## **Environment Protection Authority**

Consultancy report:

# Predicted trends for NO<sub>3</sub><sup>-</sup> concentration in the Blue Lake, South Australia

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## **CSIRO LAND and WATER**

Predicted trends for NO<sub>3</sub>- concentration in the Blue Lake, South Australia



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## **Executive Summary**

Blue Lake, the water supply for the City of Mount Gambier (South Australia), is contaminated with nitrate (NO<sub>3</sub><sup>-</sup>) originating from primary industries and the disposal of a variety of waste in the neighbouring aquifer. While the current lakewater NO<sub>3</sub><sup>-</sup> concentration (~3.5 mg N L<sup>-1</sup>) is below the recommended Australian drinking water guideline (50 mg NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> or ~11 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>), it is not clear how NO<sub>3</sub><sup>-</sup> concentration will evolve in the long term. A review of the available data for the Blue Lake was made with the following objectives:

- 1) to determine the past load of  $NO_3^-$  from groundwater entering the lake, and
- 2) to forecast future trends in lake  $NO_3^-$  concentration.

The city currently disposes of its stormwater to groundwater in the vicinity of the lake. How stormwater disposal affects the delivery of  $NO_3^-$  to the lake is unclear at present. In a third objective, the possibility of using chloride (Cl<sup>-</sup>) to quantify the contribution of stormwater to the lake's hydrological budget was assessed.

The concentration of  $NO_3^-$  in the Blue Lake increased slowly but steadily between 1970 and 1997. This increase was most likely caused by a slow increase in  $NO_3^-$  concentration in the groundwater entering the lake during that period. The forecast suggests that  $NO_3^$ concentration will continue to increase but will still remain below the drinking water guideline by 2028. It is difficult to forecast  $NO_3^-$  concentration in the lake beyond 2028, in part because not enough is known about how  $NO_3^-$  concentration will change in groundwater in the longer term. An important finding of this study was that the Blue Lake probably consumes a significant proportion of the  $NO_3^-$  added from groundwater. This self-cleaning property can be promoted. Management schemes that will increase the time water resides in the lake before being pumped out will slow down the increase in  $NO_3^-$  concentration from year to year.

Chloride concentration in the Blue Lake has decreased between 1970 and 1997, suggesting an increased input of groundwater derived from stormwater. However, with the information presently available, it is not possible to quantify the proportion of stormwater in the groundwater entering the lake. Factors other than stormwater disposal may also be involved with the decline of  $C\Gamma$  in the lake.

While the drinking water guideline for  $NO_3^-$  may not be exceeded in the Blue Lake in the short-term (decades), it may be exceeded in the longer term because  $NO_3^-$  concentration in the neighbouring groundwater may take centuries to adjust to contemporary land-use. In the light of the ongoing increase in  $NO_3^-$  concentration in the Blue Lake, the management of nitrogen use in the groundwater catchment of the lake must be actively pursued.

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## 1. Introduction

The Blue Lake is used as a water supply reservoir for the City of Mount Gambier, South Australia (Allison and Harvey 1983). The lake is groundwater fed through an extensive karst aquifer (Waterhouse 1977; Turner *et al.* 1984). Historically, agriculture, urbanisation, and the disposal of a variety of waste through bores and sinkholes has led to a widespread nitrate (NO<sub>3</sub><sup>-</sup>) contamination of the unconfined aquifer surrounding the Blue Lake (Waterhouse 1977). Presently, NO<sub>3</sub><sup>-</sup> concentration in the lake (~3.5 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>) is below the Australian drinking water guideline (50 mg L<sup>-1</sup> as NO<sub>3</sub><sup>-</sup> or ~11 mg L<sup>-1</sup> as N; NHMRC 1996). While measures for controlling waste disposal are gradually being implemented (Department of Environment and Natural Resources 1994), it is unclear at present how long it will take for water quality to recover in the aquifer and in the lake. Because of long water residence times in the lake and the aquifer, decades or centuries may be required before water quality improves in the lake.

We conducted a benchtop study to 1) estimate past groundwater  $NO_3^-$  input rates to the lake and 2) provide worst and best case scenarios for future changes in  $NO_3^-$  concentration in the lake. The first objective was achieved by *i*) reviewing the long-term  $NO_3^-$  database from the Blue Lake and *ii*) combining this database with a simple  $NO_3^-$  mass-balance model for the lake. An important feature of the model was the estimation of in-lake  $NO_3^-$  consumption, a process not accounted for in previous studies of  $NO_3^-$  cycling in the Blue Lake. Based on the results of the first part of the study, a forecast was made for trends in  $NO_3^-$  concentration for the 1998 – 2028 period using "worse case" and "best case" scenarios for future trends in groundwater  $NO_3^-$  input to the Blue Lake.

In a third objective, we evaluated the possibility to use the long-term chloride (Cl<sup>-</sup>) record from the Blue Lake to estimate the contribution of stormwater to the lake's hydrological budget. The development of the City of Mount Gambier is thought to have increased the input of stormwater to the upper unconfined aquifer feeding the lake. How this disposal of stormwater has impacted on the input of NO<sub>3</sub><sup>-</sup> to the lake is unknown at present. Chloride may be used as a hydrological tracer of stormwater because this source of groundwater has a lower Cl<sup>-</sup> concentration than the other groundwater sources. The implications of the findings of this study for the management of the Blue Lake and areas requiring additional research will also be discussed.

## 2. Methods

#### 2.1. Site Description

Blue Lake is the largest of three lakes formed in a volcanic complex in the lower South East of South Australia (Sheard 1983; Fig. 1). Typical of many crater lakes, Blue Lake is steep sided, has a very small surface catchment, and is relatively deep ( $Z_{max} \sim 77$  m) for its surface area (61 ha) (Tamuly 1970; Turner *et al.* 1984). Blue Lake has a warm monomictic stratification regime (i.e. mixes once a year; Wetzel 1983), is oligotrophic (i.e. has a low biological productivity), and algal production is probably phosphorus-limited (Allison and Harvey 1983). The age of the lake is somewhat controversial, although recent radiocarbon dating indicated that sedimentation started at least ~28 000 yr B.P. (Leaney *et al.* 1995). Striking "whiting" events (color shifts) occur on a seasonal basis (Telfer 2000). The whitings originate from the formation of small crystals of

carbonate minerals in the water column and are derived from calcite-saturated groundwater inputs (Allison and Harvey 1983; Leaney *et al.* 1995; Telfer 2000).



**Figure 1.** Location of the Blue Lake of Mount Gambier, lower South East of South Australia, and some of the sampling stations for  $Cl^-$  and  $NO_3^-$ .

#### Hydrogeology

The study area is located within the Gambier Embayment of the Otway basin, a mixed sequence of marine and terrestrial deposits, which was formed during the tectonic separation of Australia from Antarctica (Lawson et al. 1993). The main geological units in the Mount Gambier area, in a downward order, consist of Holocene volcanic deposits, the Bridgewater Formation (stranded Pleistocene beach dunes), the Gambier Limestone and the Dilwyn Formation (Fig. 2). The Gambier Limestone is a continuous system and an important aquifer throughout the region. Two distinct units occur within the Gambier Limestone: an upper bryozoal limestome sub-unit and a lower calcite/dolomite sub-unit. Karstic features are common within the Gambier Limestone. With the exception of local areas where direct disposal of organic wastes occurs, the aquifer is generally well oxygenated and with a relatively low salinity  $(300 - 600 \text{ mg L}^{-1})$ . Underlying the Gambier limestone is the Dilwyn Formation, which comprises a series of unconsolidated sandstones and gravels with carbonaceous clay interbeds. The Dilwyn Formation hosts a confined aquifer and that has a poorer water quality than the Gambier Limestone (i.e. it is anareobic and has higher salinities). A major complex of faults underlies the Blue Lake. This faulting is thought to represent a zone of regional structural weakness through which the volcanic activity occurred. Volcanic activity appears to have accelerated the formation of karstic features in the vicinity of the Blue Lake.

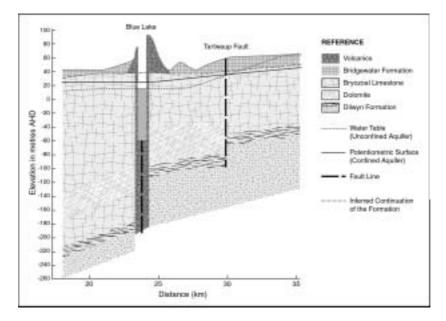


Figure 2. North-east to south-west geological cross-section of the Otway Basin in the vicinity of the Blue Lake of Mount Gambier (modified from Lawson *et al.* 1993).

#### Water balance of the Blue Lake

The hydrology of the Blue Lake has been modified substantially since European settlement (Turner *et al.* 1984; Leaney *et al.* 1995). Because the Blue Lake has a very small surface catchment, the principal sources of water are direct precipitation to the lake surface and groundwater inflow. There is no surface inflow or outflow. Regional groundwater flow is in the northeast to southwest direction, with very low gradients in the vicinity of the lake (Fig. 2). However, local flow systems occur in the upper aquifer because of the hummocky nature of the Bridgewater Formation and the preferential flow through karstic features. Groundwater flow to the lake is believed to occur as both porous media and karstic flow (Lawson *et al.* 1993). While the confined Dilwyn Formation has a positive hydraulic gradient toward the lake, its contribution to the water balance is uncertain.

Prior to European settlement, the water residence time of the lake was probably >20 years, and the main losses of water were from evaporation and groundwater outflow. Two events following European settlement may have affected the water balance of the lake: 1) Native vegetation clearance and replacement by pastures in the 1800s increased groundwater recharge rates throughout the region (Allison and Hughes 1972). Higher groundwater recharge rates should have raised groundwater levels in the region and (possibly) groundwater flow through the lake; 2) Pumping of lake water started in the late 1800s and increased rapidly during the 1950s and 60s (Fig. 3). At the peak in pumping withdrawals during the 1970's, about 15% of the lake volume was removed on an annual basis. Pumping has resulted in a large increase in groundwater inflow to the lake and shorter water residence times (<10 years; Turner *et al.* 1984; Leaney *et al.* 1995). Since the 1970s, pumping withdrawal rates have stabilised and the lake may be close to hydrological steady-state (Leaney *et al.* 1995). However, the lake level declined by ~6 metres between 1900 and 1997 (Fig. 3). Increased pumping withdrawals and a period of lower than average precipitation are thought to have contributed to the changes in water

level since 1900 (Fred Stadter, SA Department for Water, Land and Biodiversity Conservation, *personal communication*).

#### Post-1970 water balance

Because of low hydraulic gradients in the vicinity of the lake (Fig. 2) and the large uncertainties in the hydraulic properties of the Gambier Limestone aquifer (Waterhouse 1977; Lawson et al. 1993), environmental tracers have been used extensively to determine the water balance for the Blue Lake. Using tritium,  $\delta^{18}$ O, and  $\delta^{2}$ H patterns in lake and groundwater, Turner et al. (1984) estimated for the 1970 – 1976 period that groundwater inflow (4.3 to  $5.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ) and rainfall (~0.46  $\cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ) were balanced by pumping withdrawals (2.9 to  $5.2 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ), evaporation (~0.72  $\cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ) <sup>1</sup>), and some groundwater outflow. Turner et al. (1984) estimated that groundwater outflow declined from  $1.6 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$  to ~0 m<sup>3</sup> y<sup>-1</sup> between 1970 and 1976 (mean = 0.6  $\cdot 10^6$  m<sup>3</sup> y<sup>-1</sup>). Using a mixing model analysis with Cl<sup>-</sup>, uranium isotopes, and other tracers, Ramamurthy et al. (1985) estimated that 85% (±29%) of the groundwater input is from the unconfined and  $\sim 15\%$  from the confined aquifer. However, the use of Cl<sup>-</sup> mixing models in this system may be inaccurate because the end-members for some sources of water (especially the unconfined aquifer) are not well constrained (see groundwater Cl concentration and stormwater input below). Currently, the persistence of a very large hydraulic gradient towards the lake (~9 m above the lake level) is interpreted as evidence that the confined aquifer does not contribute significant amounts of water to the lake (F. Stadter, *personal communication*).

#### Groundwater NO<sub>3</sub><sup>-</sup>

Clearing of native vegetation in the vicinity of the lake and the development of the City of Mount Gambier (current population ~22 000) started during the mid-1800s. Current land use includes grazing, dairy production, horticulture, and tree plantations (Dillon 1988). Historically, a variety of waste was disposed of in the unconfined aquifer through a series of bores and sinkholes in the vicinity of the Blue Lake (Waterhouse 1977; Telfer 1994). In a survey of water quality in bores in the vicinity of Mount Gambier, NO<sub>3</sub><sup>-</sup> was the most ubiquitous contaminant in the unconfined aquifer (Waterhouse 1977). In the unconfined aquifer,  $NO_3^-$  concentration ranged between 0 and 100 mg N L<sup>-1</sup>, with a median of ~8 mg N L<sup>-1</sup>. A more recent evaluation suggests that 27% of the Mount Gambier area has groundwater NO<sub>3</sub><sup>-</sup> concentrations above the drinking water guideline (Dillon 1988). At the regional scale, diffuse pollution sources associated with primary industries would account for the bulk of the NO<sub>3</sub><sup>-</sup> input to the aquifer (Dillon 1988). However, point sources may also contribute significantly in the vicinity of the City of Mount Gambier (F. Stadter, personal communication). At the regional scale, modeling suggests that under present day loadings steady-state NO<sub>3</sub><sup>-</sup> concentration in groundwater will not be reached before 500 years, at which time 50% of the aquifer will have  $NO_3^$ concentration above the guideline (Dillon 1988).

### 2.2. Data Collection

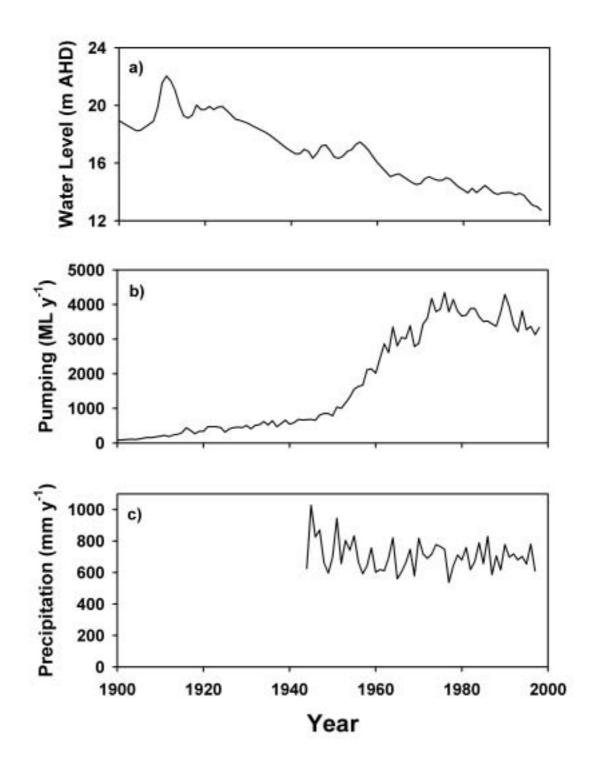
Historical information on lake water level, pumping withdrawal, precipitation, and  $NO_3^-$  concentration were obtained by contacting various government agencies (John Cugley, SA Environment Protection Authority; Andy McPharlin, SA Water; Ludovic Schmidt, SA Water). The period of records available varied from prior to 1900 for lake level and January 1968 for Cl<sup>-</sup> and  $NO_3^-$  concentrations (Fig. 3). Different analytical methods have been used to measure Cl<sup>-</sup> concentration between 1968 and 1997. Chloride was measured

using a potentiometric method (APHA 1995) up to July 1989 and then using a ferricyanide method (APHA 1995) for the remainder of the record. In the database, there was no sample with Cl<sup>-</sup> concentration determined with both methods. Thus, it was not possible here to assess if the change in analytical protocol in 1989 biased the Cl<sup>-</sup> record. Nitrate concentration was measured using an automated cadmium reduction method (APHA 1995). For 542 samples collected at the pumping station between 1981 and 1997 (*see below*), NO<sub>3</sub><sup>-</sup> concentration was determined using both an automated and a manual version of cadmium reduction method. The agreement between automated and manual measurements was excellent (*automated*:  $3.41 \pm 0.22$  mg N L<sup>-1</sup> [mean  $\pm$  standard deviation]; *manual*:  $3.43 \pm 0.21$  mg N L<sup>-1</sup>). The average difference between the two methods (automated minus manual) was 0.025 mg N L<sup>-1</sup>. Thus, analytical error is unlikely to bring significant variability in the NO<sub>3</sub><sup>-</sup> record when automated cadmium reduction alone was used.

For the purpose of annual averages, the hydrological year was defined as spanning from July 1 to June 30 (corresponding to the fiscal year). Monthly and annual average concentrations were calculated in a time-weighted fashion using:

$$\bar{c} = \frac{\left(d_{1} + \frac{d_{2} - d_{1}}{2}\right)c_{1} + \left(\frac{d_{2} - d_{1}}{2} + \frac{d_{3} - d_{2}}{2}\right)c_{2} + \dots + \left(\frac{d_{F} - d_{F-1}}{2} + d_{T} - d_{F}\right)c_{F}}{d_{T}}$$
(1)

where *c* is the average monthly or annual concentration,  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_F$  the number of days since the beginning of the month or year for the first, second, third, and last sample, respectively,  $d_T$  the number of days in the month or year, and  $c_1$ ,  $c_2$  and  $c_F$  the concentration for the first, second and last sample of the month or year, respectively.



**Figure 3.** Long-term environmental data for the Blue Lake, Mount Gambier. **a)** Water level at June 30; **b)** Annual pumping withdrawal; **c)** Annual precipitation at Mt. Gambier airport.

#### 2.3. Trends in NO<sub>3</sub><sup>-</sup> concentration

The database on  $NO_3^{-1}$  in the Blue Lake is quite extensive but heterogeneous in space and in time. Prior to the modeling exercise, the database was carefully screened and streamlined. The longest continuous record is for the pumping station, where samples have been collected since at least 1968. However, the accuracy of the NO<sub>3</sub><sup>-</sup> concentrations collected prior to 1970 is uncertain (John Cugley, SA EPA, personal *communication*). Nitrate concentration data collected prior to 1970 will not be further considered here. The intake for the pumping station is located on a raft at the margin of the lake and collects surface water. In terms of sampling frequency, there are two distinct periods for the pumping station record: from 1 to 3 times per year between 1968 and 1980 and from 17 to 50 times per year between 1981 and 1997. Nitrate concentration at other locations, at a variety of depths, was also measured between 1981 and 1997. This included station 2A along the northern margin of the lake (in an area where a large input of groundwater is believed to occur) and the more centrally located stations 1 and 6 (Fig. 1). The most extensively surveyed station was 2A, which was sampled 3 to 7 times per year, at up to 37 different depths, between 1981 and 1991. Station 1 was sampled 3 to 4 times per year between 1979 and 1987 at 4 depths. Station 6 was sampled 3 to 12 times per vear from 1991 to the present, at up to 8 different depths.

The inference of past groundwater  $NO_3^-$  concentrations using the inverse modeling approach (*see below*) requires that the estimates of  $NO_3^-$  concentration are as representative as possible of the "whole lake"  $NO_3^-$  concentration. The pumping station record was chosen for the analysis because it represents the longest time series. However, the surface water samples collected at the pumping station may not be representative of the whole lake, especially during periods when the lake is stratified. Thus, exploratory analyses were made to assess how representative the pumping station  $NO_3^-$  concentration time series was of "whole-lake"  $NO_3^-$  concentration (as defined by stations 2A, 1 and 6).

#### 2.4. Estimation of groundwater NO<sub>3</sub><sup>-</sup> concentration

The approach taken to estimate past  $NO_3^-$  concentration in groundwater entering the Blue Lake relies on the assumption that the lake behaves like a well-mixed reservoir. This modeling approach has been used extensively in limnology, especially with respect to the control of eutrophication by excess phosphorus inputs (Reckow and Chapra 1983). Because of a relatively long water residence time (6 – 10 years), Blue Lake is a good candidate for such modeling exercises. Firstly, the water balance for the Blue Lake was defined as:

$$\frac{d[V]}{dt} = (I_P + I_G - E - O_W - O_G)$$
(2),

where d[V]/dt is the change in lake volume over time,  $I_P$  the precipitation to the lake surface,  $I_G$  the groundwater input, E the evaporation from the lake surface,  $O_W$  the pumping withdrawal, and  $O_G$  the groundwater outflow. As a first approximation, it was assumed that the input from the surface catchment was minimal (Turner *et al.* 1984). By setting (1) as a finite difference equation (on a yearly basis) and by rearranging to solve for  $I_G$ :

$$I_{G} = \Delta V - I_{P} + E + O_{W} + O_{G}$$
(3),

where  $\Delta V$  (the annual change in lake volume) is equal to  $V_t - V_{t-1}$  (with *t* being the current year). *E* was assumed constant at  $0.72 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$  (Turner *et al.* 1984). Measured annual values for  $I_P$ ,  $O_W$  and  $\Delta V$  were available (Fig. 2). Lake levels were converted to lake volumes using a hypsographic curve derived from data in Tamuly (1970).  $O_G$  is not known with certainty but was estimated to range between 0 to  $1.0 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ . Thus, a range in  $I_G$  was defined for each year by using estimates of  $O_G$  ranging from 0 to  $1.0 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ .

The NO<sub>3</sub><sup>-</sup> mass-balance for the Blue Lake was defined as:

$$\frac{dM}{dt} = \frac{d[C_t \times V_t]}{dt} = \left(J_G + J_P - S - J_W - J_O\right)$$
(4),

where d[M]/dt is the change in the mass of NO<sub>3</sub><sup>-</sup> in the lake over time (mol m<sup>-3</sup> y<sup>-1</sup>),  $C_t$  the concentration of NO<sub>3</sub><sup>-</sup> at year t,  $V_t$  the lake volume at year t,  $J_G$  the load from groundwater (mol y<sup>-1</sup>),  $J_P$  the load from atmospheric deposition to the lake surface, S the in-lake NO<sub>3</sub><sup>-</sup> removal rate (mol y<sup>-1</sup>),  $J_W$  the removal by pumping and  $J_O$  the loss through groundwater outflow. By rearranging and setting (4) as a finite difference equation:

$$\Delta M = \Delta (C_t \times V_t) = J_G + J_P - S - J_W - J_O \qquad (5),$$

where  $\Delta M$  is the change in the mass of NO<sub>3</sub><sup>-</sup> in the lake relative to the mass in the previous year (with  $\Delta M = 0$  at steady-state).  $J_P$  was assumed constant at 0.0054 mol m<sup>-2</sup> y<sup>-1</sup> (0.76 kg N ha<sup>-1</sup> y<sup>-1</sup>; Blackburn and McLeod 1983).  $J_G$  was estimated by multiplying yearly pumping volume ( $O_W$ ) by yearly time-weighted NO<sub>3</sub><sup>-</sup> concentration at the pumping station. Ideally,  $J_G$  should have been estimated by weighting relative to the pumping volume between NO<sub>3</sub><sup>-</sup> sampling intervals. However, the frequency at which the pumping data was available (monthly to annually) did not match the NO<sub>3</sub><sup>-</sup> data collection intervals (weekly to bi-yearly) and this weighting could not be done. A comparison of  $J_W$  calculated with annual averages and the sum of monthly averages for the 1984 – 1994 period suggests that the bias introduced is insignificant (annual minus  $\Sigma$ monthly =  $-0.13\% \pm 1\%$ ; mean  $\pm$  SD).  $J_O$  was estimated by multiplying  $O_G$  by the yearly time-weighted NO<sub>3</sub><sup>-</sup> concentration at the pumping station.

Mass-transfer coefficients (*v*) were used to estimate in-lake NO<sub>3</sub><sup>-</sup> removal rates (*S*). Mass transfer coefficients (in m y<sup>-1</sup>) are usually determined empirically from mass-balance budgets and can be visualised as a net yearly flux from the water column to the sediments proportional to the mass of a given solute contained in *v* metres of the water column. This is an "apparent" sedimentation rate because losses through other processes (phytoplankton uptake, transformation to other forms, etc) are also included but do not necessarily involve "sedimentation" to the lake bottom. For example, in the Blue Lake, both algal uptake and denitrification at the sediment-water interface are probably important in removing NO<sub>3</sub><sup>-</sup> from the water column. The range in NO<sub>3</sub><sup>-</sup> mass-transfer coefficients for lakes found in the literature varies between 2.4 and 21.7 m y<sup>-1</sup> (Kelly *et al.* 1987; Molot and Dillon 1993; Mengis *et al.* 1997). Because of its oligotrophic state,

the  $NO_3$  mass-transfer coefficient for the Blue Lake is probably in the lower range of the literature (i.e. both algal uptake and denitrification rates should be lower under oligotrophic conditions). Following Reckow and Chapra (1983), *S* was estimated as:

$$S = A_L \cdot v \cdot C_P \tag{6}$$

where  $A_{\rm L}$  is the lake area (in m<sup>2</sup>) and  $C_{\rm P}$  the average annual NO<sub>3</sub><sup>-</sup> concentration at the pumping station (in mol m<sup>-3</sup>). Finally,  $J_{\rm G}$  was defined as  $I_{\rm G} \cdot C_{\rm G}$  (with  $C_{\rm G}$  being the average annual NO<sub>3</sub><sup>-</sup> concentration in groundwater entering the lake).  $C_{\rm G}$  was estimated by rearranging (5):

$$C_{G} = \frac{\Delta M + J_{W} + S + J_{O} - J_{P}}{I_{G}}$$
(7).

#### 2.5. Groundwater Cl<sup>-</sup> concentration and stormwater input

The concentration of Cl<sup>-</sup> in groundwater entering the lake was estimated in a similar fashion as for NO<sub>3</sub><sup>-</sup> (Equation 7), with the exception that Cl<sup>-</sup> was assumed to be conservative in the lake (i.e. S = 0 for Cl<sup>-</sup>). The possibility of determining the proportion of groundwater derived from stormwater was assessed with a sensitivity analysis. First, a mass balance for Cl<sup>-</sup> entering the lake through groundwater was defined as:

$$C_G V_G = C_U V_U + C_C V_C \tag{8},$$

where  $C_{\rm G}$  is the average concentration of Cl<sup>-</sup> in groundwater entering the lake (inferred using Equation 7),  $V_{\rm G}$  the volume of groundwater entering the lake (inferred using Equation 3),  $C_{\rm U}$  and  $C_{\rm C}$  the concentration of Cl<sup>-</sup> in the unconfined and the confined aquifer, respectively, and  $V_{\rm U}$  and  $V_{\rm C}$  the volume of groundwater entering the lake from the unconfined and the confined aquifer, respectively. Several approximations were required to estimate the stormwater component of the groundwater input. First, it was assumed that stormwater completely mixes with "native" groundwater from the unconfined aquifer but does not enter the confined aquifer. Thus, Equation 8 can be modified to yield:

$$C_{G}V_{G} = C_{NU}V_{NU} + C_{S}V_{S} + C_{C}V_{C}$$
 (9),

where  $C_{\rm NU}$  is the Cl<sup>-</sup> concentration for the "native" groundwater in the unconfined aquifer,  $C_{\rm S}$  the Cl<sup>-</sup> concentration for stormwater,  $V_{\rm NU}$  the volume of "native" groundwater derived from the unconfined aquifer, and  $V_{\rm S}$  the volume of stormwater.

The groundwater mass-balance was defined as:

$$V_{G} = V_{NU} + V_{S} + V_{C}$$
(10).

As a first approximation, the assumption was made that the volume of groundwater derived from the confined aquifer is a constant proportion of the total groundwater input from year to year. Thus,

$$V_c = a V_g \tag{11},$$

where a is a proportionality constant. By substituting Equation 11 in Equation 10 and rearranging we obtain:

$$V_{NU} = V_G(1-a) - V_S$$
 (12).

By incorporation Equations 11 and 12 to Equation 9 and by rearranging,  $V_{\rm S}$  can be solved using:

$$V_{s} = \frac{C_{g}V_{g} - C_{NU}V_{g}(1-a) - C_{c}aV_{g}}{(C_{s} - C_{NU})}$$
(13).

To determine  $V_{\rm S}$ , a realistic range in Cl<sup>-</sup> signature for each source was determined by scanning the literature (Table 1). Because the range for some sources was poorly constrained (Table 1), a sensitivity analysis was made to assess whether a precise estimate of stormwater input to the Blue Lake could be made using Cl<sup>-</sup>.

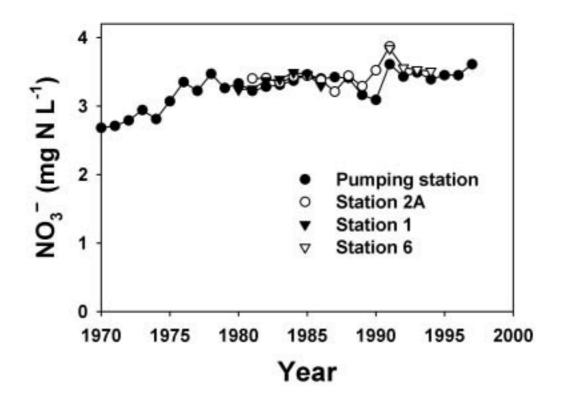
	Literature (mean and range)	This study (range)	Reference
Unconfined aquifer	55 - 277		Lawson <i>et al.</i> (1993)
	81 (65 – 96)		Ramamurthy et al. (1985)
Rainfall	10		Blackburn and McLeod (1983
"Native" unc. aquifer		70 – 110	(Estimated)
Confined aquifer	150 – 168 179 (118 – 260)	140-220	Lawson <i>et al.</i> (1993) Ramamurthy <i>et al.</i> (1985)
Stormwater	10?	10-25	Telfer (1994)
a (proportion of gw	0.15		Ramamurthy et al. (1985)
from the confined	0.20		Turner et al. (1984)
aquifer)		0.05 - 0.25	

**Table 1.** Literature values for  $Cl^-$  concentration for different sources of groundwater near the Blue Lake and parameter range used in the sensitivity analysis. All concentrations in mg  $L^{-1}$ .

## 3. Results

#### 3.1. Trends in NO<sub>3</sub><sup>-</sup> concentration

Nitrate concentration at the pumping station has increased slowly but steadily from 2.7 mg N L<sup>-1</sup> in 1970 to 3.5 mg N L<sup>-1</sup> in 1997 (Fig. 4; Table 2). The period with the greatest rate of change was 1970 to 1980, when pumping rates were also highest. With the exception of the 1990 – 1992 period, the average annual concentration measured at the pumping station was similar to the volume-integrated annual concentrations estimated at stations 2A, 1 and 6 (Fig. 4). There was also no systematic difference between station 2A and the more centrally-located stations 1 and 6 (paired *t*-test = 0.86, P < 0.4, n = 7). Overall, the pumping station appears to slightly underestimate the annual NO<sub>3</sub><sup>-</sup> concentration relative to the combined estimates from stations 2A, 1, and 6, but the difference was not statistically significant (mean difference = -0.074 mg N L<sup>-1</sup>; paired *t*-test = -1.76, P = 0.1, n = 15).

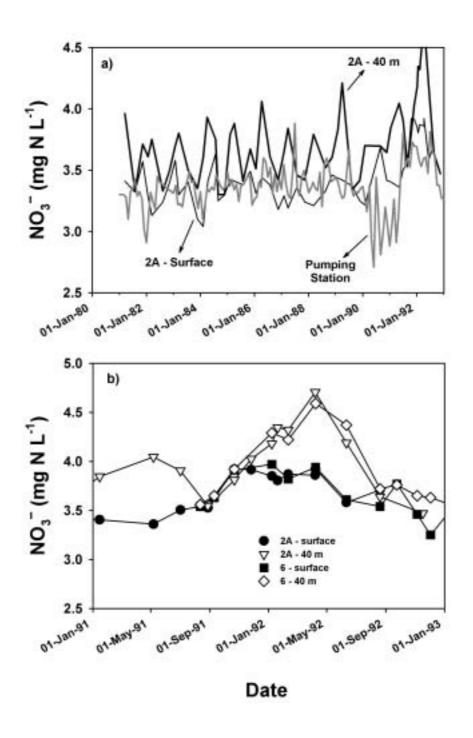


**Figure 4.** Annual average  $NO_3^-$  concentration at the pumping station and annual, volume-integrated,  $NO_3^-$  concentrations at stations 2A, 1, and 6, 1970 – 1997.

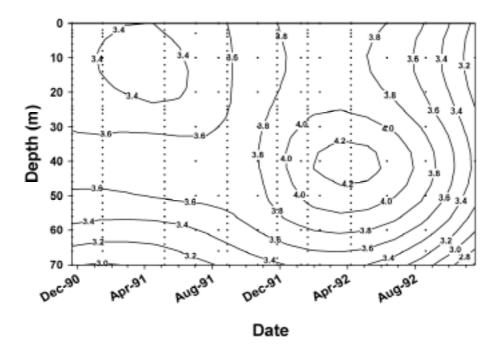
**Table 2**. Rate of increase in NO<sub>3</sub><sup>-</sup> concentration (*r*) measured at the Blue Lake pumping station for 1970 – 1997 period, and inferred for groundwater for the 1971 – 1997 period (for  $O_{\rm G} = 0.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ). Trends estimated using least-square linear regressions.

	$r \pm SE$ (mg N L <sup>-1</sup> y <sup>-1</sup> )	Probability	r <sup>2</sup>
Pumping station	$0.025 \pm 0.0040$	< 0.001	0.58
Groundwater			
$v = 2.4 \text{ m y}^{-1}$	$0.037 \pm 0.0064$	< 0.001	0.57
$v = 3.4 \text{ m y}^{-1}$	$0.043 \pm 0.0073$	< 0.001	0.58
$v = 4.4 \text{ m y}^{-1}$	$0.049 \pm 0.0083$	< 0.001	0.59
$v = 5.4 \text{ m y}^{-1}$	$0.056 \pm 0.0092$	< 0.001	0.59
$v = 6.4 \text{ m y}^{-1}$	$0.070 \pm 0.011$	< 0.001	0.60

 $NO_3^-$  concentration at the pumping station is similar to surface  $NO_3^-$  concentration at the other stations (Fig. 5a). However, there were significant variations in  $NO_3^-$  concentration across the water column. Notably, a peak in  $NO_3^-$  concentration occurs at the 40 metre depth (Fig. 5a,b) and the lowest  $NO_3^-$  concentrations are generally found close to the lake bottom (Fig. 6). Both the offshore stations and station 2A appear to have a peak in  $NO_3^-$  concentration at 40 metres (Fig. 5b).  $NO_3^-$  concentration at 40 metres has an annual cycle apparently related to the changes in pumping rate (Fig. 7). In general, a peak in  $NO_3^-$  concentration occurs ~1-2 months after the January-February peak in water extraction. The  $NO_3^-$  concentration peak at 40 metres suggests that there may be a large influx of  $NO_3^-$ -contaminated groundwater in that part of the lake. Lower pumping rates and lake turnover probably contribute to a more homogeneous vertical  $NO_3^-$  distribution pattern during winter. The rapid response of groundwater inputs to changes in pumping rates is consistent with the high transmissivity of the unconfined aquifer in the vicinity of the Blue Lake (Waterhouse 1977).



**Figure 5.**  $NO_3^-$  concentration time series at the surface and at 40 metres. **a)** at the pumping station (monthly averages; full line), station 2A at the surface (dotted line), and station 2A at 40 metres (dashed line); **b)** at stations 2A and 6, for the period when sampling overlapped (1991 – 1993).



**Figure 6**.  $NO_3^-$  concentration profiles (in mg N L<sup>-1</sup>) at station 2A between December 1990 and November 1992. Dots represent the discrete sampling points from which concentration contours were extrapolated.

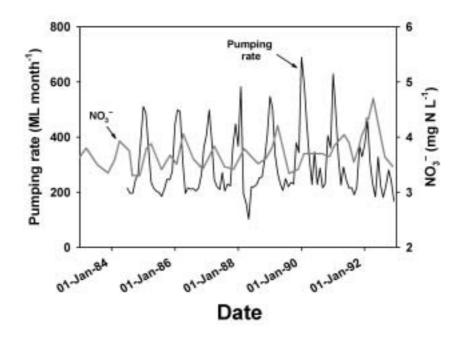
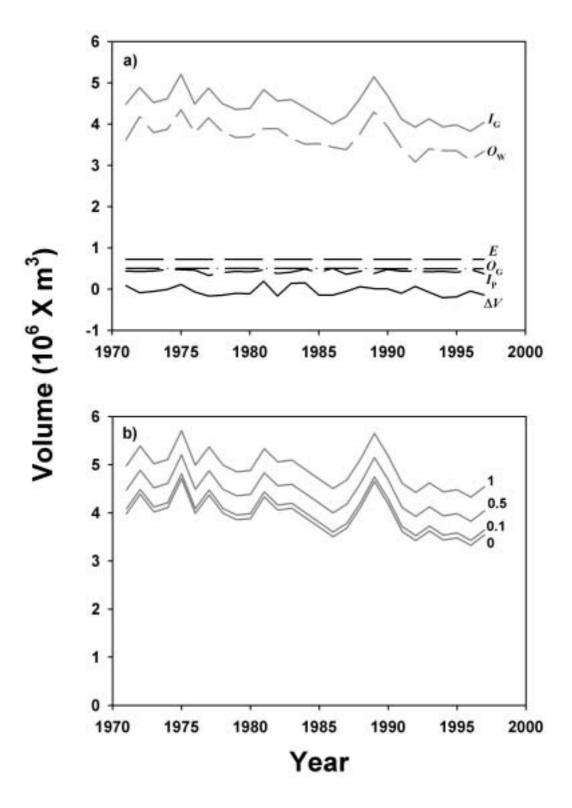


Figure 7. Monthly pumping rates and  $NO_3^-$  concentration at station 2A at 40 metres between 1983 and 1993.

#### 3.2. Water balance

Lakewater extraction by pumping appeared to be balanced mainly by new groundwater inputs during the 1970 – 1997 period, with precipitation, evaporation, and groundwater outflow being of smaller importance (Fig. 8a). The magnitude of groundwater inflow is determined, in part, on the estimate given to groundwater outflow (Fig. 8b). Despite the uncertainty with groundwater outflow, the hydrology of the lake appears primarily driven by pumping withdrawals since the 1970's. The main changes in the hydrology of the Blue Lake probably occurred between 1940 and 1970, when pumping rates were increasing rapidly.



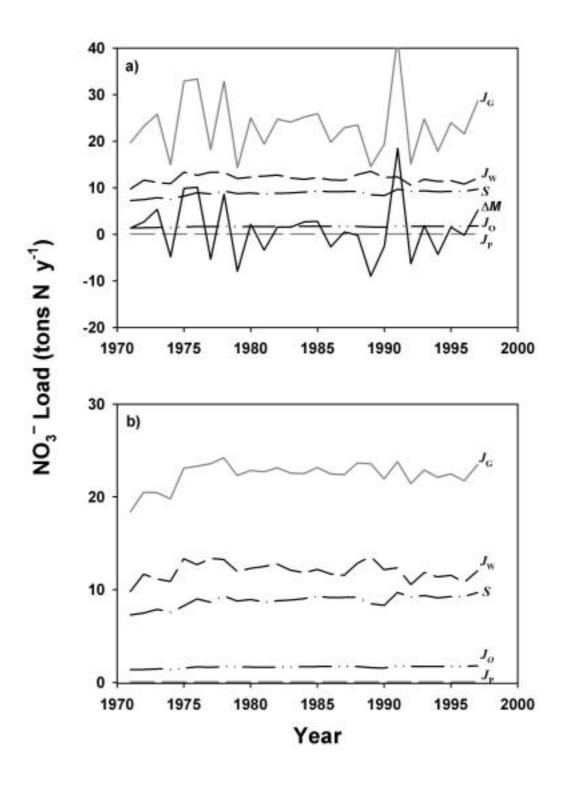
**Figure 8.** a) Estimated hydrological budget for the Blue Lake between 1971 and 1997.  $I_{\rm G}$  = groundwater input,  $O_{\rm W}$  = pumping withdrawal, E = evaporation,  $I_{\rm P}$  = precipitation,  $O_{\rm G}$  = groundwater outflow, and  $\Delta V$  = change in lake volume. b) Sensitivity analysis for the effect of different groundwater outflow estimates (in 10<sup>6</sup> m<sup>3</sup> y<sup>-1</sup>) on  $I_{\rm G}$ .

#### **3.3.** NO<sub>3</sub><sup>-</sup> loading rate to the Blue Lake

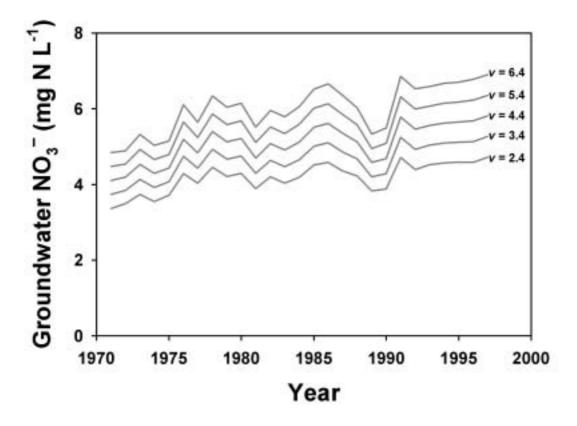
Based on the mass-balance models, the inferred NO<sub>3</sub><sup>-</sup> loading rates from groundwater  $(J_G)$  were high but variable from year to year (Fig. 9a). On average,  $J_G$  was ~20 metric tons N per year during the 1971 – 1997 period. However, closer inspection of the loading trends suggested that most of the variability in  $J_G$  arose from variability in  $\Delta M$  estimates.  $\Delta M$  estimates are prone to a large error because they are the residual of the difference between two large numbers. This was especially apparent for the 1990 – 1992 period when NO<sub>3</sub><sup>-</sup> concentrations at the pumping station were most variable (Fig. 4). In other words, small errors in the pumping station NO<sub>3</sub><sup>-</sup> concentration record may have a large impact on  $\Delta M$  estimates.

A second set of  $J_G$  estimates was calculated by assuming that the change in the mass of  $NO_3^-$  in the lake was small from year to year (i.e.  $\Delta M \sim 0$ ). Neglecting the  $\Delta M$  term will tend to underestimate  $J_G$  when  $\Delta M$  is positive and overestimate  $J_G$  when  $\Delta M$  is negative. However, because the net change in lake  $NO_3^-$  concentration was small between 1971 and 1997, neglecting  $\Delta M$  results in a negligible bias in  $J_G$ . The recalculated  $J_G$  estimates show much less variability through time (Fig. 9b). Using the recalculated estimates,  $J_G$  has been relatively constant at ~22 tons per year since 1980 (for *S* estimated with v = 4.4 m y<sup>-1</sup>). Overall, the removal of  $NO_3^-$  through pumping and through in-lake processes appear to be important sinks for  $NO_3^-$  in the Blue Lake.

While  $J_G$  appears to have been fairly constant between 1980 and 1997, the inferred concentration of NO<sub>3</sub><sup>-</sup> in groundwater entering the lake ( $C_G$ ) has been increasing at a rate of ~0.05 mg L<sup>-1</sup> per year (Table 1 and Fig. 10). Both the inferred  $C_G$  and the rate of increase in  $C_G$  are dependent on the magnitude of the estimated in-lake NO<sub>3</sub><sup>-</sup> removal rate (Fig. 10). With a low in-lake removal rate ( $v = 2.4 \text{ m y}^{-1}$ ),  $C_G$  in 1997 was 4.7 mg L<sup>-1</sup> and the rate of increase in  $C_G$  was 0.037 mg L<sup>-1</sup> y<sup>-1</sup>. With a high in-lake removal rate ( $v = 6.4 \text{ m y}^{-1}$ ),  $C_G$  in 1997 was 6.9 mg L<sup>-1</sup> and the rate of increase in  $C_G$  was 0.070 mg L<sup>-1</sup> y<sup>-1</sup>. An important conclusion from the inferred trends in  $C_G$  is that while NO<sub>3</sub><sup>-</sup> concentration in the lake is still well below the drinking water guideline, NO<sub>3</sub><sup>-</sup> concentration in groundwater entering the lake may be, on average, approaching the guideline.



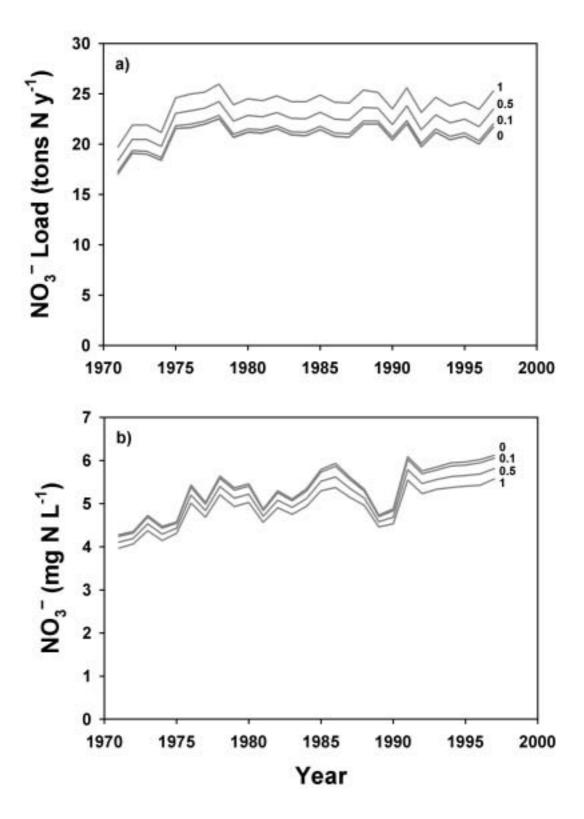
**Figure 9.** NO<sub>3</sub><sup>-</sup> mass-balance for the Blue Lake between 1971 and 1997 (for  $O_G = 0.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ ). **a)** Including  $\Delta M$ ; **b)** assuming  $\Delta M \sim 0$ .  $J_G = \text{input from}$  groundwater;  $J_W = \text{export from pumping}$ ;  $S = \text{in-lake removal (for } v = 4.4 \text{ m y}^{-1}$ );  $J_P = \text{atmospheric deposition}$ ;  $\Delta M = \text{change in the mass of NO}_3^-$  in the lake.



**Figure 10.** Inferred nitrate concentration for groundwater entering the Blue Lake between 1971 and 1997. Nitrate concentrations were estimated for a conservative range in mass-transfer coefficients (v; m y<sup>-1</sup>). These inferred NO<sub>3</sub><sup>-</sup> concentrations would represent the average for the different sources of groundwater to the lake. All simulations for  $O_{\rm G} = 0.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ .

#### 3.4. Sensitivity analysis for groundwater outflow

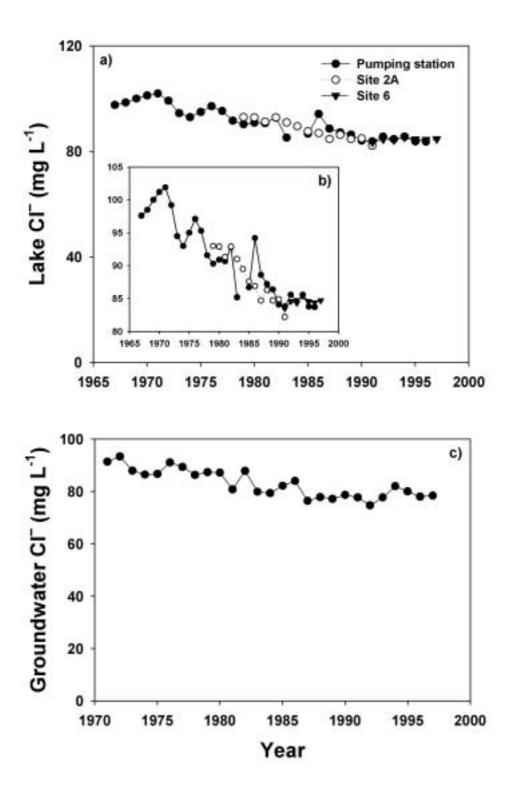
The magnitude of groundwater outflow from the Blue Lake is not known with certainty and was arbitrarily set at  $0.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$  in the above simulations. A sensitivity analysis was performed to assess the impact of varying the groundwater outflow between 0 and  $1 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$  on the inferred  $J_G$  and  $C_G$  estimates. Higher groundwater outflow rates increase the inferred  $J_G$  (Fig. 11a) but decrease the inferred  $C_G$  (Fig. 11b). In other words, while more groundwater and more groundwater  $NO_3^-$  must move into the lake if we assume higher groundwater outflow, this groundwater would have a lower  $NO_3^-$  concentration on average. Including groundwater outflow does not modify the general trend in rising  $NO_3^$ concentration in inflowing groundwater outflow from the Blue Lake will need to be resolved to obtain a more accurate picture of the  $NO_3^-$  cycle in this lake. However, the comparison of Figures 10 and 11b suggests that the unknown mass transfer coefficient for  $NO_3^-$  in the Blue Lake is presently the greatest uncertainty for the  $NO_3^-$  mass-balance.



**Figure 11.** Sensitivity analysis for the potential influence of groundwater outflow (in  $10^6 \text{ m}^3 \text{ y}^{-1}$ ) on **a**)  $J_G$  and **b**)  $C_G$  estimates (for  $v = 4.4 \text{ m y}^{-1}$ ).

#### 3.5. Trends in Cl<sup>-</sup> concentration

The database for Cl<sup>-</sup> is not as extensive as the one for NO<sub>3</sub><sup>-</sup> but bears several similarities. The longest record is for the pumping station (1968 – 1997) with a total of 52 measurements. Chloride samples were also collected at several depths at other stations, notably station 2A (1979 – 1992) and station 6 (1991 – 1996). Over the 1968 – 1992 period, there was a tendency for a decline in Cl<sup>-</sup> concentration from ~100 mg L<sup>-1</sup> to ~84 mg L<sup>-1</sup> (Fig. 12a). During the period when their records overlapped, Cl<sup>-</sup> concentration at the pumping station appeared more variable than at station 2A. However, this variability may have been caused, in part, by fewer samples being collected at the pumping station. Chloride concentrations have remained quite stable between 1992 and 1997, with a near perfect agreement between the pumping station and station 6 (Fig. 12a).

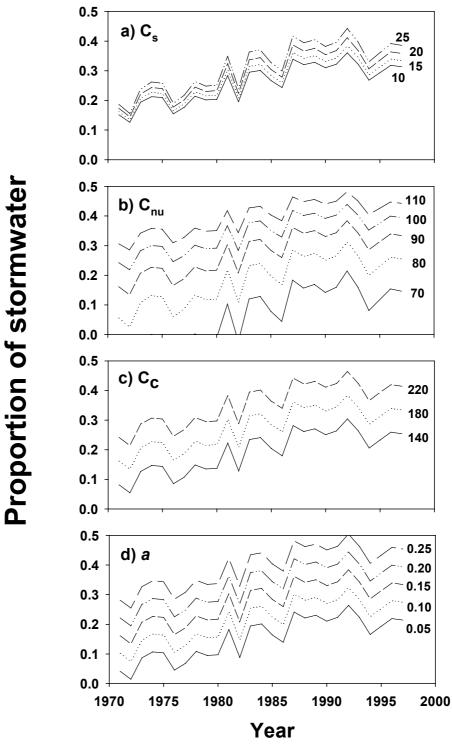


**Figure 12.** Trends in chloride concentration in the Blue Lake between the 1967 and 1997 hydrological years. **a)** Cl<sup>-</sup> concentrations at the pumping station, Station 2A, and Station 6. **b)** Same data as in a) but drawn with a broken y-axis. **c)** Inferred Cl<sup>-</sup> concentration for groundwater entering the Blue Lake between 1971 and 1997.

#### 3.6. Inferred Cl<sup>-</sup> concentration in groundwater

The same approach used to estimate the concentration of  $NO_3^-$  in groundwater entering the lake was used to estimate Cl<sup>-</sup> concentrations. However, unlike for  $NO_3^-$ , Cl<sup>-</sup> was assumed to behave conservatively during its residence within the lake. Because of a low sampling frequency at the pumping station, the time series of lake Cl<sup>-</sup> concentration used in the analysis was the combination of the record from the pumping station (1970 – 1978), station 2A (1979 – 1990), and station 6 (1991 – 1997). The inverse modeling suggested that the average concentration of Cl<sup>-</sup> in groundwater entering the lake declined from ~92 mg L<sup>-1</sup> in 1971 to ~75 mg L<sup>-1</sup> in 1992, followed by a small increase to ~78 mg L<sup>-1</sup> by 1997 (Fig. 12c). It is important to keep in mind that, as for  $NO_3^-$ , these estimated groundwater chloride concentrations are the average for the different sources of groundwater entering the lake.

The sensitivity analysis suggested that it is not possible to use Cl<sup>-</sup> concentrations to estimate the volume of stormwater entering the Blue Lake.  $C_{\rm NU}$ ,  $C_{\rm S}$ ,  $C_{\rm C}$  and a were selected for the sensitivity analysis because they appeared the most uncertain parameters (Table 1). In the sensitivity analysis, different values for one of the parameters were used while values for the other parameters were left constant. This analysis indicated that the estimated  $V_{\rm S}$  is dependent on the values chosen for  $C_{\rm NU}$ ,  $C_{\rm C}$  and a, but not the one chosen for  $C_{\rm S}$  (Fig. 13). Using 1997 as an example, the proportion of stormwater in groundwater inputs to the lake varies between 0.15 - 0.44 for  $C_{\text{NU}}$ , 0.31 - 0.39 for  $C_{\text{S}}$ , 0.25 - 0.49 for  $C_{\rm C}$ , and 0.21 - 0.45 for a depending on the value selected (Fig. 13). When using a mixed combination of values for the four parameters, the range spreads between 0.07 and 0.52 for 1997. Thus, while there is evidence that stormwater contributes to the hydrological budget of the Blue Lake and that this contribution may have increased between 1970 -1997, it is not possible to quantify the input of stormwater accurately using Cl<sup>-</sup> alone. The large uncertainty for the "native" signature of groundwater in the unconfined aquifer is the largest constraint on using CI<sup>-</sup> concentration to estimate the contribution of stormwater to the hydrological budget of the Blue Lake.

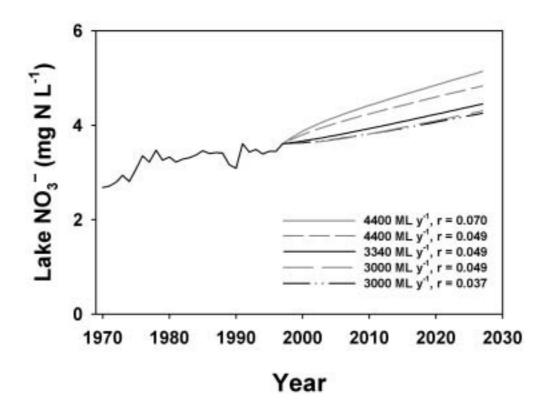


**Figure 13**. Sensitivity analysis for four parameters involved in the estimation of the stormwater contribution to groundwater input to the Blue Lake. **a**) Cl<sup>-</sup> concentration in stormwater; **b**) Cl<sup>-</sup> concentration in groundwater native to the unconfined aquifer; **c**) Cl<sup>-</sup> concentration in the confined aquifer; **d**) the proportion of the groundwater input originating from the confined aquifer. Default values were  $C_{\rm S} = 10 \text{ mg L}^{-1}$ ,  $C_{\rm UN} = 90 \text{ mg L}^{-1}$ ,  $C_{\rm C} = 180 \text{ mg L}^{-1}$ , a = 0.15.

#### 3.7. Forecast for NO<sub>3</sub><sup>-</sup> concentration in the Blue Lake

Future trends in  $NO_3^-$  concentration in the Blue Lake were estimated for different combinations of the rate of increase in groundwater  $NO_3^-$  concentration and yearly pumping rates. The trends in increasing groundwater  $NO_3^-$  concentration observed for the 1971 – 1997 period (0.04 to 0.07 mg N L<sup>-1</sup> y<sup>-1</sup>) were assumed to apply for the 1998 – 2028 period. Three different pumping scenarios were also considered: 1) "low" pumping rate (3000 ML y<sup>-1</sup>), 2) the 1997 pumping rate (3340 ML y<sup>-1</sup>), and 3) "high" pumping rate (4000 ML y<sup>-1</sup>). The combination of the low pumping rate and low rate of increase in  $NO_3^-$  concentration in groundwater represents a reasonable lower bound for the extrapolation of  $NO_3^-$  in the lake; The high pumping rate and rate of increase in groundwater  $NO_3^-$  concentration in groundwater NO<sub>3</sub><sup>-</sup> concentration based on present day conditions. While reasonable as a first approximation, it is not possible to guarantee that the rate of increase in groundwater  $NO_3^-$  concentration observed between 1971 and 1997 will be perfectly accurate for the 1998 – 2028 period.

Both the rate of pumping and the rate of increase in  $NO_3^-$  concentration in groundwater could affect  $NO_3^-$  concentration in the Blue Lake in the future (Fig. 14). However, while for all scenarios considered lake  $NO_3^-$  concentration will increase by 2028,  $NO_3^-$  concentrations should remain well below the drinking water guideline (<6 mg N L<sup>-1</sup>; Fig. 14). In the short-term (i.e. up to 2028), changes in pumping rate may be more important than increasing groundwater  $NO_3^-$  concentration to determine lake  $NO_3^-$  concentration. In other words, pumping management schemes that will increase the lake water residence time will slow down the increase in  $NO_3^-$  concentration.



**Figure 14**. Nitrate concentration forecast for the Blue Lake (1998 – 2028) under different scenarios of pumping withdrawal and increase in groundwater  $NO_3^-$  concentration (*r*, in mg N L<sup>-1</sup> y<sup>-1</sup>). All other variables (precipitation, evaporation, etc) were left constant at average values for the 1971 – 1997 period.

## 4. Discussion

#### 4.1. Monitoring and presentation of the NO<sub>3</sub><sup>-</sup> concentration data

The concentration of  $NO_3^-$  in the Blue Lake has increased slowly but steadily during the 1970 – 1997 period. This gradual change in concentration would be difficult to detect at a scale of a few years because it is small relative to natural variability. This gradual change highlights the importance of maintaining a monitoring program for the Blue Lake that minimises the noise from short-term seasonal and spatial variability at the profit of the more important long-term trends. Monitoring at the pumping station raft (which collects surface water) does provide an acceptable picture of whole-lake  $NO_3^-$  concentration but will benefit from supplementary stratified measurements at a central station.

During the production of this report, it was noted that there was a lack of consistency in the way that the Blue Lake  $NO_3^-$  record has been reported in the past. Nitrate concentrations have been expressed as either mg N L<sup>-1</sup> or mg  $NO_3^-$  L<sup>-1</sup> (which may be confusing for the general public). In addition, raw data was often presented without any spatial or temporal averaging and plotted with broken Y-axes (i.e. axes not extending to 0 mg N L<sup>-1</sup>). Figures with broken axes may be deceptive under some conditions because they convey the feeling that  $NO_3^-$  concentrations have "fluctuated widely" from year to year and have "leveled-out" since the early 1970s (see for example Mines and Energy Resources South Australia 1997). Both improper spatial and temporal averaging and broken axes distract from the important information for management purposes – the slow gradual increase in  $NO_3^-$  concentrations be averaged at a suitable spatial and temporal scale, and that data be preferably plotted with full axes (with perhaps a broken axis plot as an inset, see Fig. 12 for example).

#### 4.2. In-lake NO<sub>3</sub><sup>-</sup> consumption

The modelling exercise suggests that in-lake consumption is a significant component of the NO<sub>3</sub><sup>-</sup> budget in the Blue Lake. However, it is not possible at this stage to accurately quantify in-lake consumption rates. The N cycle in lakes is quite complex and beyond the scope of this report. Possible mechanisms for  $NO_3^-$  consumption would include *i*) algal uptake followed by sedimentation, *ii*) water column denitrification, and *iii*) denitrification at the sediment-water interface. It is not clear at present how much of the NO<sub>3</sub><sup>-</sup> is consumed by algae and bacteria in the water column of the Blue Lake. Generally, phytoplankton will first use  $NH_4^+$  as a source of N but will switch to  $NO_3^-$  when the former becomes in short supply (Wetzel 1983). In eutrophic lakes (i.e. lakes with a high biological productivity), NO<sub>3</sub><sup>-</sup> consumption by algae followed by sedimentary deposition is an important removal pathway (Teranes and Bernasconi 2000). Denitrification in the water column will occur if part of the water column becomes sub-oxic (i.e, with low  $O_2$ ) concentrations). This may occur, for example, near the lake bottom during summer stratification. The magnitude of water column denitrification would be a function of the volume of water that becomes sub-oxic (and for how long). Denitrification at the sediment-water interface is a nearly universal process in lakes (Seitzinger 1988). Most sediments have a well defined succession of oxic, sub-oxic, and anoxic conditions with depth within the sediment profile (Appelo and Postma 1993). Rates of denitrification at the sediment-water interface tend to be limited by the rate at which NO<sub>3</sub><sup>-</sup> can be delivered from the overlying water to the sub-oxic sediments by diffusive and/or advective

transport. Denitrification at the sediment-water interface becomes less important when the hypolimnion (i.e. the volume of the lake below the thermocline) becomes completely anoxic. It is recommended that the N cycle be further studied in the Blue Lake, including a detailed assessment of the magnitude of the three above-mentioned  $NO_3^-$  attenuation processes.

#### 4.3. Links between the N and P cycles

The N and phosphorus (P) cycles in lakes are closely entwined. Primary production (that is, the quantity of organic matter produced by algae during a year) is likely to be, in part, limited by the availability of P in the Blue Lake. Algae prefer  $NH_4^+$  as a source of N but will use  $NO_3^-$  once the  $NH_4^+$  pool is depleted (Wetzel 1983). Thus, for any  $NO_3^-$  to be consumed by algae, enough P must be available for all the  $NH_4^+$  to be consumed first. Primary production is also a strong determinant of how much  $NO_3^-$  will be removed through denitrification. When algae die, they slowly sink to the sediments, decompose, and thus provide "fuel" for processes such as denitrification. The highest mass-transfer coefficients for  $NO_3^-$  (21 m y<sup>-1</sup>; Mengis *et al.* 1997) have been found in eutrophic lakes (lakes with excessive algal blooms). A current dilemma facing water managers in some parts of the world is that the control of P inputs to lakes (to limit excess algal growth) may result in less efficient in-lake  $NO_3^-$  removal rates (Mengis *et al.* 1997).

The major pathways for the input of P to the Blue Lake may be quite different than the ones for N. Phosphorus is not transported as easily as N in oxygenated aquifers because phosphate (a common form of P in water) will tend to bind to surfaces and form poorly soluble minerals (Appelo and Postma 1993; Stumm and Morgan 1996). Phosphorus inputs to lakes are often associated with particles, such as sediment transport in surface runoff (Harris 2001), long-range atmospheric transport of dust (Wetzel 1983), and pollen, insects and litter from riparian vegetation (Cole *et al.* 1990). Thus, unlike for N, erosion from the small (but steep) surface catchment of the Blue Lake and the input of dust from the surrounding agricultural and urban areas may be a significant source of P. *The sources of P to the Blue Lake and how they may have changed over time should be determined*.

Whether pumping has changed the P cycle in the Blue Lake is unclear at present. Paleolimnological investigations have indicated that the inorganic carbon sedimentation rate has increased by a factor of four in the Blue Lake during the 20<sup>th</sup> century (Leaney *et al.* 1995). This is consistent with an increased input rate of calcite-saturated groundwater induced by pumping. If groundwater is a significant source for P, greater pumping rates should favor greater P inputs and increased algal productivity. On the other hand, if greater pumping rates induce more frequent and intense "whiting" events, the lake may become more P-limited. This will occur if P is lost from the water column during "whiting" events by the entrainment of algae with settling carbonate crystals (Wetzel 1983) and possibly the formation of minerals containing P (Stumm and Morgan 1996). *How pumping of the lake affects "whiting" events should be investigated because it may impact both the aesthetic value of the lake and the N and P cycles*.

#### 4.4. Water balance

It is currently unclear whether the Blue Lake is a groundwater sink or a groundwater flow-through system. Likewise, the contribution of different aquifers and sub-aquifers to the water balance is not completely understood.

Additional bores have been recently installed in distinct sections of the Gambier Limestone aquifer in the vicinity of the Blue Lake (F. Statder, *personal communication*). Hydraulic measurements and the use of environmental tracers in these new bores may shed additional light on the hydrogeology of the Blue Lake. For example, the deuterium and <sup>18</sup>O signature of bore water may be used to delineate zones of groundwater throughflow. Groundwater originating from lake recharge (i.e. throughflow) will be more enriched in these tracers relative to groundwater because of evaporation on the lake surface (Cook and Herczeg 2000). New hydrogeological tools (such as electromagnetic flow meters; P. Dillon, *personal communication*), may also be applied in bores in the Mount Gambier area to identify preferential zones of groundwater flow.

Paleolimnology and environmental isotopes may also provide useful insights in the hydrology of the Blue Lake. The sedimentary record of lakes archives several indicators of past water balances. For example, A. Herzceg and colleagues (unpublished manuscript) have used changes in the <sup>18</sup>O signature of carbonates preserved in lake sediments to estimate changes in water residence time over the last 200 years in the Blue Lake. The carbonate minerals produced in lakes (by "whiting" events, for example) have an <sup>18</sup>O signature related to the one of lake water at the time of their formation. Thus, changes in past <sup>18</sup>O signature of lake water (induced by pumping, evaporation, climate change, etc) are archived in lake sediments. Based on the sedimentary carbonate <sup>18</sup>O record, Herczeg and colleagues have estimated that the water residence time for the Blue Lake was 23±2 years prior to 1850 and decreased to 8±2 years by the mid-1990's. These water residence time estimates are similar to the ones obtained using different methods (Turner et al. 1984; this study). Herczeg and colleagues hypothesized that the two major causes for the decline in water residence time following the post-European settlement period were land use change (i.e. greater groundwater recharge rates) and pumping withdrawal. A variety of similar paleolimnological tools could be used to understand the water balance and the nitrogen cycle in the Blue Lake (Shanley et al. 1998; Herczeg et al. 2001).

A variety of tools are now available to help understand the hydrogeology of groundwaterfed lakes. These tools should be used to better understand the past and present water balance of the Blue Lake. A proper understanding of the water balance is critical to forecast future tends in  $NO_3^-$  concentration in the Blue Lake.

#### **4.5.** Use of Cl<sup>-</sup> to estimate stormwater input to the Blue Lake

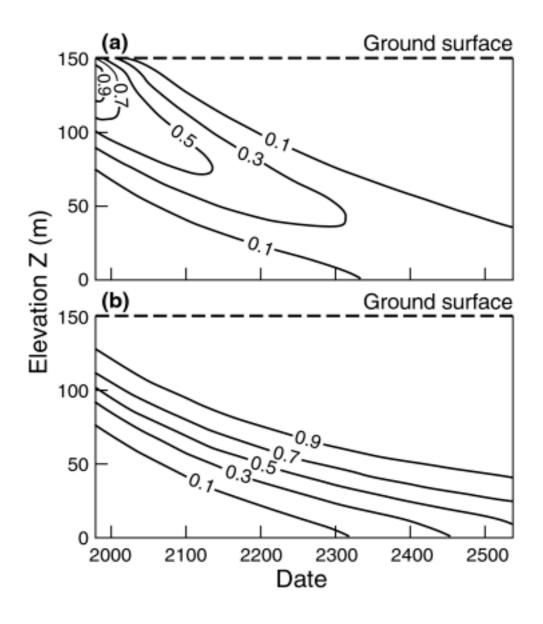
The City of Mount Gambier currently disposes of stormwater in the Gambier Limestone through sinkholes and a number of bores. How much the disposal of stormwater (and its associated potential contaminants) contributes to the lake's water budget has been a topic of concern (Emmet 1985; Telfer 1994). While it is tempting to use tracers such as Cl<sup>-</sup> to estimate the contribution of stormwater to the lake, some pitfalls should be considered. Mixing models rely on the assumptions that end-members for the different sources of water to the lake can be *clearly constrained*. This is not the case for the Blue Lake at

present because it is not possible to assign clear end-members for some of the sources, especially groundwater native to the unconfined aquifer. In addition to the large range in possible signatures for some of the sources, the assumption that the "average" Cl<sup>-</sup> concentration is fixed through time may be tenuous for some of the sources. For example, chloride concentrations in the unconfined aquifer may be slowly changing in response to changes in water and Cl<sup>-</sup> recharge rates that have followed European settlement (Allison and Hughes 1972; Dillon *et al.* 2001). Thus, the possibility exists that Cl<sup>-</sup> concentration has declined in the Blue Lake since 1970 for reasons other than increased stormwater input. How present and future inputs of stormwater from the City of Mount Gambier will impact on the water and Cl<sup>-</sup> balance in the Blue Lake will require a careful hydrogeological assessment. With the knowledge currently available, it is not recommended to use Cl<sup>-</sup> to quantify the stormwater input to the Blue Lake. A similar conclusion was reached by Lawson *et al.* (1993).

#### 4.6. Response time of the Blue Lake to changes in NO<sub>3</sub><sup>-</sup> input

The aquifer surrounding the Blue Lake is still adjusting to the changes in N input to which it has been submitted since European settlement. Even assuming that N inputs to the aquifer will decrease over the next decades,  $NO_3^-$  concentration in the Blue Lake will remain elevated for a long time because of long water residence times in the lake and the surrounding aquifer. It is interesting to note that the rate at which  $NO_3^-$  concentration is increasing in the Blue Lake is consistent with model predictions for the evolution of groundwater  $NO_3^-$  concentration in the upper Gambier Limestone aquifer (Dillon 1988; Fig. 15). The model predictions by Dillon (1988) suggest that centuries will be required for  $NO_3^-$  concentrations to reach a new equilibrium in areas of the aquifer affected by diffuse pollution sources. Thus, the effectiveness of future nutrient management plans for the Blue Lake must be designed with a long-term perspective in mind – decades to centuries.

It is difficult to forecast accurately how  $NO_3^-$  concentration will change in the Blue Lake for other than the relatively short-term (~30 years) because climate and land-use in the region will probably change substantially over the scale of centuries. For example, if tree plantations and native forests return over a significant proportion of the area, both the recharge rate of water and  $NO_3^-$  should decrease substantially (Dillon 1988). The opposite could also occur should the landscape become increasingly saturated with nitrogen (i.e. from continued use of N fertilisers and N-fixing crops). A better understanding of the N cycle in the lake and better estimates of present and past  $NO_3^$ loading trends to the aquifer surrounding the Blue Lake will be required to forecast longer term  $NO_3^-$  trends in the lake.



**Figure 15**. Forecast for  $NO_3^-$  concentration profiles in the upper Gambier Limestone aquifer for areas primarily impact by diffuse pollution sources. Simulations are for a unit recharge concentration of  $NO_3^-$  and a coefficient of vertical dispersion of 1 m<sup>2</sup> y<sup>-1</sup>; **a**) with the unit  $NO_3^-$  recharge eliminated in 1986; **b**) sustained. Modified from Dillon (1988).

#### 4.7. Conclusion

The inferences, and especially the forecast, made in this study should be taken with some caution because of the numerous approximations involved. Notably, it was assumed that climate will remain constant, and that the rate of increase in  $NO_3^-$  concentration in groundwater observed for the 1971 – 1997 period is applicable to the 1998 – 2028 period. The lake model used assumes that there is only one aquifer with an even  $NO_3^-$  concentration. In reality, both a confined and an unconfined aquifer may contribute water to the Blue Lake (Turner *et al.* 1984; Ramamurthy *et al.* 1985). Different aquifers, and systems of fractures or karstic features within aquifers, probably have different  $NO_3^-$  concentration defined here

should be interpreted as an "average" for groundwater entering the lake. A source of error is the potential for  $NO_3^-$  concentration measured at the pumping station not to be perfectly representative of whole-lake  $NO_3^-$  concentration. This is problematic on the very short-term (months to years) but probably not on the long-term (decades and centuries)

Despite some shortcomings, this simple modeling exercise has highlighted several important aspects of the  $NO_3^-$  cycle in the Blue Lake. While  $NO_3^-$  concentration in the lake will probably increase in the next decades, concentrations will probably remain below the drinking water guideline over this period. In-lake removal is probably a significant component of the lake  $NO_3^-$  budget, something that was not recognised in previous studies, and this sink may be amenable to management. Management options that will maximise the water residence time of the lake will also, indirectly, improve water quality.

## 5. Acknowledgements

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## 6. Summary of Conclusions and Recommendations

#### It is **concluded** that:

- The concentration of  $NO_3^-$  in the Blue Lake has increased slowly but steadily between 1970 and 1997.
- The slow increase in lakewater NO<sub>3</sub><sup>-</sup> concentration reflects a similar gradual increase in the concentration of NO<sub>3</sub><sup>-</sup> in groundwater entering the lake.
- In-lake removal is probably a significant sink for  $NO_3^-$  in the Blue Lake.
- *In the short-term*, variations in the pumping regime of the lake will have more impact on lake NO<sub>3</sub><sup>-</sup> concentration than the ongoing increase in NO<sub>3</sub><sup>-</sup> concentration in groundwater.
- Lakewater NO<sub>3</sub><sup>-</sup> concentration is unlikely to exceed the drinking water guideline at the scale of decades but may exceed the guideline at the scale of centuries.
- With the information currently available, chloride (Cl<sup>-</sup>) trends in the Blue Lake cannot be used to estimate the contribution of stormwater disposal to the lake's hydrological budget.

#### It is **recommended** that:

- The rate of in-lake  $NO_3^-$  removal should be measured.
- The phosphorus (P) cycle in the Blue Lake should be studied. This includes defining the sources of P to the Blue Lake, how the contribution of these sources may have changed over time, and how the P cycle is affected by pumping withdrawals.
- Primary production (i.e. algal growth) and the factors controlling primary production (nutrients, light, stratification, enhanced sedimentation, etc) must be determined for the Blue Lake. Primary production directly and indirectly controls the rates of NO<sub>3</sub><sup>-</sup> removal in lakes.
- Present and past water balances for the Blue Lake should be further investigated. An accurate understanding of the hydrogeology of the Blue Lake is required to forecast future trends in NO<sub>3</sub><sup>-</sup> concentration in the lake.
- In light of the ongoing increase in NO<sub>3</sub><sup>-</sup> concentration in the lake, ongoing efforts to control NO<sub>3</sub><sup>-</sup> inputs to the Gambier Limestone aquifer in the vicinity of the Blue Lake should be continued.

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## Appendix I

Yearly values used for physical and chemical parameters, Blue Lake Lake, South Australia. All values for the hydrological year (July 1 – June 30) unless otherwise noted. Concentrations expressed as mg N  $L^{-1}$  for NO<sub>3</sub><sup>-</sup> and mg  $L^{-1}$  for Cl<sup>-</sup>. Volume-integrated concentrations are given for stations 1 and 6.

Year	Precip. (mm)	Lake Vol. at June 30 (ML)	Pumping Withdwl. (ML)	NO <sub>3</sub> <sup>-</sup> Pump. Station	NO <sub>3</sub> <sup>-</sup> Station 2A	NO <sub>3</sub> <sup>-</sup> Stations 1 & 6	Cl <sup>–</sup> Pump. Station	Cl <sup>−</sup> Station 2A	Cl <sup>–</sup> Statior 6
1967		(1112)					97.6		
1968							98.5		
1969							100.0		
1970	818	36 750	3 440	2.68			101.2		
1971	719	36 830	3 610	2.71			101.9		
1972	691	36 740	4 180	2.79			99.2		
1973	717	36 690	3 790	2.94			94.5		
1974	778	36 680	3 870	2.81			93.0		
1975	765	36 790	4 350	3.07			95.0		
1976	747	36 720	3 790	3.35			97.1		
1977	537	36 550	4 150	3.22			95.3		
1978	642	36 400	3 810	3.47			91.6		
1979	711	36 290	3 670	3.26		(Stn 1)	90.3	93.0	
1980	679	36 180	3 690	3.33		3.24	90.9	92.9	
1981	760	36 370	3 880	3.22	3.40	3.25	90.7	91.3	
1982	620	36 190	3 890	3.28	3.41	3.37	92.8	92.9	
1983	669	36 330	3 650	3.31	3.34	3.39	85.2	91.0	
1984	790	36 480	3 510	3.37	3.43	3.49		89.5	
1985	656	36 330	3 520	3.46	3.44	3.46	86.7	87.6	
1986	829	36 180	3 440	3.40	3.38	3.30	94.2	86.9	
1987	586	36 120	3 380	3.42	3.21		88.6	84.7	
1988	707	36 180	3 770	3.41	3.44		87.2	86.3	
1989	616	36 190	4 290	3.16	3.29		86.4	84.7	
1990	779	36 200	3 930	3.09	3.52	(Stn 6)	84.1	84.9	
1991	698	36 100	3 420	3.61	3.87	3.84	83.8	82.2	83.5
1992	719	36 160	3 080	3.43		3.56	85.6		84.6
1993	681	36 080	3 400	3.49		3.53	84.6		84.3
1994	703	35 870	3 350	3.39		3.51	85.6		85.4
1995	654	35 680	3 350	3.45			83.8		84.6
1996	780	35 630	3 130	3.45			83.7		84.4
1997	610	35 490	3 340	3.61					84.7