

A wide range of techniques is available whereby various extraction reagents and experimental conditions are used. These techniques involve a 5-step [8], 4-step (BCR, Bureau Commune de Reference of the European Commission) and 6-step [13] extraction, and are thus becoming popular and adopted methods used for sequential extraction [14,15]. Several analytical methods have been used for the determination of heavy metals contents in marine environments. These include; flame AAS [16,17], atomic fluorescence spectrometry [18], anodic stripping voltametry [19,20], ICP- AES [21] and ICP-MS [22,23].

Heavy metal mobility and bioavailability depend strongly on their chemical and mineralogical forms in which they occur [24]. Several speciation studies have been conducted to determine study different forms of heavy metals rather their total metal content. These studies reveal the level of bioavailability of metals in harbour sediments and also confirm that sediments are bio- indicators of heavy metal pollution in marine environment [1,7,25,26].

Although several studies have been conducted on heavy metal pollution of harbour sediments, this paper aims to review sources, mobility, effects remediation and analytical methods used as well as to compare results that have been collected from different studies. The paper is organized as follows: Section 2 describes the sources of heavy metal pollution in harbour sediments, Section 3 discusses the mobility of heavy metals in harbour sediments, Section 4 discusses the effects of heavy metal pollution on the environment, Section 5 discusses the remediation of heavy metal pollution in harbour sediments, and Section 6 discusses the analytical methods used for the determination of heavy metals in harbour sediments.

shipping traffic especially in and close harbours. Industrial activities, vehicle emissions, agricultural activities and domestic waste can all act as a source of heavy metal pollution in the marine environment [7].

Many adverse effects have been done on human health by the environmental pollution of heavy metals. Heavy metals condition is problematic due to their persistence and non-degradability in the environments [27]. Metals distribution and association in marine sediments occur in various ways which include ion exchange, adsorption, precipitation and complexation. They are not permanently fixed by sediments [27]. Heavy metals pollution in aquatic environment and their uptake in the food chain by aquatic organisms and humans, put public health at risk.

In general, heavy metals are stable and persistence environmental contaminants of marine sediments. Interest in metals like Zn, Cu, Fe, and Mn which are required for metabolic activities in organisms depends on their nutritional value and their toxicity. Metals like Cd, Hg, Cr, Pb and As may exhibit extreme toxicity even at lower concentration under certain condition. Thus this makes regular monitoring of aquatic environment to be imperative and necessary.

Occurrence of heavy metals in marine sediments

Heavy metals are stable and persistent environmental contaminants of coastal sediments. In recent years there has been growing concern over increased contamination of estuaries and harbours from various anthropogenic sources [25]. Sediments serve as the ultimate sink for many contaminants and as a result, they pose the highest risk to the aquatic life as a source of pollution [28,29]. Bruder-Hubscherv et al. [30] worked on metal speciation in coastal marine sediments from Singapore and confirmed that sediments are the main repository and source of heavy metals in the marine environment and that they play a major role in the transport and storage of potentially hazardous metals.

A number of factors have been attributed to pollutant accumulation in harbour sediments. The design of the harbour to minimize hydrodynamic energy, industrial activities (ship repairs and traffic, accidental spills, loading and unloading), agricultural activities and urban (waste water) activities can all act as sources of heavy metal pollution in marine environment [1,2,5,31]. Heavy metal accumulation in marine sediment is due to a highly dynamic nature of the marine environment which allows rapid assimilation of these pollutants into sediments by processes such as oxidation, degradation, dispersion, dilution and ocean currents.

Phytoavailability of heavy metals depends on the characteristics of the sediment, the nature of the metal species, the interaction with sediment matrix and the duration of the contact with the surface binding. Heavy metal availability in marine organisms can be traceable to sediment characteristics such as pH, organic matter content and type, and then moisture [32]. In general,

acute or chronic damage to the nervous system. Some studies suggest that there may be a loss of up to 21 IQ points for a rise in blood lead levels from 10 to 20 µg/dl in young children. Average daily lead intake for adults is estimated at 1.6 µg from air, 20 µg from drinking water and 28 µg from food. Copper is generally remobilized with acid based ion exchange or oxidation mechanism [37].

Mercury: Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not naturally occur in living organisms. It is a global pollutant with complex and unusual chemical and physical properties. The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural bodies of water. The usage of mercury is widespread in industrial processes and in various products, (e.g. batteries, lamps and thermometers). Toxicity of mercury results in mental disturbance and impairment of speech, hearing, vision and movement [38].

It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry. Concern over mercury in the environment arises from the extremely toxic forms in which mercury can occur. Natural biological processes can cause methylated forms of mercury to form which bio-accumulate over a million fold and concentrate in living organisms especially fish. These forms of mercury: monomethylmercury and dimethylmercury are highly toxic causing neurotoxicological disorders. The main pathway for mercury to humans is through the food chain and not by inhalation [38].

Effects of heavy metals on public health

Sediments house many contaminants and therefore pose the highest risk to the aquatic environment as a source of pollution [28,29]. Environmental pollution by heavy metals impacts negatively on human health. Air remediation proves to be problematic due to the persistence and non-degradability of heavy metals [27]. High concentrations of heavy metals in biota can be linked to high concentrations in sediments.

The bioavailable metal load in sediments may affect the distribution and composition of benthic assemblages [39], and this can be linked to high concentrations recorded in living organisms [40].

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and this may be more toxic to the exposed organisms. They were able to establish that the effect of the salinity varies from metal to metal depending on the relative important of two counteracting processes, desorption from sediments to water or coagulation, flocculation and precipitation. From their results, sediments collected in area affected by chronic heavy metal contamination tend to be more efficient in trapping Zn, Cu and Pb at low salinity values. They found out that Cd tends to be more mobile as salinity increases.

In another study, [50] worked on the effect of chloride on heavy metal mobility of harbour sediments. Modified BCR-SEP was applied to harbour mobility in order to assess the extent trace element mobility (Cd, Cr, Cu, Ni, Pb and Zn) could be influenced by chloride content in sediments. Washed and non-washed sediment were compared respectively. The relative mobility order found for the six trace metals studied was not seen to be influenced by the presence of chloride in the sediments. An increase in mobility was observed for Cd and Zn (the most mobile metals) when chloride was present in the sediments. This was in agreement with findings from Riba et al. [1].

Therefore, further studies on the combine effects of pH and salinity on heavy metal mobility in marine harbour are recommended to be able to compare smaller difference in salinity values and in order to ascertain the major influence of chloride on results of heavy metals mobility

Analytical methods

Tremendous amounts of toxic pollutants have been discarded into coastal environment and the sediments of harbours represented large sink of heavy metals [51-54]. The sea and more particularly the aquatic systems are the ultimate respiratory of man's waste. Due to the dynamic nature of marine environment there is rapid assimilation of these materials by processes such as dilution, dispersion, oxidation, degradation or sequestration into sediments [2]. The release of heavy metals from sediments to water and organisms can be accelerated by processes which alter redox potentials of sediments and chemical forms of heavy metals. Toxic heavy metals are adsorbed onto organic matter and mineral surfaces in inorganic and organic forms [54,55].

Heavy metal mobility and bioavailability in sediments depend strongly on the mineralogical and chemical forms in which they occur

the environment. Corresponding metals in the exchangeable fraction

Strong acid-E tractable fraction: Residual phase: Residual phase serve as a useful tool in the assessment of the long-term potential risk of heavy metal or toxic metals entering the biosphere. Digestion in strong acid such as nitric acid, hydrochloric acid or mixture such as aqua regia that do not dissolve the silicate matrix have been commonly used to leach out the recalcitrant metals that are bound to the sediment in the residual phase. Residual phase give an estimate of the maximum amount of elements that are potentially mobilisable with changes environmental conditions. ISO 11466 [111] aqua regia digestion procedure is the known well procedure with a legal back in

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