Abstract

At elevated concentration levels metals are potentially toxic to human life and the environment. The chemical associations of heavy metals control their contaminating effect on soil and aquatic environment to a large extent. Coal thermal power plant ash and urban municipal sewage sludge are known rich sources of many bio-essential nutrients but in addition they also contain enriched levels of metals which have the potential to be toxic at higher concentration levels leading to contamination of soil, crops grown and both surface and ground water. This aspect in fact is one of the major limiting factors for their use in agriculture as soil amendments. Therefore, understanding the heavy metal adsorption behavior and chemical distribution pattern of metals in different soils subjected to amendment with either ash or sludge and their mixture will be helpful to assess the impact so as to single out the soil and metal type from the point of environmental risk.

This study was conducted to evaluate the adsorption and distribution of Cd, Cu, Ni, Pb and Zn in three soils differing in their physicochemical properties: laterite (SL1, pH=5.2), alfisol (SL2, pH=7.1) and vertisol (SL3, pH=8.6). Various mixtures of soil were prepared at different proportions with coal ash (pH=7.8) and sewage sludge (pH=4.3) either alone or in combinations at a maximum application rate of 52t ha^{-1} and were incubated up to 90 days at near field capacity. The representative soil samples were analyzed for various physicochemical properties and used for studying both single and competitive adsorption followed by sequential extraction.

Sewage sludge due to its acidic and saline nature, high organic matter and heavy metal contents had greater impact on soil properties than the coal ash. The increase in salinity, organic carbon, nitrogen, water holding capacity and decrease in pH and bulk density were observed in direct proportion to sludge content in the mixture. Ash, sludge or their mixture amendments increased "total" concentrations of both major and trace elements in all soil types while, on the other hand no significant changes were noticed in the "plant available" concentrations.

Freundlich distribution coefficient (K_D) of metals is marginally higher in amended soils compared to their respective controls. The adsorption affinity sequence based on K_D decreased in the order of SL3 > SL2 > SL1 among soils for various metals and Pb > Cu > Zn > Ni and Cd among metals for various mixtures. The degree of impact of amendments on properties and metal distribution was more in laterite followed by alfisol and vertisol.

Sequential extraction indicated that the distribution of native metals in each soil type was more in highly mobile fraction (EXC) than less mobile (CAB) and resistant (RES) fractions. Amendment application though changed the concentrations of metals extracted under each fraction but their distribution pattern remained more or less unchanged.

The sequential extraction of adsorbed metals at various equilibrating concentrations (10 to 200 $\mu M\ L^{-1}$) indicated that, there is a likely shift in their distribution pattern in each soil type due to increased concentrations. However, the changes in the partitioning of adsorbed metals were wide and clear at only higher metal loadings. As the concentration of metal addition increased, they showed a propensity to accumulate preferentially in more mobile fractions depending on the type of soil surface and substrate. Among the metals, Cd and Ni exhibited higher tendency to exist on exchangeable surfaces irrespective of soil types while Cu in organic and Pb in carbonate fractions were more predominant; but, the extent varied with type of soil. The impact of amendments on the distribution pattern of adsorbed metals was less.

The affinity sequence of metals obtained from the competitive adsorption study was largely: Pb > Cu > Zn > Ni > Cd and varied less with either soil or mixture types. The affinity sequence was in agreement with those predicted from the hydrolysis constants of metals suggesting that the adsorption of their hydrolysis products on the soil surface is one of the dominant mechanisms for adsorption.

The results of this study indicated that, application of amendments does impact the soil properties and to a lesser extent the metal adsorption capacities of soils. The distribution pattern of metals in a given soil type subjected to amendment was mainly attributed to its inherent properties, type of metal and its concentration. At elevated metal concentrations

most of the metals tend to accumulate on surface-active mobile fractions than the resistant fractions. Therefore the threat due to metal mobility is very high in laterite soils followed by neutral alfisol and alkaline vertisol. Among metals Cd and Ni are potentially more dangerous due to their higher mobility.