CHAPTER-ONE

INTRODUCTION

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Introduction

Sludges are anaerobically digested or aerated end products of wastewater (sewage) treatment and purification plants. Hence they are municipal refuses. Sludge is produced wherever wastewater purification takes place. The worldwide production of sludge is estimated to be around $20 \times 10^{12}$ kg (30 million tons) per annum of which, 70% is disposed on land per year (Nriagu and Pacyna, 1988).

1.1 Composition and Sources of Wastewater Sludge

Wastewater sludges (also known as biosolids) are organic-rich solids (more than 50% organic matter) that contain sufficient N (2-7%) and P (1-5%, equivalent to 2-10% $P_2O_5$) to make them potentially useful as fertilizers and a source of organic matter and other micronutrients (Arden, 1977). However, it has the relatively high concentration of metals, which limits both its utility as a fertilizer and its disposal to agricultural land. A number of studies has shown that the wastewater sludges contain a wide range of concentrations of many metals such as Cu, Cd, Cr, Ni, Pb, Zn, etc. Metal concentration in sludge exhibits wide variation from one city to another, reflecting the proportion of domestic and industrial input into the waste water system. In residential areas the metals are mainly derived from various components of domestic wastes. Other sewerage systems with industrial discharges will give rise to sludge differing markedly in composition and may vary considerably with time depending on the industrial activities and other factors. Some examples of industrial sources...
of metals in sludge are Ag from photographic processing work, Cd, Ni, Cr, etc. from electroplating industries, Cr from leather tanneries, Pb from car battery manufacturing and Cd, Ni, Mn from dry cell manufacturers. In the recent years there has been great pressure on the manufacturers to reduce the metal concentration in their effluents by introducing cleaner technology and recycling. Hence there are different pathways by which the heavy metals can reach the wastewater.

1.2 Wastewater Treatment and Sludge Production

Treatment in sewage work involves the following three steps. 1. Preliminary treatment, as sewage arrives for treatment, it is passed through barred grills and brushes to remove large suspended solids and floating matter (screening) 2. Sedimentation, it is an attempt made to settle out the suspended solids. 3. Biological oxidation, this stage exploits the purifying activity of microorganism. Finally in the digestion process sludge from primary and secondary sedimentation tanks are subjected to the anaerobic digestion. Gases are produced as by-products during this digestion. After digestion the sludge is dewatered and dried sludge is used as manure. This is the general plan of a conventional sewage treatment plant. Schematic diagram of sludge production from a typical treatment plant is given in appendix no.2.
1.3 Okhla Wastewater Treatment Plant

For the study of speciation of metals in wastewater sludge Okhla sewage treatment plant in Delhi was selected. Okhla wastewater treatment plant is one of the first of its own kind in India. The ultimate capacity of the plant is 124 MGD with all secondary treatments. The plant is situated on Mathura Road in south Delhi. It is conventional type of sewage treatment plant, which started functioning in 1937. It receives the highest volume of sewage in the capital city. Its catchments area consists of; I.S.B.T., Red Fort, Jama Masjid, Dariaganj, Connaught Place, Kotla Firozshah, India Gate, Pragati Maidan, Safdarjang, Sarojini Nagar, Lajpat Nagar, Greater Kailash, Dhaula Kuan, Hauz Khas and J.N.U. 90% of sewage is of domestic origin. After treatment, the sewage is released to the Agra canal, which ultimately meets the river, Yamuna. Solid waste generated during waste treatment is disposed off as manure cake to be used on city lawns, farmhouses and agricultural lands (2 truck loads per hectare per year).

1.4 Agricultural uses of the Sludge

Application to agricultural land is a major disposal option for wastewater sludge. For example in Denmark, France and Sweden, agricultural land receives over 30% of the total sludge produced. In U.K. about 40% of the sludge produced each year is applied to arable and grassland areas. These figures are likely to increase in the future due to cessation of sea disposal. There are restrictions on the addition of sewage sludge to agricultural land.
aimed at limiting the amount of potentially toxic metal added. At present however, no legally enforceable restrictions have been set for tracing toxic metal, which is present in the wastewater sludge.

Now days sludge is widely used as bio-fertilizer from agricultural point of view. Sludge can be applied to land directly or may be processed into fertilizer pellets, compost, or a liming agent (through the addition of a product such as cement kiln dust). The amount and type of industrial inputs, pretreatment of industrial discharges to reduce contaminants, and treatment of the sludge to reduce pathogens all affect the quality of sludge. Even at a specific treatment plant, sludge quality will vary over time. The application of sludge to agricultural land has been recognized as a desirable means of disposal both environmentally and economically. In addition to being inexpensive, land application results in recycling of nutrients essential for plant growth and conserve organic matter important for soil structure. Their effect may be either beneficial or harmful to crop or agricultural land depending upon the chemical compositions of the applied sludge. The organic matter and the nutrients are considered to have beneficial effects on the resulting soil characteristics in terms of crop yield and water and nutrients retaining capacities. Organic matter is added to the soil improving soil structure and increasing the ability of a soil to hold water and nutrients particularly nitrogen (N), phosphorous (P) and potassium (K) which are essential for crop growth. Plant growth is
reported to be enhanced in amended soils with sludge compared to unamended soils. In case the concentration of metals is higher than the optimum value in sludge, they may create potential hazards to agronomic plants and to the food chain. Hence it is necessary to evaluate the metals mobility within the soil and also to evaluate the bioavailability of the metal after sludge application on soil. This would help to understand what might happen in near future after prolonged agricultural use of the sludge.

Additions of sludge can improve the physical properties of soil such as bulk density, aggregation, porosity and water retention capacity. Increased crop yields with appropriate application have been documented. When amending wastewater sludge into a soil a new source of heavy metals is introduced. Unless the retaining properties of the resulting amended soil are increased in accordance with this, heavy metals may spread to the surrounding environment. It is widely reported that the treatment of the soils with sludge often results in increased concentration of metals in the food chain. This is particularly true for Cd, Cu, Ni, and Zn, which are considered to be phytotoxic (Birgitte and Ø, 1997). Most soils are amended with sludge in order to improve crop yields. The biggest concern in this context is that metal contents of plants grown on the soil may be increased. Whether the anthropogenic deposition of heavy metals in agricultural soil will become detrimental to plant growth or to the consumers of the harvested crops depends upon the chemical form of
metals present in the soils (Cheney and Giordano, 1977, Latterell et al., 1978, Mahler et al., 1980). There are four possible fates of metals once they are applied in the soils. 1. Uptake by plants and animals (immobilization). This represents as a loss from the soils when crops are harvested. 2. Fixation (adsorption/exchange) in the soils. 3. Leaching and loss in soluble form to drainage water. 4. Surface loss in solid form by runoff and erosion.

However, to date, reliable assessments of persistence following sewage sludge application have been made difficult because of the lack of long term field based experiments investigating the fate of metals and their persistence. Sewage sludge is a by-product of sewage treatment and contains not only nutrients and organic matter but also contaminants such as metals and synthetic organics discharged into the sewers from industries and businesses and leached from pipes. Because most heavy metals remain in the soil for a very long time, any additions should be considered permanent additions to the total quantity in the soil. Sludge also contains high levels of pathogens, which can be reduced or eliminated through sludge treatment.

1.5 Metals Bioavailability

The fraction that is bioavailable is usually considered to be the sum of water soluble and exchangeable metal, i.e. the fraction of the total metal content in a soil, which is available for the plant uptake. Heavy metal uptakes in contaminated soils have been extensively studied. However, in
some cases the variability of soil and plants has prevented the obtainment
of direct relationships between the total metal contents in soil and plants
(Voutsa et al., 1996; Shallari et al., 1998).

Almost all authors reporting investigations into the bioavailability of
metals in sludge applied soil found that the metals remained available for
uptake, giving anomalously high concentrations of metals in plant for
many years after application (Chaney et al., 1982, Heckman et al., 1987).
The investigation of speciation of metals both in sludge and in sludge-
amended soil may help to assess the bioavailable metal fractions and the
possibility of mobilization of these metals in soil. Various studies have
shown that some vegetables such as carrot, cabbage and spinach
accumulate metals when grown in contaminated soils. Recently, attempts
have been made to assess the bioavailability of heavy metals in
contaminated soils and sediments using sequential extraction (Xian 1987,
1989). Such assessments assume that metal bioavailability decreases with
each successive extraction step in the procedure. The beneficial and
detrimental effects associated with the use of wastewater sludge in
agriculture have been studied in details (Dowdy et al., 1976). Copper zinc,
cadmium and nickel have been regarded to be harmful to plants even in
low concentration in the soils, particularly in acidic soils.
1.6 Metals Mobility

The movement of heavy metals within a soil profile involves a complex series of processes, which are important to agriculture environment. Now a days sludge has been widely used as a biofertilizer in agricultural land. One of the major problems with agricultural use of the sludge is the introduction of heavy metals into the soil. In general, sludge solution appears to increase the metal mobility in the soil system. The heavy metal movement and accumulation in the soil have been reported in comprehensive manner in the literature. About 7% metals are taken up by the edible part of the plant out of total metal present in the soil, thus introducing the heavy metals in to the food chain (Jenne, E. A., 1968). Another effect may be the ground water pollution and surface water contamination, depending upon soil condition, mobility of metals and applied dose.

1.7 Chemical Speciation

Chemical speciation, in the context of soil and sludge-amended soil was defined in past (Ure, et al., 1993) as the description of amounts and kind of species formed and phases present. In recent years, interest in determining the speciation of metals in environmental samples has increased. This interest has arisen largely because of the awareness that it is the chemical species, rather than metal itself that plays the important role in the transfer of metals along the water-soil-plant-animal-human chain. If a soil is
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contaminated with insoluble metal containing pollutant (e.g. slag, fly ash, or mine tailing materials), sequential extraction procedure can also be applied to these materials to estimate their impact on the environment (Bunzl, K., et al., 1999). Conceptually, the solid materials can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents. Several experimental procedures, varying in manipulative complexity, have been proposed for determining the speciation of metals (Tessier et al., 1979). These procedures can be grouped into methods designed to effect the separation between residual and the non-residual metals only and more elaborate methods making use of sequential extractions. The former methods normally involve a single extraction and offer a better contrast between anomalous and background samples than does the determination of the total metal concentration. These techniques suffer from the difficulty of finding a single reagent effective in dissolving quantitatively the non-residual form of metals without attacking the detrital form. The use of sequential extraction, although more time consuming, furnishes detailed information about the mode of occurrence, biological and physico-chemical availability, mobilization and transport of metals.

1.8 Total Metal Content and Sequential Extraction

Measurement of the total concentration of metals provides inadequate information to allow us to assess the bioavailability or toxicity of metals.
An evaluation of total metal levels following a strong acid digestion of the soil may be useful as a global index of contamination, but it provides little indication of their bioavailability, mobility and reactivity in sludge amended soils (McBride, 1995).

Although some of the sequential extraction schemes were originally developed for sediment analysis (Tessier et al., 1979), their use has been extended to soil and sludge analysis (Hickey and Kittrick, 1984 Jordao and Nickless, 1989. Li, et al., 1995). Selective extraction procedure makes it possible to distinguish these associations and provide information on the chemical form of the metals. Several sequential extraction schemes for extraction of metals have been presented by many workers from time to time, such as by McLaren and Crowford (1973), Tessier, (1979), Forstner, (1985), Salomons and Forstner, (1984), Mcgualli, (1982), Emmerich et al, (1982). Shuman, (1985), Sims and Kline (1991), Ure et al, (1993), Ma and Rao (1997), Maiz et al., (1997), Luo and Christie (1998) and Basta and Sloan (1999). The procedure of Tessier et al. (1979) is one of the most thoroughly researched and widely used procedure to evaluate the efficiency of decontamination treatments (Pardo et al., 1990 Calvet et al., 1990 and Rauret et al., 1988). The procedure used here is not entirely specific. To some extent the fraction is only operationally determined. Nevertheless, this method can be widely used and valuable quantitative result on the
form and association of metals and indirectly their bioavailability can be obtained (Harrison, 1981).

1.9 Wastewater Sludge Management

The study of wastewater sludge from different aspects of environmental point of view should conclude with one important consideration, which is management of sewage sludge. Reason is that a tremendous amount of municipal sewage sludge is being generated daily. Production is increasing because municipalities are expanding sewer service areas. Wastewater treatment facilities are being upgraded to provide higher level of treatment and facilities are receiving higher amount of storm flow with improved control of combined sewer system. As a result there has been fundamental shift in the approach to sewage sludge management, resulting in a decided move from disposal to sustainable beneficial use of the sludge. Broadly, the wastewater sludge can be both disposed or reused. The disposal of sludge is carried out by means of several ways such as land fills, incineration and ocean disposal. The reuse or disposal of sludge to any part of the environment will also introduce the heavy metal present in the sludge to that part of the environment.

Nowadays the wastewater sludge has been characterized as biosolids (treated sludge) from management point of view. The standards for managing biosolids regarding use or disposal prescribe management practices designed to limit human and ecological exposure to any
contaminant and also to ensure that biosolids are used on land or disposed in ways that protect human health and the environment (Donovan, J., and Walsh, M., 1997). As a result there has been fundamental shift in the approach to wastewater sludge management, resulting in a decided move from disposal to sustainable beneficial use of the sludge. Several countries have laid down rules for the agricultural use of sewage sludge in order to limit the heavy metal input to soils. Accordingly such guidelines should only be used in agriculture if the heavy metal contents do not exceed certain limit (Webber, et al., 1984). It can be shown that the heavy metal contents lie considerably below these limiting values at present in most of the countries. Tjell, (1986) has reported that it is possible to reduce sludge metal concentrations considerably by implementing existing control on industries and wastewater authorities. The future of sludge lies in the reduction of heavy metal contents at the source. The above-mentioned controls are useful for the estimation of the time in which no damage should appear provided the valid norms are respected. It would, however, be a mistake to remain inactive during this period of time since it cannot be our aim to load the soils with heavy metals to the maximum possible amount. Once the necessity of protecting the soil by such legal means is accepted the indicative values entail the following objectives (Hani and Gupta 1984). 1. Far reaching elimination of heavy metals at the source 2.
Substitution of heavy metals in different industrial processes and products
3. Increasing efforts towards purifying the air.
Also the disposal of sludge (landfill, incineration etc.) or other alternatives instead of their use in agriculture do not represent a genuine solution to the problem at present.

1.10 Objectives of the Study
The purpose of this study was to develop and examine the merits of methods of sequential extraction for partitioning the metals into various chemicals forms, which are likely to be released in solution under various environmental conditions. Two different sequential extractions were attempted to fractionate the metals into various forms. This attempt was based on modification on the basis of literature and recent protocols summary of scheme given by different workers. The selective extraction scheme used in this study is based on operationally defined fractions, viz., exchangeable, oxidizable (bound to organic matter), acid soluble (bound to carbonate), reducible (bound to oxide and hydroxide) and residual (bound to silicates and detrital materials) to investigate the chemical fractionation of selected metals in sludge and four sludge applied soils.
This also indicates that sequential extraction can be carried out for fractionating the various “forms” of metals present in various phases of the wastewater sludge and satisfactory speciation information may be
obtained. This work is concerned with the speciation of metals in sludge and sludge-amended soils. Metals are concentrated in wastewater sludge during the treatment of wastewater according to various physico-chemical and biological processes. Depending on their nature, they are associated in a variable manner with the different phases making up the sludge. Selective extraction procedure makes it possible to distinguish these associations and provide information on the chemical form of the metals.

The present study is an attempt to assess metal speciation in wastewater sludge and sludge amended soils. It is obviously important to investigate behaviour of metals in wastewater sludge; sludge amended soils and in plant system.

The aim of this work is the investigation of speciation of metals in wastewater sludge and sludge-amended soils to assess the bioavailable metal fraction and the possibility of mobilization of metals in soil. Environmentally important metals Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Nickel (Ni) and Zinc (Zn) were taken into consideration. The objectives were:

1. To find out the total metal concentration of heavy metals in the sludge and sludge amended soils.

2. To determine the distribution of metals in the various component phases of sludge and sludge amended soils by means of sequential extraction.
3. To develop a sequential fractionation procedure capable of assessing the quantity and form of metals in wastewater sludge and sludge-applied soils.

4. To determine the bioavailability and mobility of metals in sludge amended soils. To assess the possible impact of prolonged agricultural use of the sludge as soil amendment in terms of metal pollution.

5. To suggest a possible approach for wastewater sludge management, which would involve a transition from sludge disposal to sustainable beneficial use of the sludge.