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Project Summary

Generalization of Water Quality Criteria Using Chemical Models: Development of the REDEQL-UMD System of Computer Programs for Aqueous Equilibria

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The primary objective of this research was to develop site-specific water quality criteria for metals through correlating aquatic toxicity with activities of metal species. The intent of the project was not to conduct experimental studies but use the existing literature on metal toxicity to generate the correlations. Because knowledge of the number of metal species present and the relative amounts of each was necessary to the research, a set of computer programs for finding equilibrium concentrations of metal complexes, REDEQL-UMD, was developed, along with a stability constant data base and associated reference-footnote data bases. Literature values of stability constants were adjusted to 25°C by application of thermodynamic principles.

Once speciation and toxicity data were available, a combination of factor analysis and multiple regression analysis was used to develop correlations. A detailed example involving toxicity of copper to *Daphnia magna* is included in the full report.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Correlations between aquatic toxicity and activities of metal species are important in determining water standards, because although legal limits for pollutants are most often stated as allowable total concentrations, biological activity commonly correlates best with specific forms or species of contaminants. This project makes use of existing literature reports of metal toxicity to generate the correlations. The three basic areas of activity were: developing computer programs that predict speciation in a wide variety of aqueous environments; assembling a data base of appropriate stability constants; and designing predictive modeling procedures to determine the desired correlations between aquatic toxicity and metal species concentrations.

REDEQL-UMD, the computer program used to determine the equilibrium concentrations of species of metals, was modeled after REDEQL2, a program developed at the California Institute of Technology (McDuff, *et al.*, 1975). Parameter storage was placed in linear rather than rectangular arrays in order to reduce storage requirements This allowed treatment of complexes with mixed ligands or metals and more than one precipitated form of a metal-ligand pair to be present at one time. The program was also modified to allow the redox state of the system to be specified by providing values of pE, Eh or concentration of dissolved oxygen Two options have been given for correction for ionic strength The Davies equation may be used for ionic strengths up to 0.1 molal. A new equation, the Magnuson equation, was developed as part of this study to allow for correcting of ionic strengths up to 0 5 molal (Sun, *et al.*, 1980). Provision was made to determine total carbonate from alkalinity or total inorganic carbon Finally, concentrations may be input in either mg or moles per liter.

Formation constants were stored in a data file made up from 43 metals and 65 ligands. Constants stored were for 25°C, but could be adjusted to temperatures other than 25°C with the use of a special program containing enthalphy data. All bibliographic data and conditions under which the thermodynamic data were measured have also been stored in a separate program and are available in REDEQL-UMD.

The application of data obtained from REDEQL-UMD in toxicity studies was demonstrated in a study of the toxicity of copper to *Daphnia magna* (Andrew, *et al.,* 1977) Nineteen different combinations of concentrations of components, yielding 19 sets of species concentrations and 19 measures of toxicity, were applied. Carbonate, phosphate and pyrophosphate, as well as copper, were varied. The system was found to contain 25 complexes of copper with these three ligands and hydroxide. Since the number of dependent variables exceeded the number of independent variables (LC_{50} values), factor analysis was used to reduce the number of dependent variables, and the problem was solved by the application of multiple regression analysis (Magnuson, *et al.,* 1979). Application of factor analysis is given in detail in an appendix to the full report.

Two manuals for the use of the REDEQL-UMD program are available separately, a user's manual and a programmer's manual (Harriss, *et al*, in press). The programmer's manual would be necessary only for those using the program with a different computing system or wishing to modify the program.

Conclusions

A practical procedure for the correlation of aquatic toxicity with chemical species was developed and demonstrated The REDEQL-UMD program is a versatile one with features not available in other speciation programs It was also prepared in a novice-level interactive form. Semi-empirical equations were derived that allow ionic strength corrections to be extended to higher concentration ranges. Stability constant and enthalpy data bases were obtained from the literature. Reference and footnote data accompanies each of these.

Recommendations

Correlation of aquatic toxicity with metal speciation requires the use of formation constants of both simple and mixed complexes formed in the system. Carefully designed experiments are needed to establish these correlations Temperature corrections should be used to adjust formation constants to the temperature at which toxicity is being determined. The Magnuson equation for correcting for ionic strength should be used in calculations to determine equilibrium concentrations of the various metal species. Factor analysis followed by multiple regression is recommended for determining toxicity in complex systems.

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The complete report consists of two parts, entitled "Generalization of Water Quality Criteria Using Chemical Models—Parts I and II"

"Part I," (Order No. PB 84-135 508; Cost: $17.50)

"Part II," (Order No. PB 84-135 516; Cost. $20.50)

The above reports are available only from: (cost subject to change)

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