Analysis of the Composition of Heavy Metal Pollution in Japanese River Sediments by Principal Component Analysis

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Abstract

This report describes an application of principal component analysis to heavy metal contents (Cu, Cr, Zn, Pb, Cd, Ni), HNO₃-H₂O₂ soluble metals in the upstream sediments and 0.5 N HCl soluble ones in the downstream sediments. Two principal factors were extracted, and a comparison was made between the distribution of heavy metals on the plane produced by two factor loadings and that of rivers on the plane produced by two factor scores.

Results show that the first factor represents the general pollution by heavy metals. The second factor in HNO₃-H₂O₂ soluble heavy metals in the upstream sediments represents an axis of siderophile-chalcophile element from the standpoint of geochemistry, while the second factor in 0.5 N HCl soluble heavy metals in the downstream sediments represents an axis of adsorbable-unadsorbable element in sediment from the standpoint of artificial heavy metal pollution.

1. Introduction

With the remarkable industrial development and increase in urban population, environmental pollution has become a serious problem in Japan. The authors have studied environmental analysis of heavy metals in river sediments to understand the status of river pollution (TADA et al. 1976; NISHIDA et al. 1982; NISHIDA et al. 1984a, 1984b). One of the most important problems in these investigations is to clarify the composition of pollution which consists of multivariate measurements of Cu, Cr, Zn, Pb, Cd and Ni.

In the present study, principal component analysis is applied to heavy metal data in Japanese first class river sediments to investigate the composition of heavy metal pollution in river sediments. The first class rivers were designated by the Japanese government in 1963 as important in view of national land conservation and economic program.

2. Materials and Methods

Random samples of upstream and downstream sediments were obtained by means of Eckmann-Berge bottom sampler at ten points across either bank of rivers in Japan. The upstream sediments from 72 rivers were taken at unpolluted places, and the downstream sediments from 92 rivers were taken at about 1 km upstream from the river mouth.

Each of these sediments was stirred well and dried at 80°C. The amounts of heavy metals (the average of ten measurements) soluble in HNO₃-H₂O₂ soluble and in 0.5 N HCl, respectively, of Cu, Cr, Zn, Pb, Cd and Ni, were measured in 72 upstream and 92 downstream sediments from first class rivers in Japan (AGEMIAN et al. 1976, CHESTER et al. 1981, TADA et al. 1976).

Principal component analysis was employed to clarify the composition of heavy metal pollution in river sediments. The term principal component analysis refers to a group of related statistical techniques whose primary purpose is to represent a set of variables in terms of a smaller number of hypothetical variables, that is factors. The computer program by HAGA et al. (1981) was used to implement the numerical calculation of the analysis. The data were transformed to distribute according to normal by logarithmic translation, because the raw data were distributed according to lognormal or nearly lognormal (NISHIDA et al. 1984b).
3. Results and Discussion

The results obtained by principal component analysis are shown in Tables 1 and 2, and in Figs. 1 to 4.

Table 1 presents the eigen values, contributions and cumulative contributions. According to this table, 79.1 percent of the total variations in the HNO₃-H₂O₂ soluble metals (upstream) and 86.4 percent of the total variations in the 0.5 N HCl soluble metals (downstream) are accounted for by 2 factors.

More than 2 factors were not taken into consideration, because their eigen values and contributions are too small; the 3rd eigen value of the HNO₃-H₂O₂ soluble heavy metals in upstream sediments was 0.532 and that of the 0.5 N HCl soluble heavy metals in downstream sediments was 0.298. The 3rd contribution of the HNO₃-H₂O₂ soluble heavy metals in upstream sediments was 0.088 and that of 0.5 N HCl soluble heavy metals in downstream sediments was 0.049.

Approximately 63 percent and 76 percent, for each case, of the variation in the data can be explained by the first factor which has heavy loading on Cu, Cr, Zn, Pb, Cd and Ni equally. This factor is readily interpretable as a size factor which in this study involves general pollution by heavy metals.

The second factor which has positive loading on Cr and Ni and negative loading on Cu, Zn, Pb and Cd for each case similarly explains 15.8 and 9.6 percent of the variance, respectively. This factor can be interpreted as a shape factor which means in this study the composition of heavy metal pollution.

Figure 1, which shows the relationships among the HNO₃-H₂O₂ soluble heavy metals in upstream sediments, is useful to understand Table 1 more graphically.

The six heavy metal variables are plotted on the plane of Cartesian co-ordinates in which the abscissa and the ordinate represent the magnitude of the first and second factor loading, respectively. According to Fig. 1, heavy metals have a small variance in the first factor loading but a large variance in the second factor loading. The heavy metals can be classified into two groups, the first group consisting of Cr and Ni, and the second group of Cu, Zn, Pb and Cd.

Here it can be recalled that the HNO₃-H₂O₂ soluble heavy metals in upstream sediments contain geochemical matter (Bradshow 1974; Tada et al. 1976), so Fig. 1 can be considered from the geochemical standpoint. Heavy metals in the first group, Ni and Cr, belong to siderophile elements which are contained in ultramafic rocks or ultrabasic rocks, while heavy metals in the second group, Cu, Zn, Pb and Cd, belong to chalcophile elements which are contained in basic volcanic rocks or acidic rocks and are highly active with a strong affinity to sulphur (Beus et al. 1976). In other words, the second

| Table 1. Eigen values, contributions and cumulative contributions for 1st and 2nd factors. |
|---------------------------------|----------|----------|----------|----------|
| Eigen Value | 1st   | 2nd   | 1st   | 2nd   |
| 1.000   | -     | -     | 4.600 | 0.575  |
| 0.937   | -     | -     | 0.768 | 0.996  |
| 0.833   | -     | -     | 0.768 | 0.864  |
| 0.750   | -     | -     | -     | -      |
| 0.667   | -     | 0.083 | -     | -      |
| 0.583   | -     | 0.000 | -     | -      |
| 0.500   | 0.05  | -     | -     | -      |
| 0.417   | -     | -     | -     | -      |
| 0.333   | -     | -     | -     | -      |
| 0.250   | -     | -     | -     | -      |
| 0.167   | -     | -     | -     | -      |
| 0.083   | -     | -     | -     | -      |
| 0.000   | -     | -     | -     | -      |

Fig. 1. Plot of the HNO₃-H₂O₂ soluble heavy metals in upstream sediments.
abscissa; 1st factor loading.
ordinate; 2nd factor loading.
Mark (1-6) in the Figure corresponds to Cu, Cr, Zn, Pb, Cd and Ni, respectively.
factor represents the difference between the metals which are formed within ferrous minerals earlier and the metals which are formed within sulphur minerals as sulphide later in the generative period of geochemicals.

On the other hand, data from upstream rivers are plotted in the plane of Cartesian co-ordinate as shown in Fig. 2, in which the abscissa and ordinate represent the first and the second factor scores, respectively. According to Fig. 2, the Toyo, Takahashi, Ara (Kanto) and Midori rivers contain a great amount of Ni and Cr. The Toyo and Ara (Kanto) rivers belong to the Sabagawa metamorphic belt, which is known to contain much Ni and Cr in Japan. The Tama and Niyodo rivers flow through a limestone belt and contain much Cr, Ni and Cd. The Maruyama and Sagami rivers, on the other hand, flow through an ultrabasic rock belt and contain much of all six heavy metals. The Jintsu River flows through a gneiss belt and contains much Zn, Pb and Cd. The Yoshii River has much Cu and Pb. The Yamato, Suzuka and Koze rivers contain less heavy metals; the Suzuka and the Koze flow through a granite belt which is known to contain less amounts of metals.

Thus, it becomes clear that the second factor in HNO₃-H₂O, soluble heavy metals in upstream sediments represents an axis of siderophile-chalcophile element from the geochemical points of view.

Figure 3 shows the relations among the 0.5 N HCl soluble heavy metals in downstream sediments. Heavy metals are classified into two groups in the figure; the first group consists of Cr and Ni, and the second group of Cu, Zn, Pb and Cd. Here it can be recalled that the 0.5 N HCl soluble heavy metals in downstream sediments contain nongochemical, that is, artificially polluted matter (BRADSHAW 1974; TADA et al. 1976), so that Fig. 3 was examined from the standpoint of artificial pollution. Heavy metals in the first group, Ni and Cr, are un-adsorbable in sediments and unable to be precipitated as sulphide because of the low affinity to sulphur. Also, Cr and Ni do not distribute widely as water solutions because of their high resistance to weathering. Heavy metals in the second group, Cu, Zn, Pb and Cd, are adsorbable in sediments and can be precipitated easily.

![Fig. 2. Plot of the data of upstream rivers. abscissa: 1st factor score. ordinate: 2nd factor score. Marks in the Figure are as follows.](image-url)
as sulphide because of the high affinity to sulphur. Naturally occurring Cu, Zn, Pb and Cd exist as sulphide deposits and eventually cause pollution.

On the other hand, data from downstream rivers are plotted on Cartesian co-ordinates produced by the first and second factor scores as shown in Fig. 4. The Mu and Saru rivers flow through an area polluted by Cr and Ni in Hokkaido. The Tama, Oota, Tsurumi and Ki rivers, on the other hand, flow through large cities and contain a great amount of all six metals. The Jintsu, Kitakami and Kakehashi rivers course through mining areas and thus contain much Cu, Pb, Zn and Cd, while the Agano, Gokase and Ara (Hokuriku) rivers flow through medium-sized or small cities and are polluted to some extent by heavy metals. The Sendai (Kyushu), Koze, Yahagi, Kumozu and Saba rivers flow through unpolluted areas and contain less metals. Thus, it becomes clear that the second factor in 0.5 N HCl soluble heavy metals represents an axis of adsorbable-unadsorbable element in sediments.

Principal component analysis was applied to heavy metal data found in first class river sediments in Japan in order to estimate the composition of heavy metal pollution. It became clear that the first factor for each case represents...
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sents general pollution by heavy metals, while the second factor in HNO₃-H₂O₂ soluble heavy metals in upstream sediments represents an axis of siderophile-chalcophile element from geochemical points of view; 0.5 N HCl soluble heavy metals in downstream sediments represents an axis of adsorbable-unadsorbable element in sediments from the standpoint of artificial pollution.

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