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Metal exposure profiles at metal-contaminated sites in rivers across Japan

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ABSTRACT

Understanding realistic exposure profiles of mixtures is crucial for effectively predicting the ecological risks and effects of metal mixtures in natural environments on a large scale (e.g., at a country level). In this study, we aimed to compile available measurement data for metals relevant to ecological risk assessment in rivers across Japan, identify metals of particular concern based on their relative ecological risks, and derive realistic exposure profiles of these metals based on the compiled data. We focused on six metals of concern (Ni, Cu, Zn, Pb, Cd, and Al) selected by comparing available measurement data and 10% inhibition concentrations for the daphnid *Ceriodaphnia dubia*. We then compiled measurement data on these metal concentrations, ensuring sufficiently low detection/quantification limits relevant to ecological risk assessments, from a total of 531 riverine sites. At 194 metal-contaminated sites, concentrations generally increased in the following order: Cd (median: 0.013 μg/L), Pb (0.072 μg/L) < Ni (0.45 μg/L) < Cu (1.2 μg/L) < Zn (9.1 μg/L), Al (22 μg/L). Using hierarchical cluster analysis, we classified the metal-contaminated sites into three groups (Group 1: 56 sites; Group 2: 104 sites; and Group 3: 34 sites). Group 1 and Group 3 were characterized by higher concentrations of Cd and Ni, respectively, compared to Group 2. Further compilation and accumulation of measurement data, particularly in small rivers (e.g., tributaries of major rivers), are required to more accurately assess contamination levels and ecological risks from metals in rivers nationwide.

INTRODUCTION

In aquatic environments such as streams and rivers, contamination by trace metals such as copper and zinc is a long-standing environmental issue (Luoma & Rainbow, 2008; Namba et al., 2020). The risk assessment approaches for many individual metals, such as copper, zinc, and nickel, have seen considerable advancements, particularly with the development of biotic ligand models (Adams et al., 2020). However, predicting ecological impacts of metal mixtures remains a challenging task (Farley et al., 2015), although a general risk assessment framework has been proposed to address this issue (Nys et al., 2018). To effectively understand and predict ecological risks and effects of metal mixtures in natural environments on a broad scale (e.g., a country level), it is crucial to understand the mixture exposure profiles that are likely to occur (Mebane et al., 2017).

In Japan, there has been no comprehensive attempt to compile exposure data or evaluate exposure profiles for multiple elements, including metals, on a nationwide scale. There are two national-level databases that compile results of water quality monitoring in aquatic environments throughout Japan: the Comprehensive Information Website for Water Environment managed by the Ministry of the Environment (https://waterpub.env.go.jp/water-pub/mizu-site/) and the Water Information System managed by the Ministry of Land, Infrastructure, Transport and Tourism (http://www1.river.go.jp/). However, the reported quantification limits for metals in these databases are not sufficiently low to be used for ecological risk assessments, and measurements at a majority of monitoring sites have either not been performed or fall below the reported limits. For instance, the reported quantification limits for Cu, Cd, and Pb are generally higher than 10, 0.3, and 1 µg/L, respectively, which are close to or approximately an order of magnitude higher than the U.S. EPA hardness-adjusted water quality criteria for aquatic life (e.g., 2.3, 0.21, 0.42 µg/L at water hardness of 30 mg/L; U. S. Environmental Protection Agency (2016); U.S. Environmental Protection Agency (2002)).

The objectives of this study were thus threefold: (1) to compile available measurement data of metals relevant to ecological risk assessment in rivers across Japan, (2) to identify metals of particular concern based on their relative ecological risks, and (3) to elucidate the realistic exposure profiles of these metals based on the compiled data. The outcomes of this study were expected to provide valuable insights into realistic concentration levels and ratios, which are critical for assessing the ecological risks and effects of exposure to mixtures of metals in Japanese rivers.

MATERIALS AND METHODS

SELECTION OF METALS OF CONCERN

We first selected metals of concern by comparing measurement data for as many metals as possible in rivers across Japan with toxicity test results performed under the same conditions. As the measurement dataset, we used results of dissolved metal concentrations surveyed at 450 sampling sites across 45 major rivers (i.e., 10 sites per river) in Japan during 2002–2006 (Uchida et al., 2007). For the toxicity test data, we used the IC10 (10% Inhibition Concentration) values for 50 metals, determined by chronic toxicity tests with *Ceriodaphnia dubia* (Okamoto et al., 2021). The toxicity tests were consistently conducted using filtered and sterilized tap water with a water hardness of approximately 70–80 mg/L. Although water quality parameters important for considering metal bioavailability (e.g., pH, water hardness, and dissolved organic matter; Adams et al., 2020) can vary among sampling sites and differ between the toxicity tests and sampling sites, the results of Okamoto et al. (2021) are considered ideal for the preliminary screening of metals of particular concern.

For the 15 metals for which data were available from both sources (Ni, Cu, Zn, Pb, Cd, Al, Mn, Fe, Co, Rb, Sr, Ba, Ti, V, and Cr), we calculated the ratio of the dissolved concentration of each metal to the corresponding IC10 (hereafter, toxic unit, TU) as well as the sum of the TUs at each sampling site. By calculating the contributions of each metal to the sum of the TUs at each sampling site and ranking the metals based on the 95th percentiles of these contributions, the metals in descending order were Ni (0.94), Zn (0.64), Cd (0.61), Al (0.31), and Cu (0.14) at sites where the sum of the TUs ≥ 1 (i.e., metal-contaminated sites) (Fig. 1). The 95th percentiles of the contributions for Cu, Fe, and Co were similar (0.14, 0.13, and 0.09, respectively). Among these three metals, Cu was included in the following analysis because its IC10 of 12 μg/L (Okamoto et al., 2021) was somewhat higher than the U.S. EPA hardness-adjusted water quality criterion (e.g., 6.6 μg/L at a water hardness of 70 mg/L) and because ecological risks associated with Cu have been a concern in Japan (Han et al., 2016). Lead was included in the following analysis because the IC10 for Pb reported by Okamoto et al. (2021) was 67 μg/L, which is more than an order of magnitude higher than the U.S. EPA hardness-adjusted water quality criterion of 1.7 μg/L at a water hardness of 70 mg/L. It should be noted that the IC10 of 0.37 μg/L for Ni is two orders of magnitude lower than the U.S. EPA water quality criterion of 38 μg/L at a water hardness of 70 mg/L. Alghouth the direct use of IC10 values requires some caution, IC10 values are likely acceptable for screening metals of ecological concern. The following data collection and analysis were conducted for a total of six metals (Ni, Cu, Zn, Pb, Cd, and Al).

DATA COMPILATION

In order to compile as much available monitoring data as possible for these metals in rivers across Japan, we reviewed the Comprehensive Information Website for Water Environment and the Water Information System as well as existing literature covering over 1000 sampling sites in total (excluding the two databases). The literature included peer reviewed papers (e.g., Han et al., 2013) and Japanese project reports. Based on examination of whether the measured concentrations (preferably, dissolved concentrations) of all six metals were relatively low, we selected three datasets: the large-scale measurement data of (Uchida et al., 2007); measurements from metal-contaminated rivers affected by legacy mines as well as nearby reference rivers (Iwasaki et al., 2023: 26 sites; and Iwasaki et al. unpublished data: 12 sites); and measurements from rivers to assess the ecological impacts of Ni (Takeshita et al., 2019: 50 sites). All these studies reported dissolved metal concentrations by filtering water samples through filters with a pore size of 0.45 μm and analyzing them using inductively coupled plasma mass spectrometers (ICP-MS) or inductively coupled plasma optical emission spectrometers (ICP-OES). We analyzed data from a total of 531 sampling sites (excluding 7 estuarine sites from Uchida et al. 2007; see Figure 2a). All the complied data are available in the Supporting information (Table S1).

METAL EXPOSURE PROFILES

To obtain realistic metal exposure profiles at the metal-contaminated sites where ecological risks due to the five metals were of concern, we first calculated the sum of TUs by dividing the measured dissolved metal concentrations by the U.S. EPA hardness-adjusted water quality criteria for aquatic life (U. S. Environmental Protection Agency, 2016; U.S. Environmental Protection Agency, 2002). The water quality criteria for a water hardness of 20 mg/L were used as conservative "safe" concentrations (Cu: 2.3 μg/L, Zn: 30.2 μg/L, Pb: 0.42 μg/L, Cd: 0.21 μg/L, Ni: 13.3 μg/L, and Al: 220 μg/L) because water hardness at many of the sampling sites were as low as 20 mg/L (Table S1). We used U.S. EPA water quality criteria because water quality standards for aquatic life are available in Japan for only total Zn (30 μg/L). Any concentration below the quantification or detection limit was operationally replaced with half the corresponding limit for operational purposes (see Table S1 for specific values). We then selected 194 sites where the sum of TUs ≥ 1 as metal-contaminated sites (Figure 2b). In this study, a sum of TUs >1 was used as the conservative criterion for selection, not to accurately assess risk, but rather to select sites where ecological risks could be of concern. Together with a line of empirical evidence that the exceedance of the sum of TUs beyond 1 does not necessarily lead to population or community-level effects on aquatic organisms, such as fish and macroinvertebrates (Iwasaki et al., 2023; Namba et al., 2021), it is important to note that such impacts may not always be observed at the selected metal-contaminated sites.

Based on concentrations of the six metals, the metal-contaminated sites were classified using hierarchical cluster analysis with Ward's method based on Euclidean distances (Ward, 1963). To ensure classification based on metal concentration ratios (i.e., concentration compositions) rather than absolute concentration values at individual sites, standardized values of log-transformed concentrations were used for the hierarchical cluster analysis.

RESULTS AND DISCUSSION

Based on the results of the hierarchical cluster analysis (see Fig. S1 for the dendrogram), we classified the metal-contaminated sites into three groups (Group 1, 56 sites; Group 2, 104 sites; and Group 3, 34 sites). Although there is no absolute criterion for determining the number of clusters in hierarchical cluster analysis, using more than four groups resulted in clusters with fewer than 20 sites. We therefore used a three-group classification.

Despite the observed large variations in concentrations of metals, the levels of concentrations at the 194 metal-contaminated sites generally increased in the order: Cd (median: 0.013 μg/L) ≤ Pb (0.072 μg/L) < Ni (0.45 μg/L) < Cu (1.2 μg/L) < Zn (9.1 μg/L) ≤ Al (22 μg/L) (Fig. 3). Compared with Group 2, where the overall metal concentration levels were similar to those at all metal-contaminated sites, the Cd concentrations in Group 1 were notably higher (median: 0.12 μg/L in Group 1 vs. 0.007 μg/L in Group 2). Similarly, the Ni concentrations in Group 3 were relatively high (median: 17 μg/L in Group 3 vs. 0.44 μg/L in Group 2). Each of Groups 1–3 included sampling sites from at least two of three different original datasets (Fig. 2, Table S1), and it was difficult to further interpret the geographic distribution shown in Fig. 1b. However, sampling sites from legacy mine surveys (Iwasaki et al., 2023) were more frequently included in Group 1, whereas those from the nickel survey (Takeshita et al., 2019) were more frequently included in Group 3.

CONCLUSIONS

By compiling measurement data on metal concentrations relevant to ecological risk assessments, we were able to derive realistic compositions and concentration levels of six metals (Ni, Cu, Zn, Pb, Cd, and Al) at metal-contaminated sites in rivers across Japan (see Table S2 for the percentiles of metal concentrations in individual groups). This information would be useful in choosing levels of metal concentrations relevant to those found in Japanese rivers for metal mixture toxicity tests, enabling a better assessment of their actual ecological risks. However, it should be noted that the two field studies included in our dataset focused on the impacts of specific metals such as Ni (Takeshita et al., 2019) or Cu, Zn, Cd, and Pb (Iwasaki et al., 2023). In addition, Uchida et al. (2007) have measured metal concentrations in the mainstreams of major rivers across Japan but did not make measurements in tributary streams. Because levels of contamination in small streams and rivers are more likely to be high because of their limited capacity for dilution (Büttner et al., 2022; Iwasaki et al., 2022), further compilation and accumulation of measurement data are therefore required to more accurately assess contamination levels and ecological risks from metals in rivers across Japan. To this end, it is essential to encourage the open accessibility of measurement data, along with their geographical coordinates, in easy-to-use formats in publications such as peer-reviewed papers, particularly those written in Japanese. Furthermore, the bioavailability of metals was not considered when selecting the metal-contaminated sites in this study. While important water quality variables such as Ca, Mg, and dissolved organic carbon (DOC) were collected as complementary data (Table S1), DOC was not measured by Uchida et al. (2007). Because the influence of DOC on bioavailability can be significant for some metals (OECD, 2017), compiling measurement data on such water quality variables in addition to metals, as well as developing predictive models when measurements are unavailable, will be essential for more accurate metal risk assessments.

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DISCLAIMER

During the preparation of this paper, the authors used ChatGPT to improve readability and language. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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Figure 1

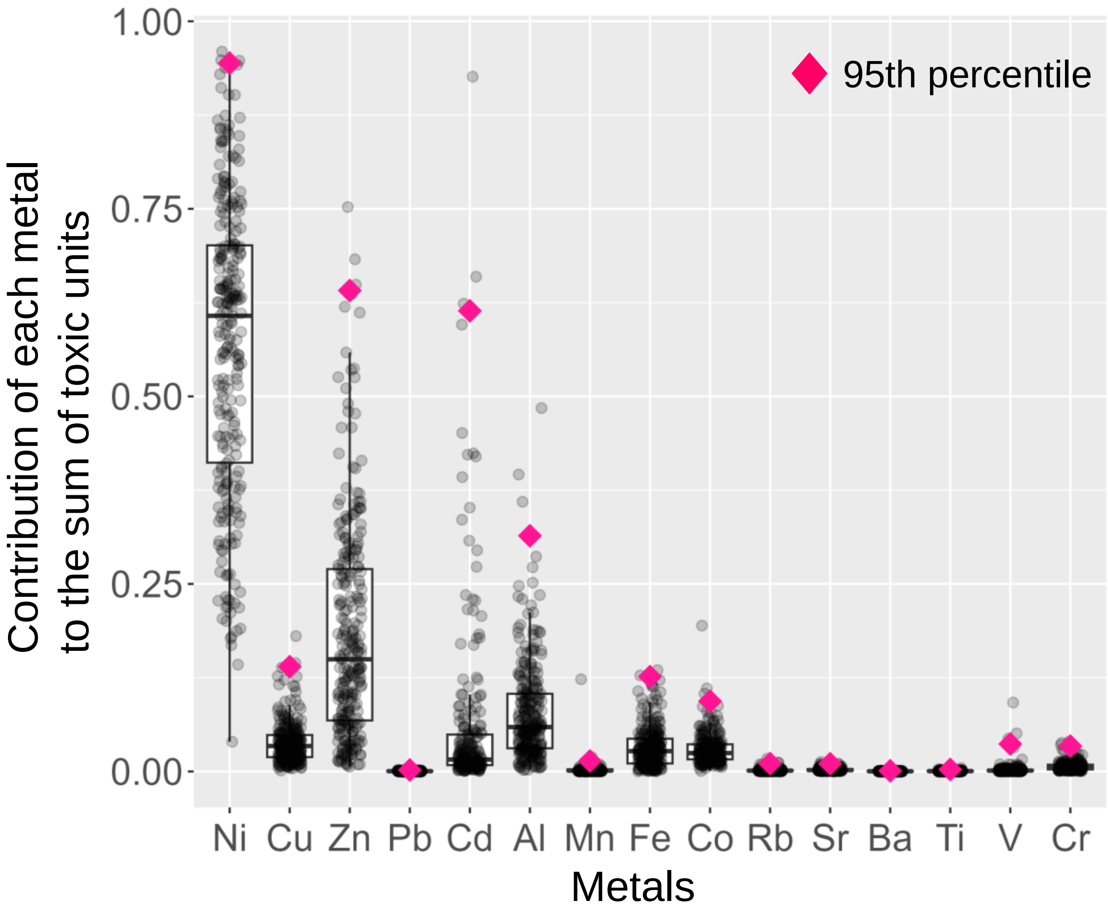
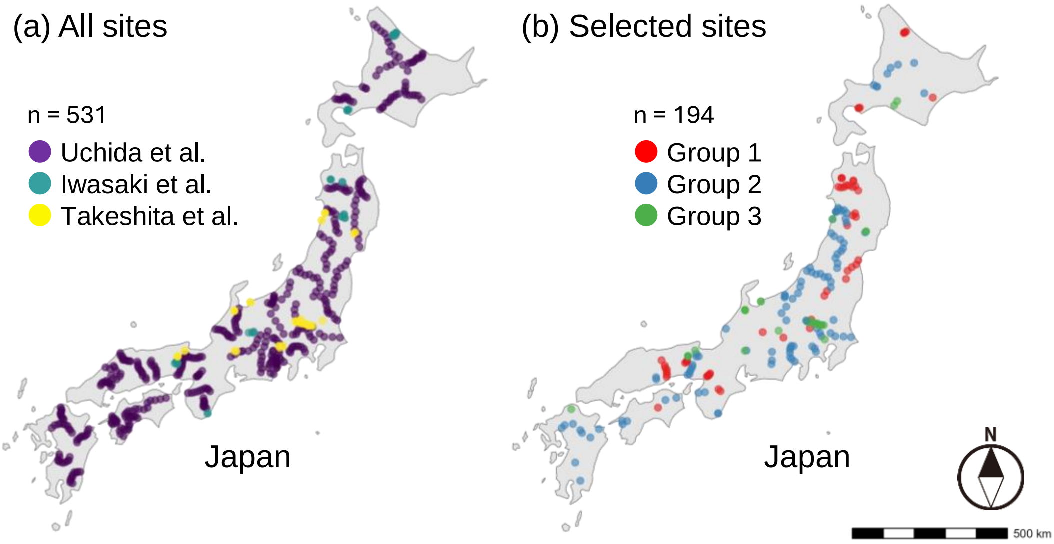


Fig. 1. Distribution of the contribution of each metal to the sum of toxic units. The central line in each boxplot represents the median (50th percentile), while the lower and upper boundaries of the box correspond to the 25th (Q1) and 75th percentiles (Q3), respectively. The whiskers extend to the smallest and largest values within 1.5 times the interquartile range (IQR) from the lower and upper quartiles. Red diamonds indicate the 95th percentiles for individual metals. Gray dots represent raw data points.

287 Figure 2



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289 Fig. 2. Maps showing (a) all sites examined and (b) selected metal-contaminated

290 sites.

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Figure 3

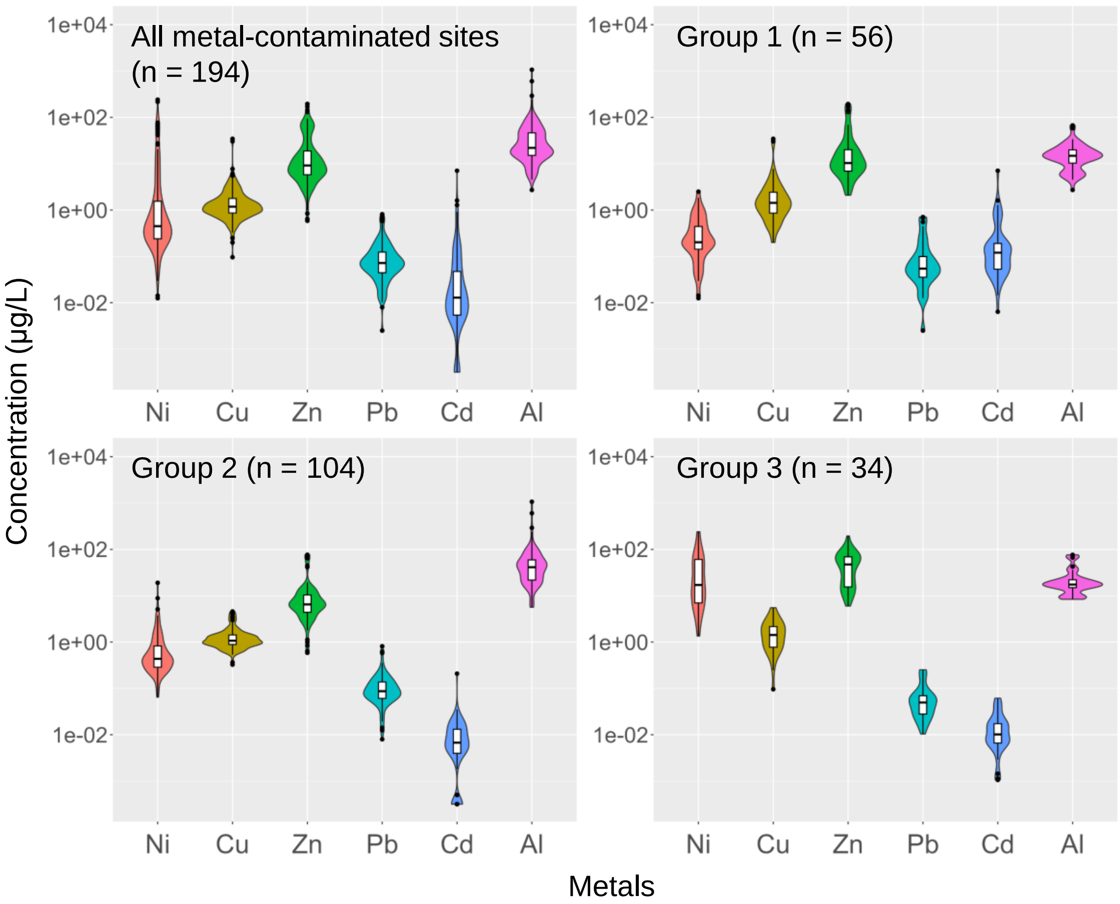

Fig. 3. Distributions of concentration of six metals (Ni, Cu, Zn, Pb, Cd, and Al) across all metal-contaminated sites, as well as in Groups 1, 2, and 3. The central line in each boxplot represents the median (50th percentile), while the lower and upper boundaries of the box correspond to the 25th (Q1) and 75th percentiles (Q3), respectively. The whiskers extend to the smallest and largest values within 1.5 times the interquartile range (IQR) from the lower and upper quartiles. Violin plots (kernel density estimates) are included to illustrate the underlying data distributions.

Figure S1

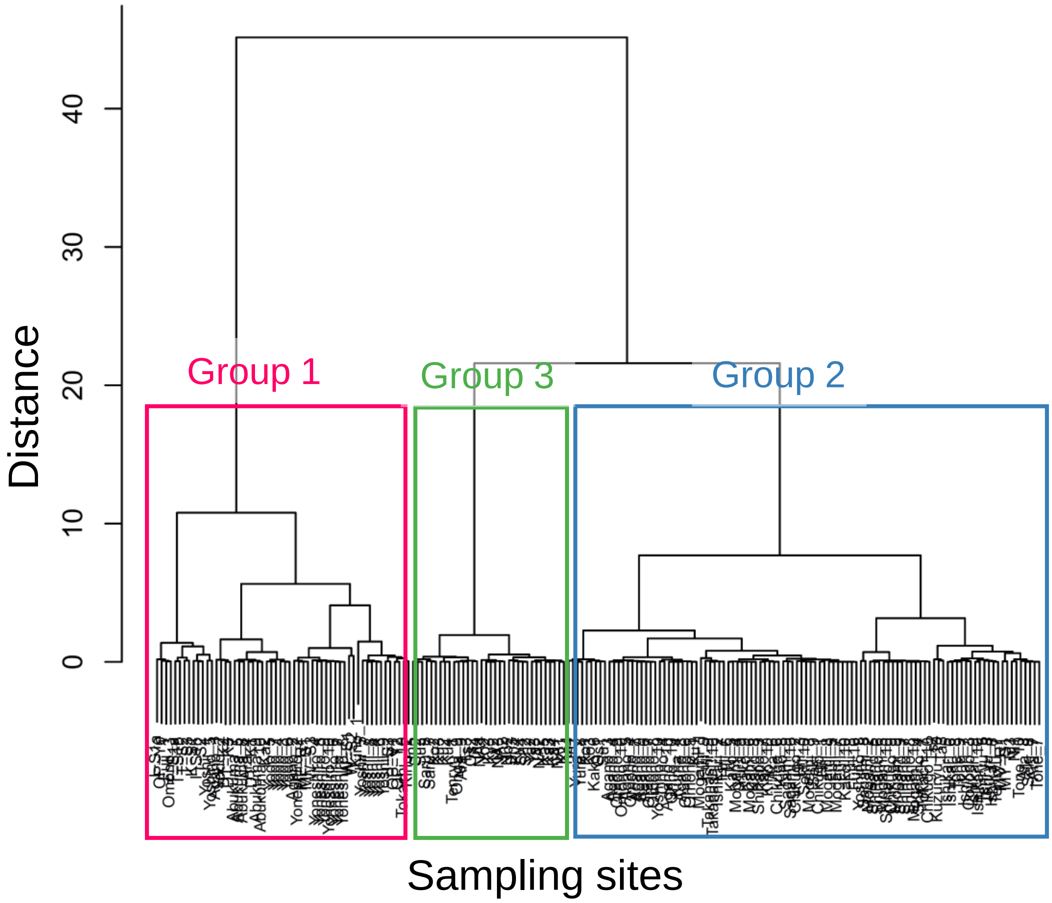

Fig. S1. Dendrogram resulting from the hierarchical cluster analysis of 194 metal-contaminated sites.