Comment On "Identifying Sources of Groundwater Pollution: An Optimization Approach" by Steven M. Gorelick, Barbara Evans, and Irwin Remson

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The paper by *Gorelick et al.* [1983] on the identification of groundwater pollution sources most certainly addresses a significant contemporary hydrologic problem. The approach that they describe could find application in detection of inputs to surface water systems as well as in detection of sources of groundwater pollution. Indeed, approaches similar to their steady state conservative model have been used recently in slightly different contexts.

Woolhiser et al. [1979, 1982] developed a technique to estimate multiple inflows to a stream reach based on a quadratic programming solution to find the unknown inflow quantities that minimized the sum of squares of normalized errors for up to eight ion balance equations, subject to a water balance constraint and a nonnegativity constraint. They used Monte Carlo techniques to investigate the sensitivity of the solution to errors in the chemical analyses and stream flow measurements.

Chemical element balances (CEB's) have also been used to identify sources of particulates for many elements which can be associated with specific types of air pollution sources [*Kowalczyk et al.*, 1982]. According to the CEB model, the composition of particles at a receptor is a linear combination of concentration patterns of particles from contributing sources. *Kowalczyk et al.* [1982] determined source strength coefficients by a least squares fit to the observed concentrations of several "marker elements."

Tsurumi [1982] utilized the multiple ion balance approach to estimate not only the relative proportions of sources present in a mixture but also the ranges of chemical composition of the sources of chemical constituents. His method requires several mixtures of the source waters at different proportions and uses an iterative least squares solution. The source compositions are also subject to an anion-cation balance constraint.

The objective of all of these techniques is to select a subset of sources, from the set of physically feasible sources, which results in simulated concentrations representing the best match with a sample. "Best" is, of course, defined in terms of the objective function and imposed constraints. The works cited above can be viewed as extensions of earlier works in which it was assumed that stream water or groundwater is a mixture of solutions derived from different steady state origins, with no loss of dissolved species occurring before or after mixing [*Piper*, 1944; *Pinder and Jones*, 1969; *Visocky*, 1970; *Hall*, 1970; *Sklash et al.*, 1976].

Previous works, however, have considered only models of complete mixing in a lumped system and have considered only conservative substances. Thus, the approach of *Gorelick et al.*

[1983] is novel because it introduces a method to treat a distributed system by incorporating a groundwater solute transport model and a nonconservative tracer. The transient case had also not been considered previously.

Although *Gorelick et al.* [1983] consider their research on the groundwater pollution identification problem to be in a formative state, certain conclusions can be drawn from their work and others. The first is that the multiple regression approach should be rejected because of the high probability of obtaining negative inputs. In their initial research, *Woolhiser et al.* [1979, 1982] tried the multiple regression approach but abandoned it when the negative input problem became apparent. They utilized the quadratic programing solution to overcome this problem and yet retain the minimum squared error objective function.

Woolhiser et al. [1979, 1982] also noted the extreme sensitivity of the quadratic programming solution to errors in the chemical analyses. They found, however, that normalizing the ion balance equations by dividing by the concentration of that ion in the mixture significantly improved the accuracy of identification. As an example of the significance of these errors, 64 mixtures of from two to eight natural waters, selected from 10 "source" waters, were prepared in the laboratory, and each of the sources and mixtures were analyzed for eight ions (D. A. Woolhiser and W. E. Emmerich, unpublished manuscript, 1984). For all samples the probability of failure to detect a source when it was present (type I error) in the mixture was 0.23, and the probability of identifying a source when it was not present (type II error) was 0.27. Because of a rather strong linear dependence among the chemical characteristics of the source waters and systematic, as well as random errors in the mixing process and chemical analyses, we feel that this is a "worst case" laboratory test. A second set of 25 mixtures was prepared by using five different source waters similar to the first 10. Laboratory procedures for preparing the samples and the chemical analysis were more carefully controlled than in the first test. The probability of a type I error was reduced to 0, but the probability of a type II error remained high at 0.33. Identification was improved by dividing each normalized ion balance equation by the error variance for that ion. This laboratory test demonstrated that there is little chance of failing to detect a source if it is present in the mixture in relatively large proportions. However, sources detected with an estimated proportion smaller than 0.10 are quite likely to be falsely identified (unless their chemical "signatures" are dramatically different from the other candidate sources), so additional investigations would be required to verify or disprove their presence. As *Gorelick et al.* [1983, p. 790] point out, field systems are usually not well-defined, and the challenging task "... of developing pollutant source identification techniques that maintain their integrity under physical, as well as data measurement, uncertainty," remains.

REFERENCES

Gorelick, S. M., B. Evans, and I. Remson. Identifying sources of groundwater pollution: An optimization approach, *Water Resour. Res.*, *19*, 779–790, 1983.

Hall, F. R., Dissolved solids: Discharge relationships, 1, Mixing models, *Water Resour. Res.*, *6*(3), 845–850, 1970.

Kowalczyk, G. S., G. E. Gordon, and S. W. Rheingrover, Identification of atmospheric particulate sources in Washington, D.C. using chemical element balances, *Environ. Sci. Technol.*, *16*, 79–90, 1982.

Pinder, G. F., and J. F. Jones, Determination of the groundwater component of peak discharge from the chemistry of total runoff, *Water Resour. Res.*, *5*(2), 438–445, 1969.

Piper, A. M., A graphic procedure in the geochemical interpretation of water analyses, *Eos Trans. AGU*, *25*, 914–923, 1944.

Sklash, M. G., R. N. Farvolden, and P. Fritz, A conceptual model of watershed response to rainfall developed through the use of oxygen 18 as a natural tracer, *Can. J. Earth Sci.*, *13*(2), 271–283, 1976.

Tsurumi, M., Self-consistent least-squares method of estimating chemical composition of the sources of chemical constituents in natural waters, *Anal. Chim. Acta*, *138*, 177–182, 1982.

Visocky, A. P. Estimating the groundwater component of storm runoff by the electrical conductivity method, *Ground Water*, *8*(2), 5–10, 1970.

Woolhiser, D. A., H. R. Gardner, and S. R. Olsen. Evaluating water quality effects of surface mining, *Pap. 79-2522*, 32 pp., Am. Soc. Agric. Eng., St. Joseph, Mich., 1979.

Woolhiser, D. A., H. R. Gardner, and S. R. Olsen. Estimation of multiple inflows to a stream reach using water chemistry data, *Trans. ASAE*, *25*(3), 616–622, 1982.

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