STATISTICAL ZONATION OF SEDIMENT SAMPLES
USING RATIO MATCHING AND CLUSTER ANALYSIS

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Abstract. A zonation technique for sediment samples based upon contaminant ratios of a series of samples is described. The technique is based on the fact that sediment samples of common origin will tend to have similar ratios of concentrations of trace pollutants such as heavy metals, PCBs, etc., despite dilution by variable amounts of inert materials such as silica or calcite. Comparison of these ratios between individual samples yields a matrix of similarity coefficients, which are then analyzed by a hierarchical agglomerative cluster analysis procedure. Sediment samples of similar origin will tend to group together in a single cluster, whereas samples influenced by unique factors such as transport patterns or proximity to point source discharges will appear as separate individual clusters. The results of application of this methodology to Great Lakes samples from Hamilton Harbour and Port Hope are presented.

Introduction

Contaminants in sediments, or as they are often called, in-place pollutants, have long been recognized as a significant problem in polluted areas, such as Areas of Concern in the Great Lakes as defined by the International Joint Commission (IJC). Even after abatement measures have been enacted, in-place pollutants can continue to be a source of continuing water quality problems. In addition, these contaminated sediments can be transported from harbours and embayments to open lake systems resulting in continuing problems in the lakes.

Full problem definition in any polluted area thus requires a knowledge of the role of sediments as a component in the overall ecosystem. This knowledge is important in the understanding and prediction of the long-term fate of contaminants. Adsorbed or precipitated contaminants are redistributed by physical processes, which concentrate contaminated sediment in depositional areas. Thereby, the benthic biota and associated food chain may become contaminated, and release to the bottom waters may occur under the proper conditions. In 1985, the IJC requested that Remedial Action Plans (RAPs) be developed for each Area of Concern. These are to include a complete description of the nature of the problems in all components of the ecosystem, sources of the contamination problems, and proposed remedial actions. These RAPs are expected to include an assessment of sediments, based upon a two-phase approach (IJC, 1988): Stage I consists of an initial assessment including physical description, bulk chemistry, benthic structure and tissue concentrations; Stage II includes four phases involving physical mapping, sediment chemistry and benthic structure, toxicity and bioaccumulation studies, and sediment dynamics.
Numerous studies have established the fact that contaminants such as heavy metals are generally concentrated in the fine grain (silt and clay) fractions of the sediments (Forstner, 1980; Forstner and Wittmann, 1983). Various researchers have separated fractions ranging from $<200 \mu m$ to $<2 \mu m$ for analyses (Forstner and Wittmann, 1983); the Ministry’s In-Place Pollutants Program (Persaud et al., 1987) has used the $<63 \mu m$ fraction as most indicative of the sediments bearing the greatest proportion of anthropogenic inputs. Larger particles are felt to consist mainly of inert minerals such as silica or calcite; in addition, these larger particles have less surface area per unit mass available for contaminant adsorption, compared to the fine-grained particles, which are often freshly precipitated metal hydroxides or carbonates with high adsorptive capacities. Furthermore, natural gravity sorting processes tend to concentrate the fine-grained sediments towards the deeper zones of any water body, whereas nearshore sediments contain relatively more coarse-grained material. Consequently, the contaminated sediments are diluted with variable amounts of inert substances, resulting in the frequently observed patterns of concentration contours paralleling depth contours.

Forstner (1980) summarizes several methods used for corrections of contaminant concentrations for these inert materials. These include: separation of grain size fractions (already referred to); extrapolation from regression curves; correction for inert materials (e.g. quartz); comparison with conservative elements (e.g. ratio element/aluminum). In this paper, ratios of trace metal concentrations are compared between various sediment samples in order to distinguish geographical zones impacted by various pollution sources. Zones so defined may also be useful in selecting sampling locations for more advanced impact studies such as chronology, bioavailability and toxicology.

**Statistical Analysis**

In order to determine the degree of similarity between various members of a series of sediment samples, a statistical technique called ‘ratio matching’ originally developed by Anders (1972) was modified. This technique is based on the fact that sediment samples of common origin will tend to have similar ratios of concentrations of trace pollutants (heavy metals, PCB, etc.) whereas the absolute concentrations of these individual pollutants may vary considerably due to dilution with inert materials such as SiO$_2$ and CaCO$_3$. This technique could also be used for developing generic relationships between individuals such as biological communities based on species populations.

For each sample, Anders divided the concentration of each chemical parameter by that of each other parameter to obtain the ‘concentration ratio matrix’, $[X_{ij}]$, which is a triangular matrix of size $m \times m$, where $m$ is the number of chemical parameters involved. Two samples A and B were compared by means of the ratio matrix $[Y_{ij}(AB)]$, which is generated by dividing each element of the $[X_{ij}]$A matrix by the corresponding element of the $[X_{ij}]$B matrix. The ratio matrix of A and B is thus: