

Contamination and dispersion of heavy metals in intertidal sediments around a military shooting range

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Introduction

Heavy metals have been generally considered as serious inorganic pollutants because of their toxic effects, high enrichment factors, and slow removal rates (Zielhuis., 1979). Although there are numerous studies on heavy metal pollution, only a limited number have investigated the heavy metal contamination in shooting range soils and sediments. In some countries, the use of ammunition (pellets and bullets) has been recognized as a significant source of heavy metal pollution. Such ammunitions contain a variety of heavy metals such as 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 is 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. In United States, about 3 million tons of lead was released as ammunitions in hunting and recreational shooting range in the 20th Century, and the lead discharge is currently increasing at an approximate rate of 60,000 metric tons per year (Craig, 1998).

In Korea, the pollution of soils and sediments by heavy metals released from ammunitions is likely serious, because a great number of shooting ranges are ubiquitous. However, there is no geochemical study for assessing the environmental degradation around shooting ranges. 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.

Sampling and Analysis

A total of 32 intertidal sediment samples were collected along a sandbar nearby the studied shooting range during December 2000 to March 2001 (Fig. 1). Each sample was prepared by mixing of 10 random spot subsamples which were collected to a depth of 5 cm using a stainless auger. The sediments were transferred to plastic bag and were kept -4°C until laboratory analysis. In the laboratory, grain-size distribution was measured by wet sieving. The pH, organic carbon and carbonate contents, and metal contents were also measured for <0.18 mm fraction. Different extraction schemes (total, partial, and sequential) were used for

the measurements of metal concentrations in this study.

Results and Discussion

To determine the degree of anthropogenic contamination of collected sediments, i.e., the concentrations above those which would naturally occur due to ammunitions, it is required to estimate the natural component of total concentration. For this purpose, 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 aluminosilicates with which the bulk of trace metals are commonly associated. However, Al cannot be successfully applied to the sediments composed mainly of immature physically weathered materials, such as feldspars, of variable grain size. Thus, Al may be present in roughly the same amounts in the coarse as well as the fine fraction, potentially resulting in poor or insignificant correlations between trace metals and Al. In those sediments, Li may give better results because most trace metals are associated in the same mineralogical components as Li, such as primary micas and ferromagnesian minerals and secondary clay minerals but not in feldspars.

Figure 2 shows the relationships between the total concentration and Li concentration for examined surface sediments (n=32). In case of Pb, Cu, Cd, and Zn, it is possible to consider the deviations from a linear trend as the result of heavy metal enrichment due to anthropogenic (ammunition-derived) effect. Those anomalous samples were collected near the shooting target. If those trace metal enriched samples are excluded from the correlation calculations, high correlation coefficients are observed between Li-Pb ($r = 0.784$), Li-Cu ($r =$

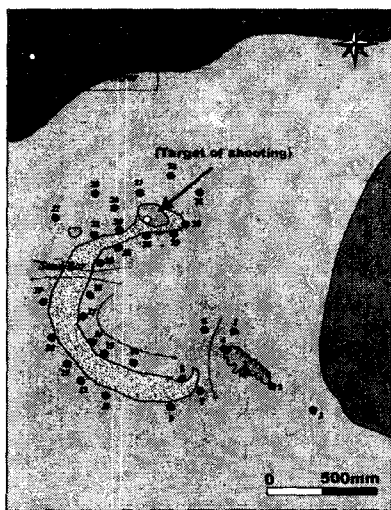


Fig 1. Sampling site

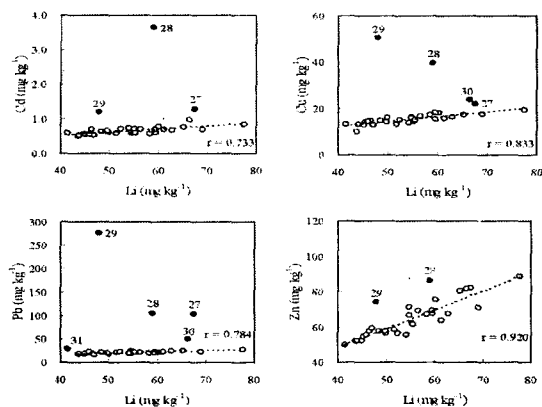


Fig 2. Plots of Li versus Cd, Cu, Pb, and Zn concentrations in the studied intertidal sediments (n = 32)

0.833), Li-Cd ($r = 0.743$), and Li-Zn ($r = 0.920$). Such a strong correlation may indicate the prevalence of mature weathering products in the sediments, which were derived from the rocks in adjacent land. We also suggest that ammunition-derived heavy metals have not been dispersed extensively in the studied area, likely as those metals are strongly retentive in the intertidal sediments due to the adsorption with organic complexes, clay minerals, or Fe-Mn- and Al-hydrous oxides.

To prove the chemical forms or ways of binding the heavy metals in sediments, sequential extraction of sediments was carried out. Pb, Cu, Cd, and Zn in sediments are found to be mostly bound to the acid-extractable and/or reducible fractions. This indicates that those elements are possibly associated with Fe-Mn hydroxides. Therefore, we suggest that Fe-Mn hydroxides in sediments play a major role for retention of heavy metals in the intertidal environment examined.

Summary

Li was proven to be a better geochemical normalizer than Al in the intertidal sediments. Using the Li versus heavy metal relationship, we could identify the extent of ammunition-related pollution in the sediments. In particular, Cd, Cu, Pb, and Zn are influenced by anthropogenic pollution. However, the metal contamination is found restrictedly around the shooting target. The results of sequential extraction show that Fe-Mn hydroxides in sediments play a major role for retention (immobilization) of heavy metals.

References

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