

## **Uncertainty in Mass-Balance Calculations of Non-Point Source Loads to the Arkansas River**

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**Abstract.** Field data on flow and solute concentrations were used in mass balance calculations to estimate the non-point source loads of salt to an upstream reach and a downstream reach along the lower Arkansas River in southeastern Colorado. A similar analysis was conducted to estimate selenium (Se) loads to the downstream reach. Electrical conductivity (EC) measurements and water-quality samples were collected numerous times at various locations along the Arkansas River and selected tributaries in the upstream reach from 1999-2005 and in the downstream reach from 2002-2005. Water-quality samples for Se concentrations and other constituents were collected along the downstream reach from 2003-2005. Data on flow rates and continuous EC records were obtained from the Colorado Division of Water Resources and the United States Geological Survey.

The unknown variable calculated to bring closure to the mass balance along each river reach for each sample period was interpreted as an estimate of unmeasured non-point load attributed to accumulated surface and groundwater interaction with ungauged tributaries and with the main stem of the river. Other possible sinks and sources were considered to be relatively small and were not included in the mass balance calculations. These unaccounted loads could be associated with changes in stored mass along the reach, ungauged point sinks or sources, dissolution and precipitation, adsorption and desorption with sediments, and volatilization. Changes in stored mass within each river reach were investigated over each sampling period to estimate how such storage changes may have influenced the mass balance calculations. Estimates of total non-point source loads were calculated as the sum of calculated unmeasured loads and the measured tributary loads.

Several sources of uncertainty in the mass balance calculations were identified and addressed: instrument error in the data sonde that collected field EC measurements at multiple locations during a sampling period, temporal and spatial uncertainty in assuming that the instantaneous EC measurements at locations represent corresponding EC averaged over the entire sampling period and over the cross section, ambiguity in using fitted regression equations to convert EC values to concentrations of total dissolved solids (TDS), and error in stream-flow measurements at gauging stations. Uncertainties associated with instrument error in EC measurements and in stream flow measurements were described using data from the literature. Uncertainties in using instantaneous point measurements of EC as values averaged over the sampling period and in using fitted EC-TDS relationships to estimate TDS concentrations were described by statistical analysis of percent errors, residual values, and correction factors for the associated data sets. Correlation between flow rate and residual values from using measured EC as continuous EC averaged over the sampling period was also estimated. For the Se mass balance, a regression equation was fit between EC measurements and Se concentrations at points where continuous EC data were available, in order to estimate the uncertainty in assuming that the grab Se samples were representative of Se concentrations averaged over the entire sampling period. These analyses rendered models of the input variables to the mass balance equations for each reach as correlated random variables with specified probability distributions.

Monte Carlo simulation was used to solve the resulting stochastic mass balance equations to predict distributions of values of the non-point source loads for TDS and Se. Statistics of the distributions, including 90% prediction limits, were described. Sensitivity of the statistics of the predicted loads to selected statistics of the input variables was also examined.