

Contamination and behavior of heavy metals in intertidal sediments around a shooting range in Korea

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1. Introduction

Heavy metals have been generally considered as important inorganic pollutants due to their toxic effects, surface enrichment, and slow removal rates. Potentially toxic heavy metals can be released into living habitats inadvertently by human activities that affect physical and chemical conditions in a natural environment. More commonly, metal contaminants have been increasingly introduced into ecosystems through chimney emissions as well as through effluents of industrial and agricultural operations. Once metal contaminants are released, they are accumulated in soils, water, sediments and biota, and accelerated to pollution. Therefore, a number of researches have been performed to investigate the heavy metals pollution and their effects.

Although there were numerous studies on heavy metals pollution, only a limited study has been investigated on heavy metals contamination in soils and sediments around military shooting range (Lin et al., 1995). In some of countries, the use of ammunition, i.e. pellet and bullets for hunting and sport, is a significant source of heavy metal pollution. Generally, ammunitions contain various heavy metals including lead, copper, zinc, antimony, arsenic, and nickel (Tanskanen et al., 1991). Jørgensen and Willems (1987) reported that the amount of Pb used in shotgun ammunition in Denmark was 800 tons annually, compared with 250 tons of Pb used annually as additives in automobile fuel. In Germany, high contents of lead, cadmium and copper were observed in the training field of NATO (Schaefer, 1997). In the United States, about 3 million tons of lead are released as munitions in hunting and recreational shooting in the 20th Century and lead discharge is presently increasing at a rate of approximately 60,000 metric tons per year (Craig et al., 1999).

Recently in Korea, the pollution of soil and sediments by heavy metals released from ammunitions has been potentially increased due to a great number of shooting ranges. Thus, heavy metal contamination has been one of the socio-political issues for several decades in Korea. Therefore, it is very crucial to determine the degree of pollution and the dispersed extent of pollutants. The aims of this study are to assess the contamination and dispersion of heavy metals in intertidal sediments around a shooting range in marine environment, and to compare the occurrence and speciation of heavy metals between contaminated and

non-contaminated sediments.

2. Sampling and analysis

For this study, a total of thirty-two intertidal sediment samples were collected around the studied shooting range during the period from December 2000 to March 2001 (Fig. 1). Each sample was prepared by mixing 10 random spot subsamples, which were taken from surface to a depth of 5 cm using a stainless steel auger. The sediments were transferred to a plastic bag and were kept at -4°C until the laboratory analyses.

Grain-size distribution was measured with wet sieving and the following fractions were determined: silt+clay (<0.05 mm), fine sand (0.05–0.18 mm), and coarse sand (>0.18 mm). The pH, organic carbon (OC) and carbonate contents, and metal content of the sediments were analyzed for <0.18 mm fraction. Different extraction schemes (total, partial, and sequential extraction) were performed for determining metal concentrations.

3. Normalization of total metal contents with lithium: source and dispersion of heavy metals

To determine the degree of anthropogenic contamination of the collected sediments, that is, the concentrations above which would naturally occur, it is necessary to estimate the natural component of the total concentration. Aluminium has been frequently used as a grain size proxy in both marine and estuarine sediments, because it is a major constituent of fine-grained alumino-silicates with which the bulk of trace metals are typically associated (Aloupi and Angelidis, 2001). However, Al cannot be successfully used in sediments composed mainly of immature, physically weathered materials such as feldspars of variable grain size. In those surface sediments, Li presents better results because the metals are associated in the same mineralogical components such as primary micas and ferromagnesium minerals and secondary clay minerals but not in feldspars (Loring and Rantala, 1992). According to XRD analysis, the mineralogy of the bulk composite sediment samples in the study area are as follows: quartz, 33.8%, potassium feldspars, 15.9%, plagioclase feldspars, 22.2%, micas, 20.1%, chlorite, 3.7%, amphibole, 2.0%, kaolinite, 0.9%, and smectite, 1.2%. This may indicate that the sediments were transported through a comparatively short distance from the provenance.

We also observed that the concentrations of Al and Fe, organic carbon content (OC), and Li correlate positively against the silt + content. Li showed better correlation with silt + clay content (correlation coefficient = 0.88) than Fe, Al and OC (correlation coefficient = 0.79, 0.71 and 0.66 respectively). Therefore, Li normalization can be useful to determine whether the origin of trace metals in the surface sediment is anthropogenic or natural. The relationships between Li and other metals in surface sediments (n=32) are shown in Fig. 2. For Pb, Cu, Cd, and Zn, it is possible to consider some of the deviations from the linear trend as a result of antropogenic enrichment. In particular, Pb is highly concentrated only at the sediments collected around the shooting range (sampling nos. 27, 28, 29, 30, and 31). On the

other hand, restricted areas around the shooting range are moderately enriched in Cu (at sites of 27, 28, 29, and 30), Cd (at sites of 27, 28, 29, and 30), and Zn (at sites of 28 and 29).

If we exclude such abnormally enriched samples nearby the shooting range from the correlation calculation, better correlations are obtained for Li-Pb ($r=0.784$), Li-Cu ($r=0.833$), Li-Cd ($r=0.743$), and Li-Zn ($r=0.920$). Such a high correlation coefficient likely indicates the dominance of non-anthropogenic, mature weathering products in the sediments (Aloupi and Angelidis, 2001) which were derived from the rocks of the adjacent land. Thus, we suggest that most heavy metals emitted from the studied shooting range have not been dispersed extensively.

4. Speciation study based on modified BCR procedure

It is important to understand the geochemical process(es) and geochemical factor(s) affecting the dispersion of Cd, Cu, Pb, and Zn. For this purpose, a modified BCR procedure was used for extracting sequentially the metals in sediments. Fig. 3 shows the results of sequential extraction. Group A samples occur in the vicinity of the shooting range and therefore record the effect of anthropogenic contamination, while Group B sediments were collected away from the shooting range and were affected only by natural process.

As shown in Fig. 3, Pb, Cu, and Zn in Group A sediments were typically enriched in the reducible fraction (Pb: 60%, Cu: 36%, Cd: 23%, Zn: 18%). This indicates that these elements are associated with Fe-Mn oxides (Ure et al., 1993). They are also partitioned in the carbonate fraction (Pb: 27%, Cu: 20%, Cd: 28%, Zn: 16%). In the case of Cd, relatively high proportion of the metal was also released from the exchangeable fraction. On the other hand, most of the metals in Group A sediments are bounded to residual fraction.

Lin et al. (1995) reported that the principal mechanisms of Pb retention in soils include the adsorption onto organic complexes, clay minerals, and Fe-, Mn- and Al-hydrous oxides. They also suggested that weathering products of Pb pellets tend to be retained primarily in the weathering crusts as secondary mineral phases. The secondary mineral phases of the pellets consists dominantly of hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], with small amounts of cerussite (PbCO_3), anglesite (PbSO_4), and massicot (PbO) (Lin et al., 1995; Lin, 1996). The solubility of such secondary minerals may be influenced by pH as well. The results of sequential extraction in this study suggested that Pb is preferentially associated with the carbonate fraction. Therefore, cerussite or hydrocerussite are considered as the dominant secondary minerals controlling the mobility of Pb. The carbonate fraction also controls the geochemistry of Cu and Zn in the study area. However, the carbonate fraction does not control the behavior of Cd in both Group A and B sediments.

In summary, the heavy metals (Cd, Cu, Pb, and Zn) have not been dispersed extensively from the shooting range. The results of sequential extraction also show that secondary minerals (possibly, carbonates) and Fe-Mn oxides play a major role in controlling the behavior of Pb, Cu, and Zn.

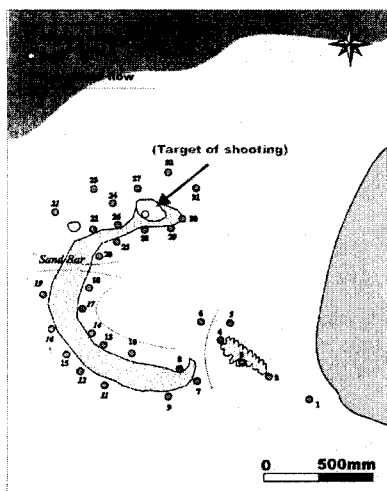


Fig. 1 Sampling site

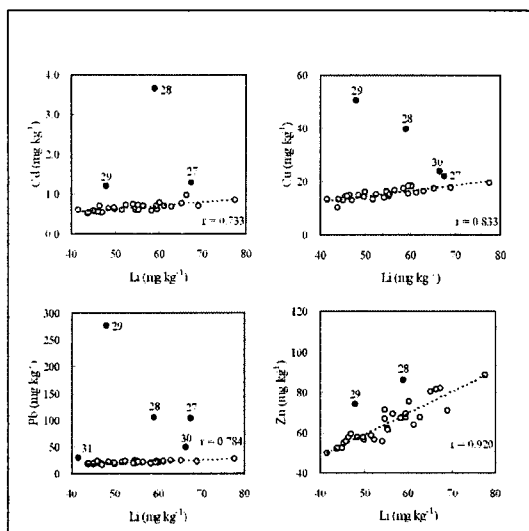


Fig. 2 Plots of Li versus Cd, Cu, Pb and Zn in surface sediments (n=32)

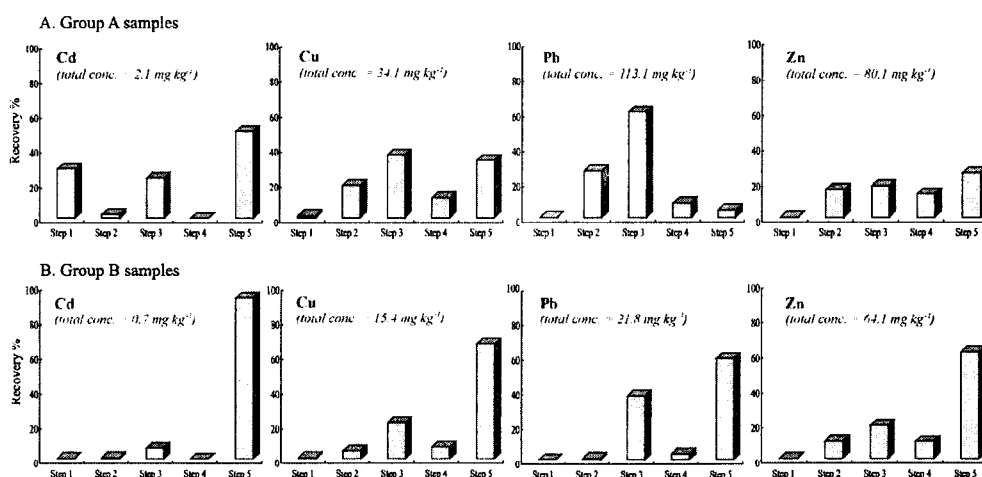


Fig. 3 Partitioning of Pb, Zn, Cu and Cd in surface sediments

(Step 1: exchangeable, Step 2: carbonate, Step 3: reducible, Step 4: oxidizable, Step 5: residual)