

Modelling Solute Transport Through An Arid Zone Ephemeral Lake System: Joint Use Of Geochemical And Hydrological Techniques

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EXTENDED ABSTRACT

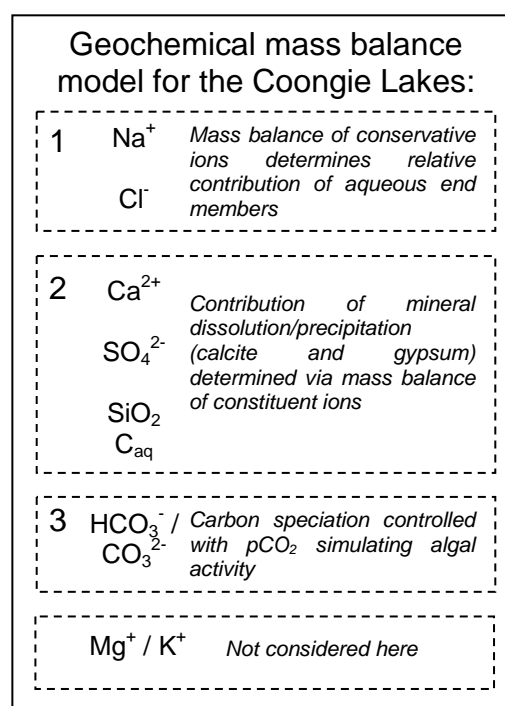
In an ephemeral, interconnected lake system in Australia's arid zone, where data traditionally required for water balance studies is approximate at best, geochemical based models are being developed to assist in the understanding of system-level salt transport and salinity dynamics.

Previous work based on gross salt and hydrological balances in the area has identified that salt loading via inflow and evapoconcentration over time does not sufficiently explain the observed variability in lake salinity, noted on both spatial and temporal scales. Lakes become more saline with increasing distance downstream during both the filling and post flow phases. It is postulated here that lake-bed interstitial water (soil water) and dissolution/precipitation of minerals in near-surface substrate can act as local sources and sinks of salt and thus contribute to the observed salinity and chemical composition of the lakes.

The geochemical based models developed for the study area (see figure right) have quantified the contribution of these local sources and sinks of salt to each of the lakes over a large flood event. During the rising limb of the event, minor amounts of soil water (up to 6% for a downstream lake in a terminal position), mineral precipitation and dissolution account for subtle differences observed in inter-lake chemistries. Inter-lake variability in the speciation of dissolved carbon is attributed to algal growth and photosynthesis. With use of gross salt balances (e.g. total dissolved salts) the contribution of local processes to lake chemistries is unlikely to have been resolved.

Following the flow event, the amount of surface water evaporation from the lakes over a six-month period has also been constrained using geochemical based models. This technique is particularly useful in an area where volumetric data are unavailable. The potential for processes other than evaporation to contribute to the

evolution of the lake waters following a flow event has also been identified.



Above: Design of a geochemical-based mass balance model used to evaluate the contribution of local salt sources and sinks to the salinity of an ephemeral, arid zone lake system.

1. INTRODUCTION

Large flood events dominate the transport of water and solutes in surface water systems in Australia's arid interior. Over time, concentration of solutes by evaporation (evapoconcentration) is considered to be a principle salinisation mechanism. In an ephemeral lake system located in Australia's arid zone however, previous work based on gross salt and hydrological balances has identified that these processes alone do not sufficiently explain the variations in surface water salinity over both space and time (Costelloe et al., 2005). This paper presents a geochemical mass balance model within a hydrological framework to evaluate the potential of local salt sources and sinks to explain the salinity variability in this lake system.

1.1. Study Area

The Coongie Lakes are a series of large, shallow, interconnected, generally freshwater lakes located on the Northwest branch of Cooper Creek, central Australia (Figure 1). Flows of Cooper Creek are highly variable and when in flood, the Coongie Lakes fill, providing essential refugia and breeding opportunities for many species of waterbird, fish and other aquatic biota (Kingsford et al., 1999).

Transport of water and salt from Cooper Creek, both into and out of the Coongie Lakes, and evapoconcentration over time are considered to be the major influences on lake salinity. However, it has been observed that lakes become more saline with increasing distance downstream during both the filling and post flow phases (Costelloe et al., 2005). It is postulated here that lake-bed interstitial water (soil water) and dissolution/precipitation of minerals in near-surface lake substrate can also act as potential sources and sinks of salt.

1.2. Field data collection and observations

To determine the relative influence of the above-mentioned salt sources and sinks on observed lake salinities, the surface waters of lakes Toontoowaranie, Goolangirie and Apanburra (in order of filling – Figure 1) were sampled during the rising limb (May 2004) and post flow phase (November 2004) of a large flood event.

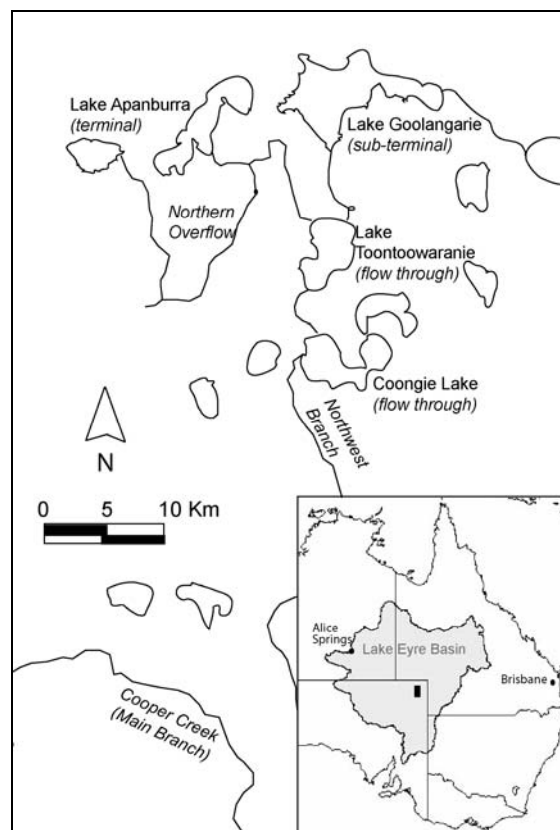


Figure 1: The Coongie Lakes, located in the Lake Eyre Basin, central Australia (inset).

At the time of sampling during the rising limb of the flood, flow was receding in the channel connecting lakes Coongie and Toontoowaranie and rising in the channels connecting lakes Toontoowaranie with Goolangirie and Apanburra. Water level monitoring data confirmed that Lake Toontoowaranie had reached or was approaching its maximum fill level at the time of May 2004 sampling and lakes Goolangirie and Apanburra were in the process of filling. At the time of sampling in November 2004, all lakes were disconnected and had been since the flood recession. Surface water samples were analysed for the major ionic constituents (Alkalinity, Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , Mg^{2+} , K^+) and the isotopes of water ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$). Electrical conductivity, pH and temperature were measured in the field. Surface waters were turbid and alkaline (pH 8 -10) at all sample locations on both sampling occasions, and algal blooms were observed in each of the three lakes during the flood sampling. Total dissolved salt (TDS) results from the surface water samples demonstrate the high inter-lake salinity variability (Table 1). Surface soils collected from drill holes close to the lake margins were also

sampled at these times, inspected for the minerals calcite and gypsum and analysed for soil moisture content and soil water chloride.

Table 1: Observed salinity and chemical composition of the Coongie Lakes, 2004.

	TDS (mg/L)	Water type
Lake Toontoowaranie		
May 2004	198	Na-Cl-HCO ₃
November 2004	385	Na-HCO ₃
Lake Goolangirie		
May 2004	230	Na-HCO ₃
November 2004	418	Na-HCO ₃
Lake Apanburra		
May 2004	780	Na-Cl-SO ₄
November 2004	1070	Na-HCO ₃

2. ANALYSIS FRAMEWORK

Potential source water and mineral chemistries form the basis of the geochemical model applied to this problem using the hydrogeochemical transport program PHREEQC (Parkhurst and Appelo, 1999). Through the PHREEQC program, the effects of evaporation, multi-part mixing and mineral precipitation and dissolution in an aqueous system can be elucidated through a series of batch reactions or step-wise mole-balance models. The particular advantage of using PHREEQC in systems where values for discharge and volume are approximate at best, is that unless otherwise specified, the program considers all reactions to occur in 1kg of water (analogous to a 1L bucket model) with all chemical constituents input in concentration units. The model output describes the input constituents as a percentage of the target water.

2.1. Lake salt budgets

The mass of salt in a terminal ephemeral lake ($V_L C_L$) can be described as:

$$V_L C_L = V_{in} C_{in} + V_{LB} C_{LB} + M_{dis} - M_{pre} \quad 1$$

where the inflow ($V_{in} C_{in}$) mass is accumulated over the period since the lake was last dry, $V_{LB} C_{LB}$ represents the lake bed solute storage when the lake began to refill, M_{dis} is the total mass of salt that has been dissolved and M_{pre} is the total mass of salt that has been precipitated since the lake began to fill. In flow through lakes, outflow, whilst affecting lake volumes and net salt loads, is

considered to have no effect on the observed lake chemistry (i.e. $C_{out} = C_L$) (Figure 2). An analogous budget can be calculated for water, with additional terms for rainfall and evapotranspiration (ET).

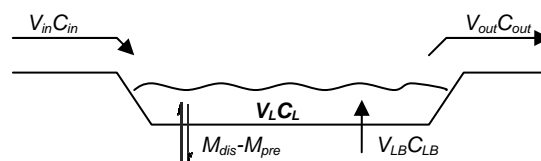


Figure 2: During filling phases, lake chemistries are dependent on the chemical composition of inflow and local solute sources and sinks such as interstitial water and mineral dissolution/precipitation.

2.2. Initial mass balance analysis

Three of the above components are considered to contribute to the chemical composition of each lake during the rising limb of an event: inflow (V_{IN}, C_{IN}) (including any salt that had been stored in upstream lakes), lake-bed interstitial water (V_{LB}, C_{LB}) and dissolution of substrate minerals, M (calcite and gypsum considered here). Rainfall does not contribute significantly to either the salt or water balance during the rising limb of the 2004 flood, with local rainfall over the study period totalling 39mm. The effects of ET were not considered significant for the model describing lake filling, but are considered in describing temporal changes in the system. Similarly, any solute or water loss or gain from shallow groundwater is, for the purposes of this modelling exercise considered negligible.

Algal growth, photosynthesis and decay are also expected to have an impact on the observed chemical compositions, causing changes in dissolved carbon dioxide concentrations and hence, affecting pH and carbonate/bicarbonate ratios.

As lakes Toontoowaranie, Goolangirie and Apanburra were dry prior to the 2004 flood event, the conditions observed during the first sampling resulted from the initial lake filling. This filling stage is analysed here to determine if the conditions during the first sampling can be explained by inflow alone or whether other local processes are important. This was achieved by estimating the approximate contribution of salt of each of the three components for the 2004 event.

The inflow of salt to the downstream lakes (i.e. the transfer from Lake Coongie to Lake Toontoowaranie) includes that flowing in via the Northwest Branch of Cooper Creek and any residual salt remaining in Lake Coongie. The flow volume in the Northwest Branch was estimated as

$5 \times 10^8 \text{ m}^3$ being 50% of the total discharge recorded at Cullyamurra with the remaining 50% being transported down the main branch of Cooper Creek (Knighton and Nanson, 1994). A discharge weighted median TDS concentration of 214mg/L was calculated which translates to a total salt load of $1.07 \times 10^8 \text{ kg}$. The amount of pre-existing water in the lake system was estimated from satellite imagery. Lake Coongie contained approximately $5.6 \times 10^5 \text{ m}^3$ of water prior to the 2004 flood event. Determining the salt load in this pre-event water however proved problematic as no measured salinity data was available for the period immediately preceding the flood event. Previous studies however have recorded the EC of Lake Coongie during dry periods with values ranging from $600 \mu\text{S/cm}$ to $4,000 \mu\text{S/cm}$ (Mollema et al., 1984). As such, a median conductivity of $1000 \mu\text{S/cm}$ was adopted. If EC is considered to be related to TDS by the relationship $\text{TDS}(\text{mg/L}) = 0.6\text{EC}(\mu\text{S/cm})$, the total available salt load of pre-event water is estimated as $3.3 \times 10^5 \text{ kg}$.

It was assumed that salt in soil water solutions in the top 0.5m of the lake bed could be transferred into the lake water via interflow. The amount of available near surface soil water was determined as the volumetric soil moisture (approximately 5% v/v for 0-0.5m depth) multiplied by each lakes' surface area (averaging approximately 15 km^2) and was found to be in the order of $4 \times 10^5 \text{ m}^3$ for each lake. Near surface soil water chloride concentrations were determined as 800mg/L for Lake Toontoowaranie, implying a total available salt load in the order of $6 \times 10^5 \text{ kg}$ of salt for this lake. The same value was adopted for Lake Goolangirie. Near surface soil water chloride contents at Lake Apanburra were significantly higher, with a total available salt load estimated as $2 \times 10^6 \text{ kg}$.

Calcite (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are either absent, or present only in minor (0-5%) quantities within the near surface. Applying an average density of 2.5 g/cm^3 for these minerals, this translates to a possible maximum contribution of $9 \times 10^8 \text{ kg}$ of salt through dissolution. Despite the large near-surface store, any dissolution of these low solubility minerals would be minor. Any precipitation of these minerals would invariably reduce the aqueous concentration of the constituent ions.

From the above approximations, it is expected that inflow contributes the vast majority of water to the lake system with lake bed interstitial water contributing only minor amounts (three orders of magnitude less) i.e. $V_{IN} \gg V_{LB}$. Inflow is also expected to contribute the majority of salts transported into the system. Interstitial salts and

near surface minerals expected to make only a minor contribution to the total salt loads observed in the system; i.e. $C_{IN} \gg C_{LB} \approx M_{dis}$.

During the lake filling phase, transport of solutes through the Coongie Lakes is conceptualised to occur in what can be described as a 'batch' model. Firstly, as each lake fills, surface waters are well mixed with any pre-existing surface and/or interstitial water. The well-mixed body of water then equilibrates with the low solubility substrate minerals. The water and solutes are then transported to the next lake. For transport from Lake Toontoowaranie to Lake Goolangirie, this occurs at an approximate lake stage of 1.5m depth. For transport from Lake Toontoowaranie to Lake Apanburra, this occurs at an approximate lake stage of 2.5m depth (Reid and Puckridge, 1990).

2.3. Quantitative geochemical model design

Using the PHREEQC program a series of geochemical mass balance models were developed to firstly, determine if reaction of the local salt sources and sinks with inflow could sufficiently describe the spatially variable salinities and chemical compositions observed in lakes Toontoowaranie (C_{TOON}), Goolangirie (C_{GOOL}) and Apanburra (C_{APAN}) during the rising limb of the 2004 flood event. Secondly, evaporation models were developed to determine if evapoconcentration could sufficiently describe the increases in each of the lake salinities observed between May 2004 and November 2004.

Determination of input solutions

The target lake compositions were available, but as there is no data for initial conditions, the major ion compositions of inflow (C_{IN}) (including pre-event surface water) were estimated. C_{IN} was calculated as the discharge weighted median (DWM) major ion composition of event flow. Similarly, to simulate the expected composition of the pre-event surface water in Lake Coongie, the DWM major ion composition of surface waters at the Cullyamurra gauging station over the period 2001-2003 was calculated. This solution was then evaporated in PHREEQC by removing water until the target salinity was reached (approximately 5.8-fold concentration). The evaporated solution was then tested for saturation with respect to the main lake-bed minerals, calcite and gypsum, and was found to be close to saturation with respect to these minerals. As such this composition was considered to be realistic and was used as the input component C_{IN} .

The composition of shallow interstitial water, C_{LB} , was estimated by assuming an equimolar mix of

chloride and sodium¹. The lake bed mineral gypsum and calcite were assumed to be pure in composition.

Model structure

The PHREEQC models are based on mixing (or, in the case of solid phases, reacting) the above described input end-members to obtain the target (observed) chemical composition via a series of mass balance or equilibrium reactions (Figure 3).

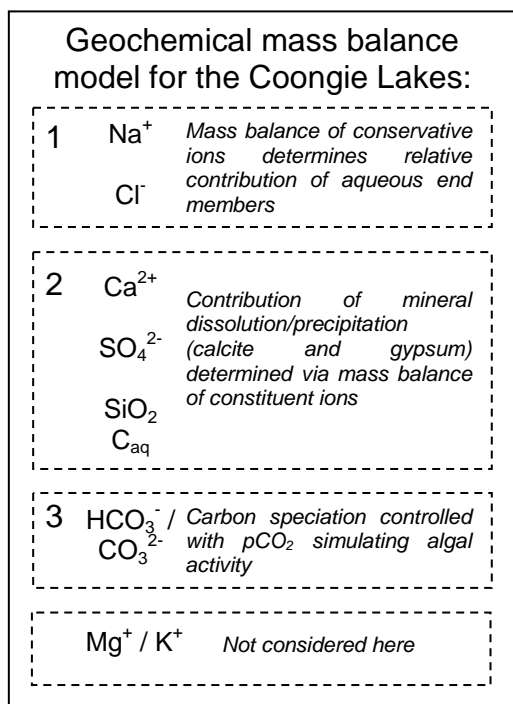


Figure 3: Step-wise mass balance model used to evaluate the contribution of local salt sources and sinks.

Using PHREEQC's 'inverse modeling' function, the relative contribution of each of the aqueous end members to the target composition was derived via a mass-balance based on the ions considered to be conservative (sodium and chloride). The inverse modeling function provided a number of valid solutions to the mass balance or mixing problems where a unique solution could otherwise not be found; i.e. when the number of unknowns (the number of input water compositions) exceeds the number of balances (conservative tracers). The valid output solutions were then reviewed in consideration of the results of the initial mass balance analysis in order to find a 'best-fit' solution.

¹ Actual results of soil water chemistry are currently pending and will be incorporated into the model when available.

To balance the non-conservative ions, namely Ca^{2+} , SO_4^{2-} and $\text{CO}_3^{2-} + \text{HCO}_3^-$, the minerals gypsum and carbonate were allowed to precipitate or dissolve with the modeled aqueous mixture. Similarly, the amorphous silica phase ($\text{SiO}_{2(s)}$) was introduced into the model to arbitrarily control dissolved silica concentrations.

To account for any changes in dissolved $\text{CO}_2(\text{g})$ concentrations resulting from algal growth and photosynthesis (decreased pCO_2) or organic matter decay (increased pCO_2), CO_2 gas was also allowed to be added or removed from the modeled solution as required.

3. RESULTS AND DISCUSSION

3.1. Geochemical model results – lake filling

For each of the modeled lakes, several solutions were derived. The 'best-fit' model was defined as that with the smallest root mean square error (RMSE) between the observed and modeled compositions. The 'best-fit' models resulting from this process are shown in Figure 4.

Lake Toontoowaranie was found to be best modeled by a mixture of inflow (>98%) and soil water (<2%) with the precipitation of amorphous silica and the removal of carbon dioxide. This is consistent with uptake by algae observed at Lake Toontoowaranie at this time (Figure 4a). It is noted that the contribution of soil water is higher than estimated from the initial mass balance.

Lake Goolangirie was best described by simply equilibrating the inflowing water (i.e. out flowing from Lake Toontoowaranie) with carbon dioxide to the observed partial pressures (Figure 4b). This resulted in an overall reduction in the concentration of dissolved CO_2 , again consistent with algal uptake. An excess of chloride outside the acceptable error range in the modeled composition is however noted, suggesting scope for improvement in the model or input data.

As shown in Table 1 and Figure 4c the salinity and chemical composition of Lake Apanburra was markedly different in comparison to lakes Toontoowaranie and Goolangirie. As such, a suitable model for Lake Apanburra, using the input compositions as described in section 2.1 was not found. Higher relative concentrations of sulphate were noted in the surface water sample, so the composition of the local soil water was altered to reflect this. This approach proved successful for the purposes of this modeling exercise with the composition of Lake Apanburra successfully modeled by mixing inflow (94%) (i.e. outflow from Lake Toontoowaranie) with soil water of a Na-Cl- SO_4 composition (6%). Again, pH and

bicarbonate concentrations were controlled by removing carbon dioxide from the system (Figure 2c).

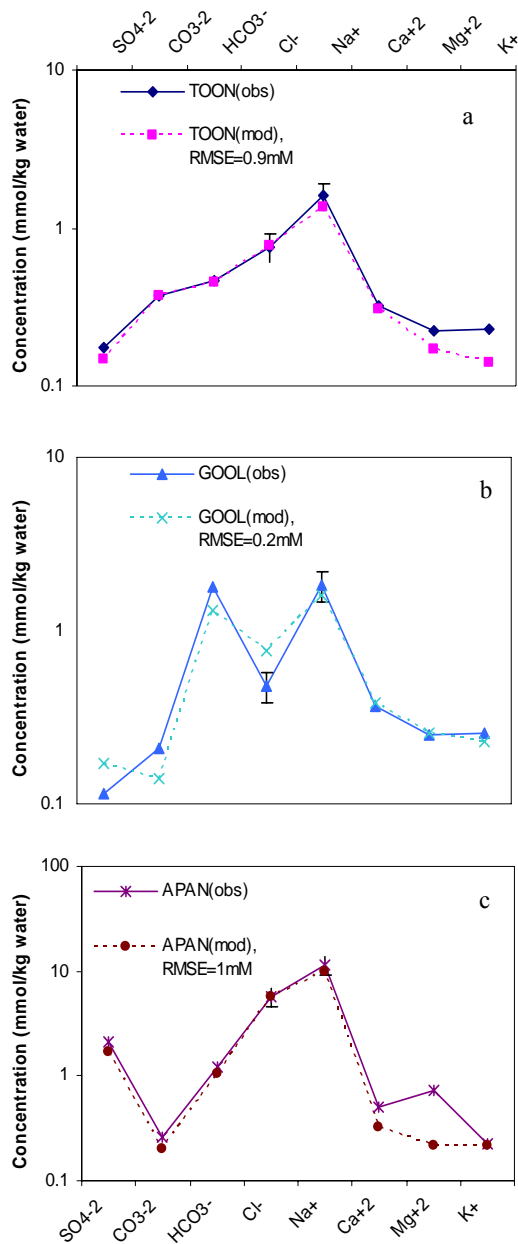


Figure 4: Observed and modeled lake compositions for the rising limb of the 2004 flood.

3.2. Evaporation modeling

Evaporation modeling in PHREEQC is achieved by removing water from a solution, thus increasing the salinity of the residual fraction. Similar to the rising limb modeling, the resultant mixture can be equilibrated with soil minerals and gases.

The increase in salinity of lakes Toontoowaranie, Goolangirie and Apanburra over the six-month

period between sampling dates was modeled using this technique with varying degrees of accuracy.

The evolution of Lake Toontoowaranie was best modeled by concentrating the rising limb sample by a factor of 1.6, or imposing 37% evaporation. The pH and alkalinity were controlled in this model by increasing the dissolved carbon dioxide content to that observed in the evaporated sample. This is consistent with the cessation of algal growth and respiration (no algal bloom was observed in November 2004). The modeled result however shows that chloride concentrations, considered to be a conservative ion, are not sufficiently modeled by this approach.

A similar degree of evaporation (33%) was noted to account for the observed changes over time in cation chemistry in Lake Goolangirie. Increasing the concentration of dissolved CO₂ to simulate the cessation of algal activity closely approximated changes in alkalinity, however significant errors were again noted in the simulation of chloride and sulphate concentrations.

Based on a gross TDS balance, the changes in salinity of Lake Apanburra over time should be attributed to evaporation of 23%. Following the above approach however models were unable to converge on values of chloride, sulphate and alkalinity. Given that the model could not be resolved suggests the occurrence of a local salt or solute source or sinks not already considered. High levels of uncertainty for several of the input compositions (C_{IN} , C_{LB}) may also have had a detrimental impact on the model results. Future work, considering other local conditions such as groundwater-surface water interaction and sensitivity analysis will aim to rectify this discrepancy.

4. CONCLUDING COMMENTS

In an arid, ephemeral system such as the Coongie Lakes where data traditionally required for water balance studies is approximate at best, geochemical modeling is proving to be a promising technique for increasing understanding of water and solute transport.

The models developed for the Coongie Lakes system over a large flood event have allowed inputs to the system other than inflow to be constrained. During the rising limb of the event, minor amounts of soil water (up to 6% for a downstream lake in a terminal position), mineral precipitation and dissolution account for subtle differences observed in inter-lake chemistries. Inter-lake variability in the speciation of dissolved carbon is attributed to algal growth and photosynthesis. With use of gross salt balances

(e.g. total dissolved salts) the contribution of local processes to lake chemistries is unlikely to have been resolved.

The amount of evaporation from the lakes over a six-month period has also been constrained using geochemical modeling. The potential for processes other than evaporation to contribute to the evolution of the lake waters following a flow event has also been identified.

5. ACKNOWLEDGMENTS

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