Short communication

# Ion chromatographic determination of lithium at trace level concentrations
## Application to a tracer experiment in a high-mountain lake

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**Abstract**

The water residence time of a high-mountain seepage lake in the Austrian Alps was derived from the flushing rate of a tracer substance. A diluted lithium chloride solution was injected into the lake during holomictic conditions in order to favour the homogeneous distribution of the tracer. The exponential decline of the mass of lithium in the lake revealed a water residence time of 1.5 to 3 months for summer and almost no lake water exchange during winter. Lithium concentrations ranged from background values of 0.06 $\mu$g l$^{-1}$ to about 3 $\mu$g l$^{-1}$ immediately after the tracer injection. Lake water samples were analyzed with ion-exchange chromatography using a Dionex device with a CS 12A separation column. The method detection limit determined according to the definition of the US Envirinmental Protection Agency amounted to 0.009 $\mu$g l$^{-1}$. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Water analysis; Lithium chloride; Metal cations

## 1. Introduction

The quantification of mass fluxes in remote mountain lakes was among the main topics of the European Union project MOLAR (ENV4-CT95-0007). The water residence time, which is defined as the time required to exchange the entire volume of a lake once, represents a key parameter in this context. Generally, it is derived from components of the water balance of a lake and its catchment, and may be expressed as the ratio of lake volume to the sum of discharge and evaporation rate. A major shortcoming of this approach, however, is the restricted reliability of the result when the individual com-

ponents of the water balance (e.g. discharge) are not measured directly, but instead are inferred from the differences of other components [1]. This applies especially to seepage lakes, i.e. lakes without superficial inlets and outlets, fed only by groundwater and precipitation. The water residence time is then preferably derived from the flushing rate of a tracer substance injected into the lake, independently of the water balance. Here, this method is applied to Lake Gossenkölle, a small high-mountain seepage lake in the Austrian Alps (2413 m above sea level, 47°13′ N, 11°01′ E). A diluted lithium chloride solution was injected into the lake, and from the exponential decline of the lithium mass contained in the lake the water residence time was determined.

With regard to the cristalline bedrock (gneiss, granite) of the lake catchment, background lithium concentrations in Lake Gossenkölle were expected to

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be at trace levels, i.e. in the $\mu$g l$^{-1}$ range or less. Therefore, ion chromatography, which has proven in various studies to be a very practicable and sensitive method for the analysis of water samples at low level concentrations (e.g. [2–4]), was the selected analytical technique for this study.

Only a few references were found to studies in which lithium was employed as a tracer substance in hydrological field experiments or in which the lithium content of groundwater and surface water was investigated [5–9]. In these studies, however, flame atomic absorption spectrometry or inductively coupled plasma-MS was employed for chemical analysis rather than ion chromatography.

This paper describes the ion chromatographic method applied and gives a short overview of the tracer experiment. A detailed discussion of the results will be published elsewhere.

## 2. Experimental

### 2.1. The tracer experiment

When deriving the water residence time of a lake from the flushing rate of a tracer substance, one major prerequisite is that the tracer be homogeneously distributed within the lake. Therefore, the time span of holomixis, i.e. when circulation occurs throughout the entire water column of a lake, was considered to be the appropriate period for the tracer injection. In July 1997, during the period of holomixis that persisted for a few days after Lake Gossenkölle thawed, a dilute lithium chloride solution was introduced into the lake by spray injection. Along horizontal transects at various depth levels, a total of 240 g Li$^+$ was injected into a lake volume of about 76 000 m$^3$, thus causing the weighted mean lithium concentration to rise from 0.06 to 3.1 $\mu$g l$^{-1}$.

During the subsequent decline in the lithium concentration samples were taken at weekly to biweekly intervals. At three selected sampling points in the lake, water was collected with a metal-free Ruttner sampler along vertical profiles at intervals of 1 m, from the surface down to the bottom of the lake. Samples from each depth were poured into pre-cleaned polyethylene bottles and kept at 4°C until the chemical analysis was carried out (generally

performed within 1 week after sampling). The sampling period lasted from July 1997 through September 1998.

A detailed description of the experiment, reasons for the selection of lithium chloride as a tracer and a discussion of its potential effects on aquatic organisms can be found in [10].

### 2.2. Ion chromatography

A Dionex DX-100 instrument was used for the analysis of lithium. The original system, however, had been extended by adding components such as the UI 20 Universal Interface, a SRS Controller and a Thermal Stabilizer Module for the conductivity cell, and was combined with a DX-500 instrument for concomitant anion analysis. System control, data collection and processing were performed by Dionex PeakNet software (release 5.1).

The analytical column used was a CS 12A (4 mm) with the equivalent guard column CG 12A (4 mm). The eluent was 11 m$M$ sulfuric acid, and the flow-rate was 1 ml min$^{-1}$. Detection was done by suppressed conductivity. The CSRS-Ultra cation suppressor was run in the auto suppression recycle mode with the SRS current set to 300 mA. The sample loop had a volume of 200 $\mu$l. Samples were delivered by a Dionex automated sampler to the loop.

Eluents and standard solutions were prepared with deionized water of resistivity >17.8 M$\Omega$ cm. A 1000 mg l$^{-1}$ lithium stock solution (Merck) was diluted down to the $\mu$g l$^{-1}$ to ng l$^{-1}$ range immediately before calibration. All standards and samples were analyzed at the 0.3 $\mu$S cm$^{-1}$ detection range using a four-level quadratic calibration.

## 3. Results and discussion

### 3.1. Detection limit

The method detection limit (MDL) was derived according to the definition of the US Environmental Protection Agency (EPA) [11]:

$$MDL = t_{(n-1,\ 1-\alpha=0.99)}\sigma \tag{1}$$

where $\sigma$ is the standard deviation of a series of measurements, n is the number of replicates and $t$ is Student's $t$ value for $n - 1$ degrees of freedom at the 99% confidence level. The concentration of the sample used to determine the detection limit lay according to the EPA [11] in the concentration range of the expected MDL, i.e. up to five times the MDL.

Ten replicate measurements of an artificial sample gave an MDL of 0.009 $\mu$g l$^{-1}$ lithium, which corresponded well to the few values found in the literature. Kaiser et al. [12] determined for lithium a detection limit of 0.007 $\mu$g l$^{-1}$ at a signal-to-noise ratio of 3 using a Dionex device with a CS12A separation column. The authors achieved this low value by a high-volume direct-injection method, using a sample size of 1000 $\mu$l. In [13] a lithium detection limit of 0.005 $\mu$g l$^{-1}$ was reported at a signal-to-noise ratio of 10. The method employed comprised the use of a 7.5 ml sample loop, a concentrator column and a CS12A separation column. Both in [12] and [13] a considerably bigger sample size was used compared to the 200 $\mu$l loop we applied. However, the 200 $\mu$l injection volume had turned out to be the most practicable one taking into account both the need for a low detection limit and the ion content of the lake water [14].

The chromatogram of a real sample is shown in Fig. 1. Lake water sampled 5 weeks after the injection of the lithium tracer is analyzed according to the chromatographic conditions given in Section 2.1. The chromatogram clearly reveals that there is no interference between the lithium and sodium ions,
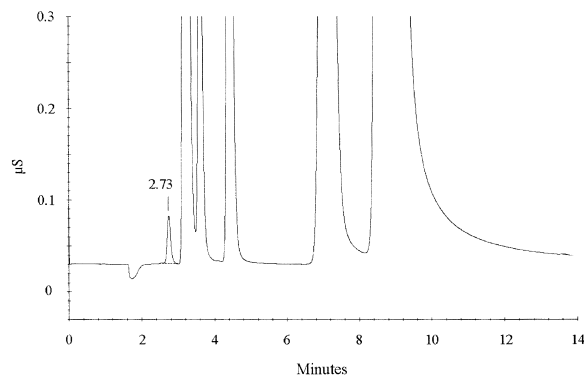
i.e. the lithium peak is completely separated from the subsequent sodium peak.

## 3.2. Water residence time

The water residence time $\tau$ was derived from the exponential decline of the lithium mass contained in Lake Gossenkölle:

$$m(t) = m_0 \, e^{-t/\tau} \tag{2}$$

with $m(t)$ as the lithium mass at time $t$ and $m_0$ as the injected mass of lithium. The water residence time could then be expressed as:

$$\tau = t/[\ln m_0 - \ln m(t)] \tag{3}$$

The lithium mass $m(t)$ was determined from the lithium concentrations measured at the various distinct depths by multiplying each concentration value with the respective partial lake volume. A bathymetric chart and the continuous registration of the lake water level helped to take into account the temporal variability of the lake volume.

The volume-weighted mean lithium concentration amounted to 3.1 $\mu$g l$^{-1}$ immediately after the tracer injection in July 1997 and had declined exponentially to the natural background value of 0.06 $\mu$g l$^{-1}$ by September 1998. Concomitantly the total mass of lithium in the lake decreased from the injected 240 g down to about 5 g Li$^{+}$. The decline of the lithium was most pronounced during the first 4 months of the experiment. It slowed down during the winter half year, when snow was the predominant form of precipitation and no major melting occurred. In May 1998, when both the snow pack in the catchment of Lake Gossenkölle and the lake ice cover started to melt, an enhanced decline of the lithium mass was again observed, until background values were reached in September 1998.

Due to the varying decline of the lithium mass, the water residence time $\tau$, determined according to Eq. (3), also revealed a pronounced temporal variability. $\tau$ was shortest for the period July to September 1997, amounting to about 1.5 months. The mathematically derived 23 months of water residence time for the winter period indicated almost no exchange of lake water from December 1997 to April 1998. During Summer 1998 a water residence time of 3 months



Fig. 1. Chromatogram of a lake water sample. Lithium peaks at 2.73 min, the concentration is 1.236 $\mu$g l$^{-1}$. Chromatographic conditions as described in Section 2.1.

was determined. The difference with respect to the value found during the previous summer was attributed largely to the increasing relative importance of lithium input by groundwater, which was assumed to have a lithium concentration similar to that of the lake background value (i.e. 0.06 $\mu g\, l^{-1}$).

## 4. Conclusion

The investigation confirmed the practicability of ion-exchange chromatography for the analysis of water samples at trace level concentrations. The method detection limit of 0.009 $\mu g\, l^{-1}$ Li$^+$ served as a basis for a hydrological tracer experiment with lithium chloride, which aimed at the determination of the water residence time of a seepage lake. Due to the sensitivity of the analytical method and the low lithium background concentration (0.06 $\mu g\, l^{-1}$), the amount of injected lithium necessary to follow the flushing of the tracer substance properly, could be reduced to a minimum. This was particularly important in order to reduce the potential impact of the lithium used in the experiment on the aquatic environment of the lake.

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