11 Towards Better Prediction of Water Quality in Ungauged Basins

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INTRODUCTION

In Australia, land and water resources are being adversely affected by the degradation of our basins from a range of land-use practices that place strain on the environment. One such example is the impact of dryland and stream salinity arising from the large scale clearing of native vegetation causing a hydrological and salt imbalance resulting in increased salt loads to river systems. These in turn degenerate the potential beneficial use of the resource, so affecting biodiversity, human uses and even public health and recreational value.

Whilst there is better understanding of the interrelationships between the environment and human impact, this does not necessarily translate to more appropriate landuse practices for a sustainable natural resource base in the longer term. By the development of prediction models for water quality, better awareness and information can be provided to stakeholders for making responsible decisions.

Water quality prediction is fundamentally associated with a good understanding of the hydrological processes. In the reverse, water quality parameters can provide a means in understanding hydrological flow paths. Additionally, stable water isotopes have been applied in basin studies to partition various basin hydrological flow paths. These have been presented in the scientific literature for several decades (Turner *et al.*, 1987, 1991; Sklash, 1990; Ogunkoya & Jenkins, 1993; Bradd, 1996).

There are two components to predicting water quality in rivers. These are spatial and temporal considerations. Prediction of solute concentrations in streamwaters in the literature originally took four approaches (Foster, 1979):

- Rating equations that relate solute concentration to stream discharge
- Mixing models
- Multiple regression equations
- Analysis of statistical properties of output data

Many field studies have identified several variables likely to influence solute behaviour, apart from discharge which is regarded as the most important control (Johnson *et al.*, 1969; Hall, 1970; Foster, 1979; Reynolds *et al.*, 1983, 1986). These include antecedent moisture conditions, rainfall volume and intensity, seasonality, and background characteristics such as altitude, geology, localized hydrogeological conditions, precipitation chemistry, evapotranspiration, rates of biological activity, solubility and cation exchange controls, and residence times of water in the soil.

END-MEMBER MIXING ANALYSIS—SPATIAL PREDICTION OF WATER QUALITY

Streamwater chemistry reflects the integration of solute concentrations from the source areas of the stream. The chemistry of waters from these source areas are determined by the nature of atmospheric inputs, biogeochemical processes such as mineral weathering, ion exchange and plant uptake, and by climatic factors such as evapotranspiration. The solutes are then transported to the stream by the mechanisms of runoff generation prevailing in the catchment.

Hydrogeochemical modelling conducted by Christopherson *et al.* (1990) and Hooper *et al.* (1990) applied these concepts of extreme water chemical composition from source areas, called end-members, to explain the mechanisms of runoff generation. They called this method "end-member mixing analysis" or EMMA, and used this approach to predict the streamwater chemical response to different levels of acidic deposition by examining the change in concentration of each end-member under different loads. No hydrological model is required under this approach. End-member mixing analysis modelling is a different approach to multiplayer models because it assumes that the streamwater originates from spatially different soils or landscape units in a catchment. Also, rather than calculating the soil chemistry with a mathematical model, end-member mixing modelling measures the water chemistry of different possible sources directly.

The advantage of adopting this approach is in using measured water chemistry as end members that are a mix in various proportions depending on hydrological flow paths that provide a resultant stream chemistry. According to Mulder *et al.* (1991), however, this kind of modelling does not adequately describe the water flow path or the changes in chemistry of the water passing from upland positions to the stream through lowland soils.

OTHER WATER QUALITY TEMPORAL PREDICTION APPROACHES

In order to predict stream chemistry through time, the physical, chemical and biological reactions of water entering a catchment with the soil, bedrock and the water flow path through catchment materials, need to be understood. This requires the understanding of catchment hydrogeochemical processes.

There are several types of mathematical models to predict streamwater chemistry at a particular point. The simplest model type is the lumped parameter model. Cosby *et al.* (1985) demonstrated that a lumped parameter model, which treats the whole catchment as a single homogeneous soil horizon, provides a reasonable estimate of stream chemistry. Others have used multilayer models that differentiate between surface and subsurface soils (e.g. Bobba & Lam, 1990; Stone & Seip, 1990). These investigators have used three layer models that take into account vertical variability of chemistry in a soil profile, but do not take into account spatial variability.

According to Cosby et al. (1985), "quantitative stream chemistry prediction modelling requires physically based process-oriented models of catchment soil water and streamwater chemistry. A desirable characteristic of such models is that they include terms to describe the important phenomena controlling a system's chemical response to [in this case] acidic deposition, yet be restricted in complexity so that they can be implemented on diverse systems with a minimum of priori data." p.51.

THE MASS BALANCE APPROACH

The mass balance approach (Mast *et al.*, 1990) involves determining input–output budgets for dissolved constituents in surface waters and can be expressed as:

 $[output] - [input] = [weathering \pm \Delta soil exchange pool \pm \Delta biomass]$

where [input] represents elements added to the watershed in precipitation and [output] represents dissolved constituents leaving the catchment in streamwater, or groundwater if subsurface flow is significant.

MODELLING STREAMWATER CHEMISTRY AS A RESULT OF HILLSLOPE PROCESSES

Waters are often analysed for the major ions K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and alkalinity. Different ions are analysed for different reasons to aid in overall interpretation of catchment hydrogeochemical processes. For example, according to Hooper *et al.* (1990), if the chloride concentration varies little between soil horizons in a catchment, the pattern is consistent with aerosol input. Potassium is influenced by biological activity and is usually retained within the root zone. Alkalinity and sulphate reflect acid–base reactions in the catchment; the remainder are products of primary mineral weathering and ion exchange.

INTEGRATING WATER QUALITY PREDICTION APPROACHES

Bradd (1996) reviewed and assessed a range of water quality prediction methods with a view to adopting the best approach to predicting salt loads from dryland salinized catchments in the upland regions of the Murray Darling Basin, Australia. He found at an investigation site that stream chemistry is controlled by the mixing of water reaching the stream via several distinct pathways. These pathways were found to be primarily from soil moisture seepage at a depth between 30 and 50 cm below ground surface. A three component isotopic hydrograph separation technique was used to determine the proportion of pre-storm event and storm event water in the stream. Hydrogeochemical analyses of the various flow paths were also examined both spatially and temporally at different scales from storm event to seasonal within an annual timeframe. Multivariate statistical analysis was conducted to gain insights on the existence and nature of correlation between discharge and ionic concentration, and to assess the predictability of electrical conductivity. By manually linking data from these approaches to a physically distributed model (TOPOG), Bradd (1996) was able to reasonably predict streamwater quality and salt loads in the study area.

This work concluded that future investment in research should focus on integrating physically-based models, hydrograph separation approaches based on three or more components using isotopes or tracers, water balance approaches and hydrogeochemical data. If such a model was developed, the model could predict the time taken for the groundwater levels to rise to a critical level as well as determine when this might happen. Finally, the model would provide what the likely salt content is in this shallow groundwater and in surface seepages, and thus estimate the salt export leaving the catchment.

More recently, an integrated approach to streamwater quality prediction has been developed by Tuteja *et al.* (2003) which incorporates many of the recommendations of Bradd (1996). These researchers have developed an integrated and comprehensive

framework for the assessment of water and salt balance for large catchments. The framework comprised three models each operating on a different scale. The data was assembled under a GIS framework. The method is unique in that a process model is implemented at the hillslope scale to create useful information for the sub-catchment scale model. A groundwater model "Flowtube" was used to implement the long term effects of land-use change on groundwater discharge. They concluded that some new algorithms that enable effective transfer of information across the scale warrant consideration.

Finally, in order to produce a successful streamwater quality prediction package, the developments to date suggest the need for close interaction between a wide range of disciplines including, hydrologists, hydrogeologists, geochemists, isotope hydrologists, modellers, programmers and GIS analysts.

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