CHAPTER 3
3. Review of Literature

3.1 Arsenic in groundwater

Sonderegger and Ohguchi (1988) reported that the arsenic (As) concentration in 13 water samples from wells in Montana, USA ranged from 26 to 150 \( \mu g \) per litre with a mean As concentration of 51 \( \mu g \) per litre. Evaporative concentration of the river-derived irrigation water was believed to have been the overwhelming factor in the contamination of this shallow aquifer.

Robertson (1989), while studying the concentration of dissolved As in groundwater in alluvial basins of Arizona, reported that the As concentration commonly exceeded 50 \( \mu g \) per litre and reached as high as 1300 \( \mu g \) per litre. The As occurred in the fully oxidised state (pentavalent As), most likely in the form of \( \text{HASO}_4^{2-} \) under the existing oxidising and pH conditions, and was presumably oxidised to soluble As before getting transported into the basin. It was also observed that arsenic content of alluvial materials ranged from 2 to 88 mg As/kg.

Korte and Fernando (1991) reported that trivalent As was more prevalent in groundwater than previously believed and the reducing conditions in the alluvial aquifers may be responsible for the exposures of the local population to naturally occurring As (III). Arsenic (III) is both more toxic and mobile in the environment than As (V). A complex series of geochemical reactions undergone by As renders the investigation of As (III) in the environment quite difficult. The mechanisms, which promote the mobility of As (III) in groundwater, are reducing conditions in alluvium in which iron oxides have sorbed As. Such conditions may result in concentrations of As in groundwater as high as several hundred micrograms per litre.

Boyle et al. (1998), while reporting some geochemical factors that control the concentration and mobility of As in groundwater in British Columbia, included anion exchange of As from clay minerals during cation (divalent/univalent) exchange processes (water softening) which leads to waters of high pH and high anion exchange capacities desorption of As from Fe and Al oxyhydroxide minerals during pronounced shifts in pH from acid to alkaline conditions brought on by the water
softening process; and stepwise oxidation of arsenopyrite mineralization to form arsenous sulphate-bearing groundwater.

While conducting experiments with sixteen irrigated (> 20 yr irrigation) and non-irrigated (never irrigated) soils in Madison and Upper Missouri rivers, Jones et al. (1999) concluded that Madison River water containing approximately 0.6 to 1.3 mM As had the potential to alter the soil solution As concentrations through a variety of mechanisms. The sorbed As concentrations may increase due to irrigation, thereby supporting higher equilibrium solution As concentrations. Flood irrigation may decrease redox potentials, favouring the formation of As (III) and possibly decreasing the As sorption.

Bhattacharya et al. (1997) reported that exploitation of As contaminated groundwater in the Gangetic alluvial aquifers from delta plains, eastern India had caused adverse health effects among the population within a span of 8 to 10 years. They also reported that the sources of As in natural water are a function of local geology, hydrology and that the geochemical characteristics of the aquifers and arseniferous groundwater belts were mainly located in the upper delta plain and in abandoned meander channels. The mineralogical investigations had established that As in silty clay and sandy layers occurred as coatings on mineral grains. Clayey sediments intercalated with sandy layers occurred as coatings on mineral grains. Clayey sediments intercalated with sandy aquifers at depths between 20 and 80 m are reported as a major source of As in groundwater and an integrated knowledge on geological, hydrological and geochemical characteristics of the multilevel aquifer system of the upper delta plains is, therefore, necessary in predicting the origin, occurrence and mobility of As in groundwater in West Bengal.

Acharyya et al. (1999, 2000) reported that arsenic toxicity in groundwater in the Ganges delta and some low-lying areas in the Bengal basin was confined to middle Holocene sediments. Dissected terraces and highlands of Pleistocene and early Holocene deposits were free of such problems. Arsenic-rich pyrite or other As minerals were rare or absent in the affected sediments. Arsenic appeared to occur as adsorbed species on iron hydroxide, coated sand grains and clay minerals and was transported in soluble form and co-precipitated with, or was scavenged by, Fe (III) and Mn (IV) in the sediments. Preferential entrapment of arsenic in fine-grained and
organic rich sediments occurred during mid-Holocene sea-level rises in deltaic and some low-lying areas of the Bengal basin which was subsequently liberated under reducing conditions and mediated further by microbial action. Furthermore, the recent release of As to groundwater was due to intensive extraction of the same for irrigation together with the application of phosphoric fertilizer, which has also induced groundwater flow, mobilizing phosphate derived from fertilizer, as well as from decayed organic matter, thereby promoting the growth of sediment biota and aided in further release of As (Acharyya et al., 1999, 2000). Saha and Chakraborty (1995) also suggested that large-scale seasonal withdrawal of groundwater along with application of phosphoric fertilizers had major role in As contamination.

Acharyya (1997) concluded that the arsenic-affected areas in West Bengal, India occurred along a nearly 400 km long linear tract extending from Kaliachak in Malda district through Raninagar block in Murshidabad district, parts of Nadia and 24 Parganas (North) districts up to Baruipur in 24 Parganas (South) district and the belt mostly lay on the eastern side of the Bhagirathi-Hugli river basin, except for Purbasthal in Barddhaman district which was situated on the western side of the river. Moreover, it was also reported that the arsenic affected area in West Bengal and Bangladesh were entirely confined within parts of the Ganga delta east of the Rajmahal hills and was further restricted mainly between the Bhagirathi-Hugli and Ganga-Padma river channels.

The information regarding mechanism of groundwater contamination by As is quite scanty. Chakraborti et al. (1992) inferred that iron pyrites might be responsible for As contamination of groundwater. Arsenic was possibly associated with pyrites formed due to chemical combination of sulphur with iron containing minerals brought along by rivers as a part of the alluvial sediment or formed in situ under reducing conditions. The pyrites underwent oxygenated decomposition due to excessive withdrawal of groundwater especially during the lean period resulting in formation of Fe (II) and Fe (III) sulphate and sulphuric acid, which in turn, were responsible for As-mobilization.

Roy (1997) reported that when large amount of water was withdrawn from the borewells for agricultural purposes, a cone of depression was created in the water table, the radius of influence and drawdown of which was directly proportional with
the time of withdrawal of underground water by pump sets. When large number of
pumps were operated for a long period in a particular area, water withdrawal through
different borewells of varying depths caused a situation when drawdown of any
particular borewell reached a depth where extended aerated zone (vadose zone) may
have interacted with arsenopyrite pockets, resulting in oxygenated decomposition of
pyrites and creation of pollution plume, which, in turn, was responsible for the
secondary pollution upon withdrawal of such contaminated water by wells.

Arsenic contamination was more or less confined to the Indo - Gangetic plains
of West Bengal, but some cases had also been reported outside this belt. Pandey et al.
(1999) reported such an incident from Rajnandagaon district in Madhya Pradesh
where about 400 people (30% of the population) were affected and 130 people were
critically affected due to As poisoning. Out of 390 water samples from tubewells, 26
sites were found to be contaminated with As with the total As content ranging
between 0.01 and 1.01 mg/L. Statistical analyses revealed that the mean concentration
of As was about 0.35 mg/L in the village of Koudikasa.

Chakraborti et al. (1998) conducted a eight year study on groundwater As
contamination in a residential area in an industrial zone of Kolkata, West Bengal. The
sufferings of people were due to industrial effluent discharge and more than 7000
people who lived around the discharge point were exposed to As contaminated water
and also some of the distant tubewells which were earlier free from As were
contaminated with As. This was due to the fact that an industry, producing 20 - 30
tons of Paris Green per year, discharged most of the effluents without proper
treatment in an open land just outside the boundary of the factory and due to high soil
porosity, As percolated and contaminated the underground aquifer.

The presence of As in groundwater in West Bengal was first noticed in 1978
(Muralidharan, 1998). Though the exact mechanism of As contamination was not
clear, the increase in the affected areas corresponded with the increased groundwater
utilization for irrigation in those areas and deeper sources previously found to be As-
free showed As contamination with time thereby suggesting the need to protect the
presently uncontaminated deeper aquifers through effective hydrological
management. He (1998) also reported the absence of well - defined aquifer stages in
the As affected areas of Bengal Basin apart from the shallow water table aquifer. The thickness of the shallow aquifer varied from a few meters to a few tens of meters and was under-exploited while the middle level aquifers (depth range 30 - 80 m) were exploited to a maximum extent for irrigation wells.

Incidentally the maximum reported As contamination in groundwater in West Bengal was from the middle level aquifers which was under semi-confined condition due to the presence of semi-pervious silt-clay layers (Saha et al., 1997). Wide variations were reported in As content within the same aquifer zone. During 1990, the Public Health Engineering Department (PHED), Government of West Bengal had drilled eight deep tube wells to depths of 150 m to tap safe water at Ghentugachhi village in Chakdah block, Nadia district, West Bengal. Initially these wells reportedly supplied As-free water but later with time, As contamination was reported (PHED, 1991). The analysis of litholog and construction details of irrigation wells of Chakdah block in Nadia district of West Bengal indicated that the aquifers at different depths were interconnected through positioning of strainer slots at different levels in many cases. Though it was difficult to understand the actual aquifer interaction processes during non-pumping periods, exchange between the aquifers was expected to occur due to pressure differences created through pumping. This process may lead to migration of contaminants from one level into another and was, therefore, necessary to have the drinking water wells away from such irrigation well clusters in the affected areas.

According to Nickson et al. (1998, 1999) As derived from reductive dissolution of arsenic-rich iron oxyhydroxide was derived from weathering of base-metal sulphides. The Fe oxyhydroxide existed in the aquifer as dispersed phases such as coatings on sedimentary grains. As dissolved iron was oxidised it got precipitated as iron oxyhydroxide, which was instrumental in scavenging the As from solution.

3.2 Arsenic in soils

Limited information was available on the concentration and nature of As in soil and soil solutions under field conditions. The main source of As in soils was the parent materials from which the soil was derived (Yan-Chu, 1994). Background
concentrations do not generally exceed 15 mg As/kg (NRCC, 1978). In 1995, Azcue reviewed the environmental significance of elevated natural levels of As. Globally, As introduced into the biosphere by human activities has surpassed As from natural sources, the supply of the element from these two sources being approximately 60% and 40% respectively. Water in numerous regions of the world has elevated concentration of As from natural sources. Arsenopyrite may contain up to 6000 µg As/kg and the weathering of such geological materials increased the levels of As in groundwater. Long-term consumption of groundwater containing elevated concentration of As has caused natural chronic As intoxication in local populations in Taiwan, Mexico, Chile, Argentina and other countries. An endemic disease, commonly called “Black Foot” disease, which can be caused by As in drinking water was documented in Taiwan in 1963. For more than 80 years local population has consumed well water with As concentrations as high as 1829 mg/L. The widespread geographical distribution of minerals with a high As content suggested that new regions with natural As contamination will be identified in future (Azcue, 1995).

Ori et al. (1993) reported that the total As content of representative soils from Louisiana, USA ranged from 0 to 73 mg/kg with a mean of 23.2 mg/kg and observed that in general As levels increased or remained about the same with increasing profile depths and total As was significantly related to soil texture. Also soils with higher clay content had higher As contents. Generally alluvial soils of Red and Mississippi River valleys had the highest As contents while the Ohachita River alluvial soils had the lowest As contents.

Lund and Fobian (1991) conducted studies on As distribution in profiles from Denmark and observed large variations in the profile that could not be explained by the compositions of the soil horizons. Generally, As was retained in the A and B-horizons of the profiles studied. In the A horizon, the retention of As was associated with high organic-matter content, whereas retention in the B horizon may be associated with adsorption by Mn, Fe, and Al oxides.

Arsenic content of the topsoil in about 400 randomly sampled surface soils and various soil profiles of the Upper Austria ranged from 1 to 39 mg/kg (Aickberger and Hofer, 1989). They reported that the soils from different geological regions of the Upper Austria differed widely in their average As contents and indicated strong
relationships with parent materials for As, which also showed even distribution in the studied soil profile.

Kalbitz and Wenrich (1998) in Germany studied the mobility of As and the influence of dissolved organic matter on the mobility of As and reported that the acid-soluble concentrations which were mostly equal to the total content were up to 265 mg/kg for As. They also observed that the arsenic mobility was low and As concentration in the soils was positively correlated with dissolved organic matter (Kalbitz and Wenrich, 1998).

Chen et al. (1992) concluded that the range of As in the soils of Hong Kong (China) was between 76 and 5092 mg/kg with an average of 810 mg/kg. The arsenic content in different soil horizons varied greatly and leaching was weak in the profiles.

Klose and Braun (1997) conducted studies on As transfer and recommendations for agricultural use in a highly As polluted region in Germany. The soil As content was over 50 mg/kg. Crops studied included fodder plants, spring barley, potatoes, maize, winter rape, pasture grasses and clover. In experiments with maize, rape, barley and potatoes, As content ranged from 0.04 to 1.31 mg/kg dry-matter when grown on soils containing 60 - 362 mg As/kg soil and experiments with pasture grasses, soil As content ranged from 90 to 1050 mg As/kg soil while the plant As content ranged from 0.18 to 6.7 mg As/kg dry-matter.

3.3 Soil arsenic map

A soil arsenic map illustrates the geographic distribution of soil As in an area. It contributed to better understanding of the correlation between soil As content and occurrence of any As related diseases. In addition, these maps would be useful in considering the effects of As content in groundwater and crops. These soil As maps helped in identification of high risk zones in any study area and studied the effect of arsenic containing irrigation water on As build-up in the soils. Inherent in this process was the assumption that a property measured at a given point represented the surrounding unsampled neighbourhood. The validity of this assumption depended on the spatial variability of the soil property (here arsenic).
Engel et al. (1996) deduced the spatial pattern of As distribution in Jamaican soils using the Geographical Resources Analysis Support System (GRASS) and data from an island wide soil survey. The frequency of distribution of As was discussed in relation to major lithological groups. Arsenic background levels for different areas of Jamaica were also determined.

Chang et al. (1999) developed a soil arsenic map of Taiwan by using data collected from a study targeting agricultural soils in Taiwan and reported that the As content of the surface soils (0 - 15 cm) ranged from 0.01 to 16.16 mg/kg, while the mean value was 5.65 mg/kg. These authors (1999) used geostatistics and geographical information system (GIS) to develop the map illustrating the geographic distribution of As in surface soil horizons of Taiwan. According to them, the soil As map would be useful in future research to determine the geographical distribution of regional patterns of plants and groundwater As contents, the relationship between As and parent soil material and correlation with the occurrence of blackfoot disease in Taiwan.

### 3.4 Arsenic in crops

Arsenical compounds have been widely used as pesticides and herbicides in agriculture. Attention had focussed on the accumulation of As in agricultural soils and the possible toxic effects on plant production. Extensive research on the effects of As on plant production are well documented (Jacobs et al., 1970; Steevens et al., 1972; Anastasia and Kender, 1973; MacLean and Langille, 1981; Jiang and Singh, 1994). Uptake of As by plants occurred primarily through the root system, and the highest As concentrations were reported in plant roots and tubers (Anastasia and Kender, 1973; Marin et al., 1993).

Arsenic content in rice grain and in root tubers of sweet potato and total As content in the soils showed significant correlations (Chen et al., 1992). When the As content in soils ranged from 202 to 350 mg/kg, the As contents in edible parts of rice and sweet potato reached a critical value of 0.7 mg/kg. Several vegetable crops grown in silt loam soil treated with 100 mg As/kg showed that total As contents of the edible plant parts were generally low, ranging from 3 mg/kg for potato peel to trace.
quantities in cabbage and maize. The highest As concentration in broccoli, cabbage, maize, green beans, lettuce and potato peel were found in the methanol/water phase, whereas the arsenic in the non-extractable or chloroform phase was predominant in beets, potato flesh, swiss chard and tomato (Pyles and Woolson, 1982).

Jonnalagadda and Nenzou (1997) studied the bioaccumulation of As in *cynodon dactylon* (couchgrass), *pinicum sativum* (thatchgrass) and *amaranthus hybridus* (amaranthus or mhowa) in Zimbabwe and reported that high concentrations of accumulated As was detected in the roots of couchgrass. Amaranthus had high levels of As in the leaves. Elemental uptake varied with the plant species and it was observed in all the species that the rate of uptake was rapid at the early stages of plant growth (Jonnalagadda and Nenzou 1997). Wang - Ya Gu *et al.* (1997) studied the contents of some heavy metals in vegetables in Shangai suburbs, China. They suggested a tolerance limit of 0.2 mg/kg for As in vegetables based on the quality requirements for green food.

Carbonell - Barrachina *et al.* (1997) reported the uptake of As and accumulation among roots, stems, leaves and fruits. Arsenite was the more phytotoxic form in plant species; tomato plants were more tolerant to As than bean plants. The strategy developed by tomato plants to tolerate As was avoidance, limiting As transport to shoots and increasing As accumulation in the root system. Arsenic in tomato tissue seemed to be so effectively compartmentalized that its impact on plant growth and metabolism was minimal. However, in bean plants upon uptake, As was readily transported to shoots and accumulated in high concentrations in leaf tissue. The observed differences in absorption and translocation of arsenite or its metabolized species by tomato and bean plants were probably responsible for the difference in plant tolerance to As pollution (Carbonell - Barrachina *et al.*, 1997).

Xie and Huang (1994) studied the detailed relationships between As content and rice tillering in soil - rice systems and concluded that rice tillering was promoted by small As contents in soil but was inhibited by large contents. Kiss *et al.* (1992) examined the dangers of As in drinking and irrigation water to humans and plants and also the antagonism of As and Mg. They (1992) reported that the uptake of As was greater in leaves than in roots in onions and irrigation with water containing As

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increased plant As content more than did the soil As treatment. In solution culture trials with rice, As markedly reduced plant weight, while Mg increased plant weight.

Uptake, accumulation and translocation of arsenical compounds by cotton was reviewed by Marcus-Wyner and Rains (1982). When As was applied as arsenic trioxide it was readily taken up by the roots but not translocated to shoots but when supplied as cacodylic acid, As was found in all parts of the plant. Plants treated with herbicides, MSMA and DSMA, also accumulated As in roots and shoots. Cotton seeds accumulated As at levels below the tolerance limit in treated bolls (Marcus-Wyner and Rains, 1982). Liu and Gao (1987) investigated the As content in red soils in China and its effect on several plants and noted that arsenic was toxic to azolla and sweet potato, but blue green algae tolerated up to 10 ppm As.

Hattemer-Frey et al. (1996) evaluated the effect of some soil properties on root uptake of As. They used multiple linear regression analysis to develop simple, predictive models for estimating the concentrations of metals (here As) in homegrown vegetables. The concentrations of As in plants were typically estimated by multiplying the total concentration of metal in soil by a metal-specific soil-to-root uptake factor (RUF). They used preliminary predictive equations for estimating root uptake of As in fruit and root vegetables so that the importance of this pathway and subsequent influence of human exposure could be accurately assessed.

Marin et al. (1993), while studying the soil redox potential and its influence on As uptake by rice, found that an increase in pH led to higher dissolved As concentrations. When the soil redox potential dropped below 0 mV, most of the As was present as trivalent As and under more oxidizing conditions both As (III) and As (V) were present. Chemical speciation of As in water-soluble fraction affected its phytoavailability. More indigenous As taken up by the plants remained in the root. Plant As availability increased with increasing As concentration in solution (lower soil pH) and with increasing amounts of soluble As (III) (lower soil redox) (Masscheleyn et al., 1991). Amended monomethylarsonic acid (MMAA) was approximately two times more phytoavailable than the indigenous inorganic As forms which increased with decreasing pH and redox potential.
3.5 Arsenic sorption and desorption

Adsorption and desorption processes are the principal factors affecting the transport, degradation and biological availability of compounds in soils (Sanyal and DeDatta, 1991). The concentration of As in the soil solution was controlled both by soil physical and soil chemical properties that influenced adsorption-desorption processes. Scanty information is available on As adsorption and transport in soils. Arsenic has a high affinity for oxidic surfaces, although reactivity of oxides may vary considerably, depending on pH, and soil solution composition. Soil texture (Wauchope, 1975; Frost and Griffin, 1977), nature of constituent minerals (Walsh et al., 1977; Pierce and Moore, 1980), pH and the nature of competing ions have all been shown to influence adsorption processes.

Arsenic (III) and arsenic (V) adsorption on three California soils were studied by Manning and Goldberg (1997) and they concluded that the soil with the highest citrate-dithionite extractable Fe and clay percentage had the highest affinity for As (III) and As (V) and displayed adsorption behavior similar to pure ferric oxide. Adsorption isotherms indicated that As (V) species were adsorbed more strongly than As(III) under most conditions. These authors (1997) applied the Langmuir and the Freundlich adsorption isotherms which gave comparable and highly significant fits of As(III) and As(V) experimental data on all soils (Manning and Goldberg, 1997).

The adsorption of arsenate on kaolinite, montmorillonite and illite was investigated by Manning and Goldberg (1996) at varying pH and competing anion concentration, while holding As (V) concentration, clay suspension density and ionic strength constant. The effects of two concentrations of phosphate or molybdate on As (V) adsorption envelopes gave evidence for direct competitive adsorption [in case of As (V) + P] and possibly site-specific non-competitive adsorption [As (V) + Mo]. Distinct As (V) adsorption maxima occurred at approximately pH 5.0 for kaolinite, 6.0 for montmorillonite and 6.5 for illite (Manning and Goldberg, 1996).

Elkhatib et al. (1984a) found that the Elovich and the modified Freundlich equations described the sorption rates of trivalent As successfully. The modified
Freundlich equation proved to be superior to the Elovich equation. Arsenite sorption conformed to the Freundlich isotherm over the entire concentration range for all soils (Elkhatib et al., 1984b). The rate of As (III) sorption was rapid initially and decreased with time. Arsenite sorption was not reversible; only a small amount of sorbed As (III) was released after five desorption steps. The desorption kinetics of As (III) was only described by the modified Freundlich equation. They concluded that iron oxides and $E_h$ were the main soil properties controlling arsenite sorption rate.

3.6 Arsenic sorption by clay minerals

Among the soil properties that influenced sorption of As, clays played an important role. Both the amount of clay and the nature of constituent clay minerals controlled As adsorption in soils. According to Frost and Griffin (1977) arsenate sorption on the clay minerals, namely kaolinite and montmorillonite, increased below pH 4, exhibited a peak between pH 4 and 9. Montmorillonite sorbed both arsenate and arsenite more strongly than did kaolinite, and that arsenite was sorbed much less than arsenate by both clay minerals. The higher adsorption by montmorillonite is attributed to a higher edge surface area and the external surface area of montmorillonite, which is 2.5 times larger than that of kaolinite. Another explanation for the higher adsorption by montmorillonite with respect to kaolinite is due to the inter-layer hydroxy aluminium polymers which by virtue of the very reactive $\text{Al(OH)}_x$ adsorbed on the clay probably accounted for the higher adsorption capacity of the former.

Huang (1975) studied the As retention by hydroxy-Al on external and interlamellar surfaces of micaceous mineral colloids. Depletion of K from muscovite and biotite decreased As retention. This effect was attributed to the exclusion of arsenate ions by the K-depleted layers. Changes in solution pH from neutral to strongly acidic and variable concentrations of NaCl did not promote As retention by hydroxy - Al in interlamellar space of the micaceous minerals. Huang (1975) concluded that hydroxy - Al on the internal surfaces of the micaceous mineral colloids was significant in retention of As, particularly when the particle size was $< 0.2 \mu m$. When the mica particles decreased in size, the Langmuir adsorption maximum of hydroxy-Al mica complexes for As increased whereas the bonding energy of the complexes for As decreased.
Johnson and Hiltbold (1969) reported that approximately 90% of As present in the soil was associated with the clay fraction. Iron and iron coatings on clay surfaces may be important in controlling As adsorption – desorption processes in soils. Clays may often be coated with Fe and Al oxides (Shuman, 1976; Naidu et al., 1990; Naidu et al., 1994).

3.7 Extractant efficiency

Extractants for various chemical constituents may serve several purposes and were designed to meet different criteria in estimating supply and solubility of soil components. Environmentalists and soil scientists evaluated the potential pollution in runoff and groundwater by leaching from contaminated soils, landfills and mine tailings under different conditions while agronomists would be interested in constituents that were readily available to the roots and which are present in the economic produce of the different crops.

Jacobs et al. (1970) studied the As residue toxicity to vegetable crops grown on Plainfiled sand in Wisconsin. The yield decreases of the crops were related highly to total, 1N NH₄OAc extractable and Bray 1 extractable As. These extractants were chosen as they are commonly used in routine soil testing procedures and can give an available As test. NH₄OAc extracted on an average about 1 to 5% of the total As in the soil. Due to difficulty of accurately determining low levels of As, the Bray 1, which extracts about ten times as much As as does NH₄OAc, would be preferred “available” As extractant (Jacobs et al., 1970).

Vandecaveye et al. (1936) found no correlation between phytotoxicity and the solubility of soil As in distilled water, 0.1 N NH₄OAc, 0.1 N NH₄NO₃, 0.1 N KNO₃ or hot concentrated HNO₃. The effectiveness of As extraction by water and 0.1 N NH₄NO₃ was low for a soil sample from an orchard sprayed with lead arsenate in Yakima Valley, Washington. Vandecaveye (1943) reported that As not soluble in 0.1 N NH₄OAc had little injurious effect on plant growth. Reed and Sturgis (1936) reported that a better correlation existed between plant growth and 0.5 N HCl extractable As than with water soluble As. Johnston and Barnard (1979) studied the
comparative effectiveness of 14 solutions for extracting As from four Western New York soils. The relative effectiveness of the basic solutions in removing As was in the order of 0.5 (M) NH$_4$F ≈ 0.5 (M) NaHCO$_3$ < 0.5 (M) (NH$_4$)$_2$CO$_3$ < 0.5 (M) Na$_2$CO$_3$ < 0.1 (M) NaOH; for acid solutions the order was 0.05 (N) HCl + 0.025 (N) H$_2$SO$_4$ ~ 0.5 (M) HCl < 0.5 (M) KH$_2$PO$_4$ < 0.5 (N) H$_2$SO$_4$. Almost invariably the concentrations of As extracted by the nine more effective extractants increased with shaking time for all the soil types. Even after 18 hours of shaking, no extractant removed more than 80% of the As extracted sequentially for any sample.

3.8 Sequential extraction

McLaren et al. (1998) reported a sequential extraction scheme, based on a soil P fractionation process, to assess the chemical nature, and thus the potential bioavailability and mobility of As. Soil As was separated into six fractions with (i) anion exchange resin, (ii) NaHCO$_3$, (iii) NaOH, (iv) NaOH following sonification, (v) HCl and (vi) HCl / HNO$_3$. Most of the sites contained substantial concentrations of As in the two most labile fractions, which indicated high potential for phytotoxicity and leaching. Arsenic seemed to be associated with soil amorphous Fe and Al minerals. Resin - extractable As, in particular, might provide a good index of potential As bioavailability and mobility (McLaren et al., 1998).

Woolson et al. (1973) studied the effect of 1 N NH$_4$Cl, 0.5 N NH$_4$F, 0.1 N NaOH and 0.5 N H$_2$SO$_4$ on solubilising As. The dissolved arsenates were designated as Ws - As (water soluble), Al - As, Fe - As and Ca - As, respectively. Arsenic became fixed predominantly as Al - As (0.5 N NH$_4$F soluble) and Fe - As (0.1 N NaOH soluble). The percent of Ws - As present was proportional to As added and inversely proportional to time, and to the Fe and Al content. Woolson et al. (1971a) conducted another experiment on correlation of available soil As and response of corn. Iron - As was the predominant form in most soils with Al - As usually the second most abundant form. Few exceptions to this pattern also existed. In some soils the Al form was highest in abundance and in two soils Ca - As was predominant. The high reactive Al or Ca contents of these soils could explain this behaviour.
3.9 Soil - site suitability

Verma et al. (1999) characterised some alluvial soils of West Bengal, India and evaluated their soil - site suitability for rice cultivation. The soils varied in their morphological and physicochemical properties and also in degree of profile development. *Chuchura* and *Simla* soils (both Aeric Haplaquepts) were highly suitable (S1) for rice due to imperfect to moderately well drainage and fine silty clay loam texture. *Banabharui* (Typic Ustifluvent) and *Maheshpur* (Tropic Ustochrepts) soils were moderately suitable (S2) for rice. They had limitations of light to medium texture (sandy loam to loam) and needed frequent irrigation and fertilization.

Rao et al. (1998) evaluated the soil-site suitability for rice, wheat and pigeonpea in Etawah, Uttar Pradesh, India. Old alluvial plain soils were suitable (S1) for rice but recent alluvial plain soils were only moderately suitable (S2). They had limitations of soil fertility, texture and rainfall. The active floodplains were marginally suitable (S3) for all the three crops viz. rice, wheat, pigeon pea whereas eroded soils (areas under ravines) were marginally suitable to unsuitable. Active flood plains and eroded soils had limitations of slope, texture, CaCO₃ content, erosion, drainage and soil fertility.

According to Bhaskar et al. (1996) soil-site and climatic parameters were very important for determining the wheat yield in Saongi watershed in Maharashtra. High temperature and low humidity coupled with high wind velocity were important in contributing to low yields through creating water stress. Soil factors, viz. soil depth, clay content, cation exchange capacity (CEC), available water capacity (AWC) and organic carbon were positively correlated with grain yield. The effective range for soil depth was 65-100 cm; AWC was 170-200 mm; clay content was 48-56%; CEC was 43-53 cmol(+)/kg; and organic matter content was 0.63 to 0.74%. Out of the six different soils studied, three soil types showed satisfactory yields. The sites were deemed moderately suitable (S2) to marginally suitable (S3) for wheat cultivation under prevailing climatic conditions.
Srivastava et al. (1994) studied the soil-site suitability for rice in Barddhaman district of West Bengal, India and evaluated the same for effective crop planning and better utilization of land resources. The soil-site suitability of some dominant soils of Barddhaman were selected under rainfed rice. Both the limitation and parametric approaches were used for assessing the soil-site suitability. The Kalyaneswar soils were not suitable for rice. The major limitations were steep slopes, undulating terrain, shallow rooting depth, gravelly texture, low nutrient and water retention capacity and hence the soil could be considered for some horticultural, plantation crops and agro-forestry. The Beldanga soils were moderately suitable (S2) for rainfed rice and the major limitations observed in these soils were undulating slopes, low organic matter status and poor water and nutrient retention capacity. The Hansgram and Balidanga soils were highly suitable (S1) for rice cultivation. They were developed on lower alluvial plain and meander flood plains.