value of Nickel is highest in the industrial zone. Cadmium has been found in traces in the air. There have been similar studies in
other cities of India as well viz. vishakhapatnam\textsuperscript{241-243}, Ahmedabad\textsuperscript{244}, Sindri\textsuperscript{245}, Firozabad\textsuperscript{246}, Kanpur\textsuperscript{247}, and Patiala\textsuperscript{248}.

The increment in the level of ambient air aerosol and gaseous pollution in and around Patiala was studied\textsuperscript{249} due to wheat and rice crop stubble burning practices. The crop stubble burning performed after the wheat and rice crop harvesting had changed the chemistry of ambient air in Patiala in 2007 by increasing the concentration of aerosols, \(\text{SO}_2\) and \(\text{NO}_2\) in the province. Although levels of \(\text{SO}_2\) and \(\text{NO}_2\) were fluctuating at different monitoring sites, high concentrations were obtained in the months of April and May (wheat crop stubble burning months) as well as October and November (rice crop stubble burning months).

\textbf{2.6.1 Sources for Particulate Matter}

1. The ultrafine particles less than 0.1 \(\mu\)m are formed by condensation of low vapour pressure substances formed by high temperature vaporization or by chemical reactions to form new particles, such as from wood smoke, automobile exhaust and emission from generators or diesel engines\textsuperscript{250-252}.

2. Fine particles of size range from 0.7-1 \(\mu\)m are formed by coagulation of ultra fine particles. The fine particles concentration was 58-68\% in close vicinity of road, due to exhaust released from traffic\textsuperscript{253}.

3. Biomass burning is an important source of fine organic aerosol and gaseous pollution in the atmosphere\textsuperscript{254-257}.

4. Coarse particles from 1- 200\(\mu\)m are emitted into atmosphere by mechanical sparing of rock or soil material. These particles are also found in the wind blown dust from agricultural processes, mining operation and uncovered soil. In urban environment dust arise due to agitation of soil through vehicular movement\textsuperscript{258} and earth moving\textsuperscript{234}.
5. During harvesting periods, open burning of agricultural residues releases a large amount of pollutants to the atmosphere, including aerosols and hydrocarbons. Due to traffic in urban region about 80% of coarse dust particles from traffic settle within 150m, about 40% at 200-270 m and about 20% at about 1500m from the road.

In 1987, the primary standard for Total suspended Particles was replaced with PM10, which includes the particles with diameter of 10µm or less. Then in 1997, the primary standard for PM10 was replaced with PM2.5 standard.

PM 10 fraction originated from three sources have significant effect on health
1. Primary fine particles from industrial and combustion sources mainly traffic.
2. Secondary aerosol formed from photochemical reactions, mainly ammonium sulphate and ammonium nitrate.
3. Windblown soil and resuspended street dust present in course fraction 2.5-10 µm.
4. Pollutants emanated from biomass burning can also affect properties, materials and moreover health problems when they inhaled, causing respiratory problems.

Particles deposit within the respiratory tract by several mechanisms inertial impaction, sedimentation, diffusion, electrostatic precipitation and interception. The interception or depth to which these particles can penetrate in the respiratory system depends upon the particle size as shown in figure. Electrostatic precipitation is deposition related to particle charge.
Figure 2.3: Respiratory system, showing the depth to which particles can penetrate
Source: U.S. EPA, Air Pollution Training Institute APTI, Course No. 435
It has been observed that smaller particles are typically man-made. Total Suspended particles have a bimodal distribution, with naturally occurring particles centred at about 10µm and man-made particles centered at about 0.4µm as shown in figure.

Figure 2.4: Bimodal distributions of Total Suspended particles
Source: U.S. EPA, Air Pollution Training Institute APTI, Course No. 435
References


20 Brassicaceae accessions from a wide geographic area. New Phytol. 159,421-430.


