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Spatial distribution of physico-chemical properties and function of heavy metals in soils of Yelagiri hills, Tamilnadu by energy dispersive X-ray florescence spectroscopy (EDXRF) with statistical approach

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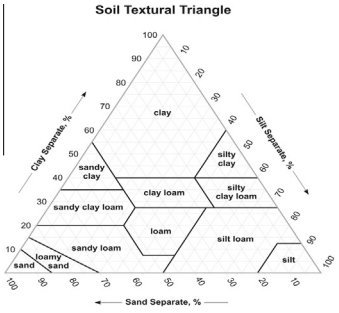
HIGHLIGHTS

- The relationship of physico-chemical properties and heavy metals are studied.
- Geo-spatial distribution maps give the distribution pattern of soil parameters.
- Red and yellowish-red color soils identified due to presence of Fe^{3+} and Mn^{2+}.
- Soil pollutant identified using PCA and CA.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil physico-chemical properties were thought to be important factors in obscuring clear identification of pollutant sources. In the present study physicochemical properties such as, pH, electrical conductivity, bulk density, porosity density, soil texture and color were determined to identify the pollution status using different conventional analytical methods in soils of Yelagiri Hills, Tamilnadu. Soil pH ranges from 5.39 to 8.43 which indicate that the soils are acidic to alkaline in nature. The concentrations of selected heavy metals were determined using energy dispersive X-ray florescence spectroscopy (EDXRF) technique. In all the locations Al is the most abundant metal and Co is the least amount in soil. The relationship between the physico-chemical properties and heavy metals were studied by Pearson correlation. The statistical technique shows that strong significant correlation among the heavy metals. The Chemometric approaches namely: principal component analyses (PCA), hierarchical cluster analysis (HCA), were used for identify the soil pollutant. Spatial distribution of physico-chemical properties of soil such as pH, soil texture (sand, silt, clay) electrical conductivity was studied by geo-statistical methods such as kriging identified areas. The heavy metal mapping also attempted to know the distribution pattern in soils.

Introduction

Soil pollution is the major problem in the environment. The surface soils polluted due to usage of several biodegradable materials (like vegetables, animal wastes, papers, wooden pieces, carcasses, plant twigs, leaves, cloth wastes as well as sweepings) and many non-biodegradable materials (such as plastic bags, plastic bottles, plastic wastes, glass bottles, glass pieces, stone/cement pieces). The usage of these bio and non-bio degradable materials leads the variation of physical, chemical, and biological properties of soil affects the soil quality and plant growth. The physical properties of

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a soil largely determine the ways in which it can be used. The size, shape, and arrangement of the primary soil particles are known as the physical properties of soil. Other important physical properties center on the size and shape of the spaces between the particle arrangements, called the pore space, which has a direct effect on the movement of air and water, the ability of the soil to supply nutrients to plants, and the amount of water available to the plant. The physico-chemical properties such as soil texture (sand, slit, clay), pH, electrical conductivity (EC), bulk density (BD) and porous of the soil very often changed by natural and anthropogenic activities.

Clayey soil has been studied more than any other soil type for interactions between soil and pollutants. The main difference between clays and other soils is that clay has a large specific surface area, a high number of available active sites and a dynamic crystalline structure which makes it different in bulk physical properties in respect of sand or silt soils [1]. For the last two are characterized by their larger pore size and gritty texture, as well as low specific surface, and low holding capacity for water and nutrients [2]. Sand and silt textures are mainly composed of quartz with some fragments of feldspar, mica and traces of other heavy minerals [3], their composition evidences colloidal properties absence, and so far the physical, chemical and electro kinetic properties of soils composed mainly of these particles cannot be modified as it happens for clayey soils [4–5].

The proportions of the four major components of soils are inorganic particles, organic materials, water and the air can vary greatly from place to place and with depth. The amount of water and air in a soil can also fluctuate widely from season to season. However, the physical characteristics of the solid components, inorganic and organic particles, are essentially unchanging. Chemical properties of soils are important in that, along with their physical and biological properties, they regulate the nutrient supplies to the plant. Without these nutrients supplied by the soil or applied as inorganic fertilizers, organically by manures, and other vegetative materials, plant growth would cease.

Heavy metals are elements that exhibit metallic properties such as ductility, malleability, conductivity, cation stability, and ligand specificity. They are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 [6]. Some heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V, and Zn are required in minute quantities by organisms. However, excessive amounts of these elements can become harmful to organisms. Other heavy metals such as Pb, Cd, Hg, and As (a metalloid but generally referred to as a heavy metal) do not have any beneficial effect on organisms and are thus regarded as the "main threats" since they are very harmful to both plants and animals. Metals exist either as separate entities or in combination with other soil components. These components may include exchangeable ions sorbed on the surfaces of inorganic solids, nonexchangeable ions and insoluble inorganic metal compounds such as carbonates and phosphates, soluble metal compound or free metal ions in the soil solution, metal complex of organic materials, and metals attached to silicate minerals [7]. Metals bound to silicate minerals represent the background soil metal concentration and they do not cause contamination/pollution problems compared with metals that exist as separate entities or those present in high concentration in the other 4 components [8].

Generally topsoil layer contain largest amount of pollutants. The contaminant concentration in soil mainly depends on the adsorption properties of soil matter. The solubility of heavy metal ions in soil was mainly influence by many factors such as pH, conductivity, moisture content etc. In the municipal sewage water in which it contains the domestic liquid waste and industrial effluents are commonly found. The pollution level in the environment is increasing due to industrialization, urbanization, anthropogenic activities and natural sources.

Soil properties affect metal availability in diverse ways. Harter [9] reported that soil pH is the major factor affecting metal availability in soil. Availability of Cd and Zn to the roots of *Thlaspi caerulescens* decreased with increases in soil pH [10]. Organic matter and hydrous ferric oxide have been shown to decrease heavy metal availability through immobilization of these metals [11]. Significant positive correlations have also been recorded between heavy metals and some soil physical properties such as moisture content and water holding capacity [12]. Other factors that affect the metal availability in soil include the density and type of charge in soil colloids, the degree of complexation with ligands, and the soil's relative surface area [13]. The large interface and specific surface areas provided by soil colloids help in controlling the concentration of heavy metals in natural soils. In addition, soluble concentrations of metals in polluted soils may be reduced by soil particles with high specific surface area, though this may be metal specific [7]. For instance, Mcbride and Martınez [14] reported that addition of amendment consisting of hydroxides with high reactive surface area decreased the solubility of As, Cd, Cu, Mo, and Pb while the solubility of Ni and Zn was not changed. Soil aeration, microbial activity, and mineral composition have also been shown to influence heavy metal availability in soils [15].

The concentrations of heavy metals in environmental samples had been studied by several authors using either atomic absorption spectrometry (AAS) [16–20] or XRF analysis [21–24]. Most of these studies indicate high concentrations of heavy metals in the environment. Pollution of natural environment by heavy metal is a worldwide problem because these elements are indestructible and many of them have toxic effects on living organisms, especially when they exceed threshold values [25].

XRF is a rapid, non-destructive multi-elemental analysis technique with sensitivity in the range of 10^4 ppm to % [26] and it is ideal for environmental research. This analytical method has been widely and routinely applied to the analysis of various archaeological samples, historical relics and works of art [24,27]. X-ray fluorescence (XRF) analysis is based on the measurement of characteristic X-rays resulting from de-excitation of inner shell vacancy produced in a sample by means of a suitable source of incident radiation. EDXRF analysis employs detectors that will directly measure the energy of the X-rays in a suitable detecting medium [28].

Multivariate statistical methods are used to interpret the data in environmental research by several authors [12,29–30]. Pearson correlation is powerful tool to know the relationship between the physico-chemical properties and heavy metals [12]. Principal component analysis (PCA) and Cluster analysis (CA) are used to identify the source of the pollutant [31]. In the present study multivariate statistical methods are used to analyze the physico-chemical and heavy metals data's for soil samples.

In the last few years, anthropogenic activities like construction, waste disposal, domestic heating system and motor vehicles are continuously contributing towards an increase in the soil pollution in the tourist and picnic spots. So there is demand is necessary in the tourist place of Yelagiri hills to appraise the physico-chemical and heavy metal concentration in the soil to understand the present condition of the soil quality and to compile the baseline data for future monitoring. From the best knowledge, there is no data is available on the soil properties and the distribution of heavy metals in Yelagiri hills, Tamilnadu. The main objective of the present work is to study (i) physico-chemical properties of soil (ii) heavy metal concentration in the soil (iii) relationship between the physico-chemical properties and heavy metals using Pearson correlation (iv) identification of soil pollutant by principal component