

## Radium-226 and Alkaline Earth Elements in the Water Column, Interstitial Sediment Water, and Sediments of Zürichsee (Switzerland)\*

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Distribution of alkaline earth elements Mg, Ca, Sr, Ba and Ra (<sup>226</sup>Ra) was measured in the water column and in the sediments (solids and interstitial water) of Zürichsee (Lake Zurich), Switzerland. With the exception of Ra, the concentrations of alkaline earth elements were always quite uniformly distributed throughout the water column and did not show seasonal variations. Our results indicate removal of Ra from the water column in winter, probably due to scavenging effects during the turnover period of the lake. Furthermore, during the lake stagnation in summer, the concentrations of Ra (and to a lesser extent of Ba) increased in the bottom layer of the water column. We postulate that the increase in the concentrations of these elements during stagnation results from their release from the sediments together with Mn when the sediments and the interstitial water become more anoxic. Ra and Ba were found to be enriched in the interstitial water of the sediments. Their concentrations in solid sediments decreased with increasing sediment depth and showed a sediment distribution pattern resembling that of manganese.

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## INTRODUCTION

The concentrations and behaviour of alkaline earth elements (AEE's) Mg, Ca and Sr have been investigated in various aquatic environments (*e.g.*, Refs. 1–3). In contrast to these AEE's, investigations of Ba and especially of Ra ( $^{226}\text{Ra}$ ) in lakes are scarce because their concentrations are low (very low for Ra) and difficult to measure.

Whereas Mg, Ca and Sr were found to be uniformly distributed in the water column of Lake Biwa, Japan, Ba was reported to decrease in the bottom layer of this lake.<sup>3</sup> Contrary to these results, the concentrations of Ba increased in the anoxic hypolimnion of Estwaite Water (English Lake District).<sup>4</sup>

Durham and Joshi<sup>5</sup> have measured  $^{226}\text{Ra}$  in Lake Huron, and Drndarski and Lavi in the impoundment of the Grliška.<sup>6</sup> Hesslein and Slavicek<sup>7</sup> have measured elevated concentrations of artificially added  $^{226}\text{Ra}$  near the sediment/water interface in small Canadian shield lakes. Elevated  $^{226}\text{Ra}$  concentrations near the sediments have also been reported for Lake Pavin (Massive Central, France).<sup>8</sup>

Contrary to lakes,  $^{226}\text{Ra}$  distributions have been measured in a wide variety of marine and estuarine environments.<sup>9–13</sup> These studies have suggested that enhanced  $^{226}\text{Ra}$  in the water column can result from the dissolution of ferro-manganese oxy-hydroxides during cyclic redox processes.<sup>11</sup> In the Black Sea, maxima of Ba and  $^{226}\text{Ra}$  near the  $\text{O}_2/\text{H}_2\text{S}$  interface have been explained by a bacteria-mediated breakdown of particulate organic matter and the subsequent release and partial dissolution of associated barite.<sup>13</sup>

In the present paper, we report on the distribution of AEE's (including  $^{226}\text{Ra}$ ) in the water column, in the interstitial water, and in sediments of a fairly anoxic sediment core from Zürichsee (Lake Zurich), Switzerland. This publication of the results for  $^{226}\text{Ra}$  coincides with the 100th anniversary of the discovery of radium by Pierre and Marie Curie in 1898.

## EXPERIMENTAL

### *Sampling and Methods*

A map of Switzerland with Zürichsee and its environments is presented in Figure 1. Zürichsee (volume  $3.3 \text{ km}^3$ , area  $65 \text{ km}^2$ , mean depth 51 m) is a well investigated lake.<sup>14–20</sup> It receives major inputs from agriculture, industrial and domestic discharges, and from atmospheric fallout. The allochthonous flux is small to the main basin of the lake where the sampling for the present study was performed, because the particle freight of the main inflowing River Linth is mostly deposited upstream in Walensee and in the upper part of Zürichsee (Obersee), which is today separated by a dam (Figure 1). Our studies were performed in the deepest part (136 m depth) of the lake.

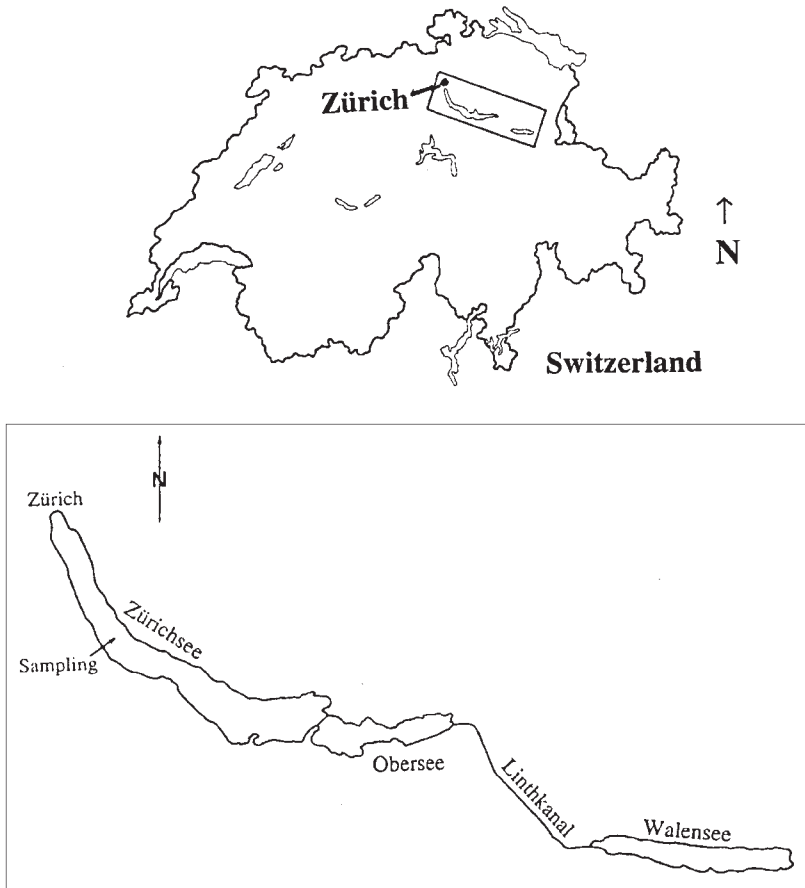


Figure 1. (Top) Map of Switzerland with insert. (Bottom) Expanded view of the insert showing Zürichsee (Lake Zurich) and environments. The coring position (sampling) is also indicated.

Water temperature, pH, alkalinity, dissolved  $O_2$  and the chemical composition of the water were regularly measured by the Water Supply Laboratory of the city of Zürich.<sup>16</sup> Water samples for the measurement of AEE's (including  $^{226}\text{Ra}$ ) were taken between August 1991 and April 1992.

A sediment core was recovered in August 1991 with a gravity corer (12 cm inner diameter) at the sampling location of water samples. The core was dissected at 2 cm intervals on-board the boat. The core sections were immediately frozen in tightly closed centrifuge tubes. After thawing in the laboratory, the samples were centrifuged (25 min, 8000 rpm) and filtered (0.45  $\mu\text{m}$ ). AEE's were determined in the interstitial water and in solid sediments. Solid sediments were dissolved in  $\text{HNO}_3/\text{HClO}_4/\text{HF}$ . In all samples (lake water, interstitial water, and sediments) Mg and Ca were assayed by flame AAS, Sr by graphite furnace AAS and Ba by ICP-AES.

## <sup>226</sup>Ra Analysis

We have adapted a method of Sill<sup>21</sup> and S. Short (personal communication) with <sup>133</sup>Ba as yield tracer. For details see Ref. 22. The <sup>133</sup>Ba tracer was added to 20 L of lake water. <sup>226</sup>Ra and <sup>133</sup>Ba were adsorbed onto 1 g of freshly prepared and dispersed MnO<sub>2</sub> which was then decanted and dissolved in 1 mL 30% H<sub>2</sub>O<sub>2</sub> and 50 mL 0.75 M HBr. This solution was passed through a 5 mL column of Dowex<sup>®</sup> 1x2 (50–100 mesh, Cl<sup>-</sup>-form). The effluent from the column and 25 mL of a 0.75 M HBr wash solution were combined and diluted to 900 mL with water. Then, the procedure of Ref. 21 was applied. The blank value for the full <sup>226</sup>Ra procedure was 0.32 ± 0.05 mBq.

## RESULTS AND DISCUSSION

### *Properties of the Water Column*

Figures 2 and 3 present typical examples (October 1991 and February 1992) of the distribution of temperature, pH, dissolved O<sub>2</sub> and AEE's (including <sup>226</sup>Ra) in the water column of Zürichsee.

In October 1991 (*i.e.*, near the end of the lake stagnation period), the thermocline was at about 12 m depth (Figure 2). The maximum of dissolved O<sub>2</sub> (0.3 mM) was at the top of the water column. At 15 m depth, the oxidation of biota led to a decrease of the concentration of O<sub>2</sub> to about 0.05 mM. Between 60 and 100 m water depth the O<sub>2</sub> content increased again to ≈ 0.2 mM. Near the bottom of the lake (*i.e.*, at ≈ 135 m depth), it was at ≈ 0.05 mM (*i.e.*, ≈ 10% of O<sub>2</sub> saturation). The pH was > 8 near the lake surface and dropped to a practically constant value of about 7.5 between the 15 m depth and the bottom of the lake. Mg, Ca and Sr were uniformly distributed throughout the water column. Ba was also evenly distributed for the major part of the water column, but was somewhat enriched close to the bottom of the lake. The uniform distribution of these AEE's contrasts to the radioactivity concentrations (given in mBq/100 L) of <sup>226</sup>Ra which varied considerably with depth. The latter had a maximum activity concentration at about a 50 m depth, then it decreased to a minimum at the 120 m depth and was enriched near the bottom layer of the water column. Elevated concentrations of Ra and Ba near the bottom of the water column were found during the stagnation period and are probably the result of a release by the 'fairly anoxic' lake sediments (O<sub>2</sub> ≈ 0.05 mM). The decrease in the redox potential close to the bottom of the lake during stagnation enables Mn (hydr)oxides and associated Ba and Ra compounds to dissolve. Speciation calculations (MINTEQA2) show that Ba is completely dissolved as Ba<sup>2+</sup> under the prevailing conditions. Further discussions of the Ba and Ra enrichment at the bottom of the water column are given below.

In February 1992 (Figure 3), *i.e.*, during the temperature induced convection of the lake water, the concentrations of dissolved O<sub>2</sub> remained prac-

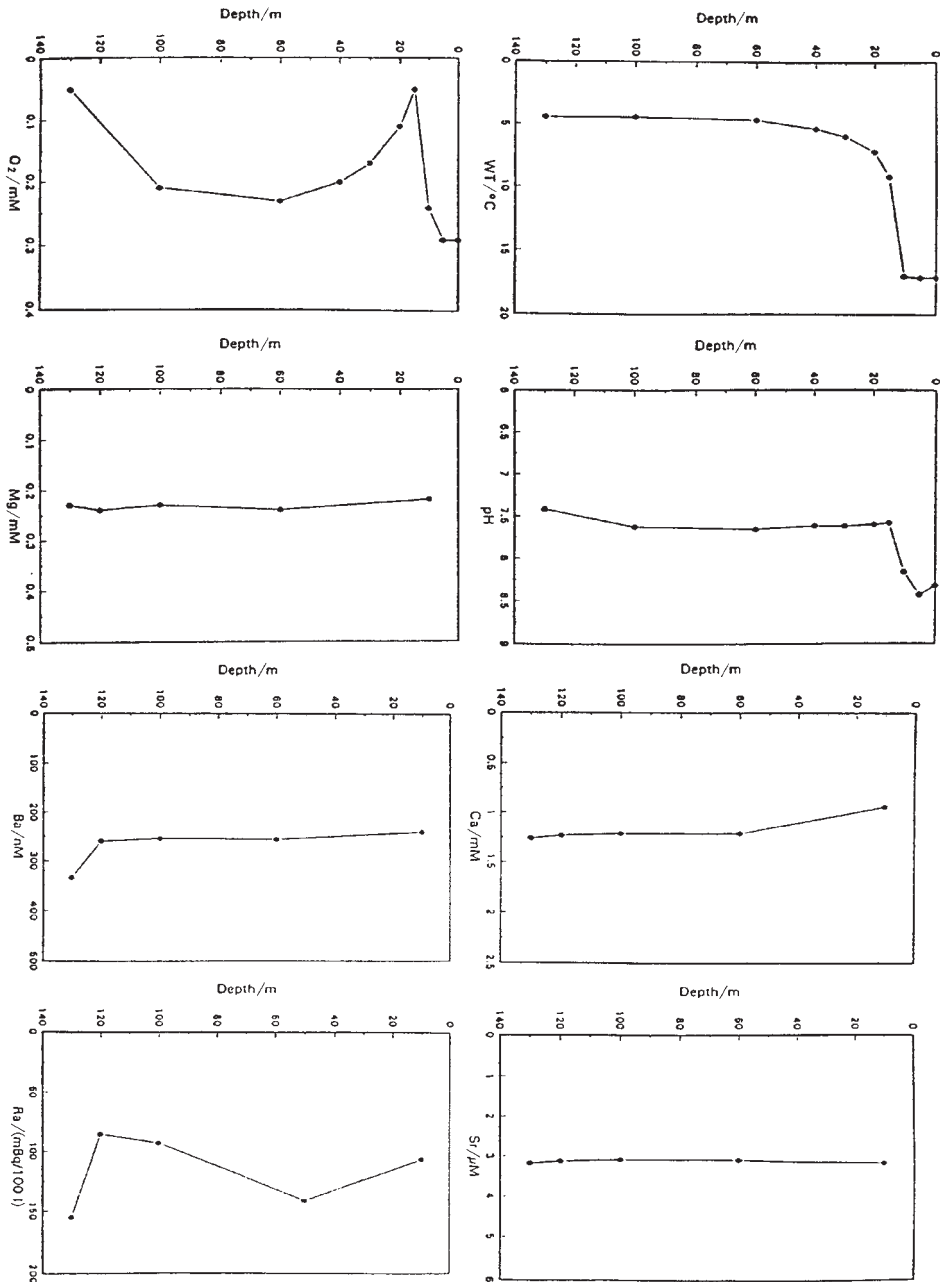


Figure 2. Vertical distribution in the water column of dissolved oxygen, water temperature (WT), pH and alkaline earth elements on 9th October 1991. Analytical errors ( $1\sigma$ ) are 5% for Mg and Ca, 5–7% for Sr and Ba. See Table I for errors of  $^{226}\text{Ra}$ . 1 Bq (1 disintegration per second) corresponds to a  $^{226}\text{Ra}$  concentration of  $\approx 1.2 \times 10^{-13}$  mol.

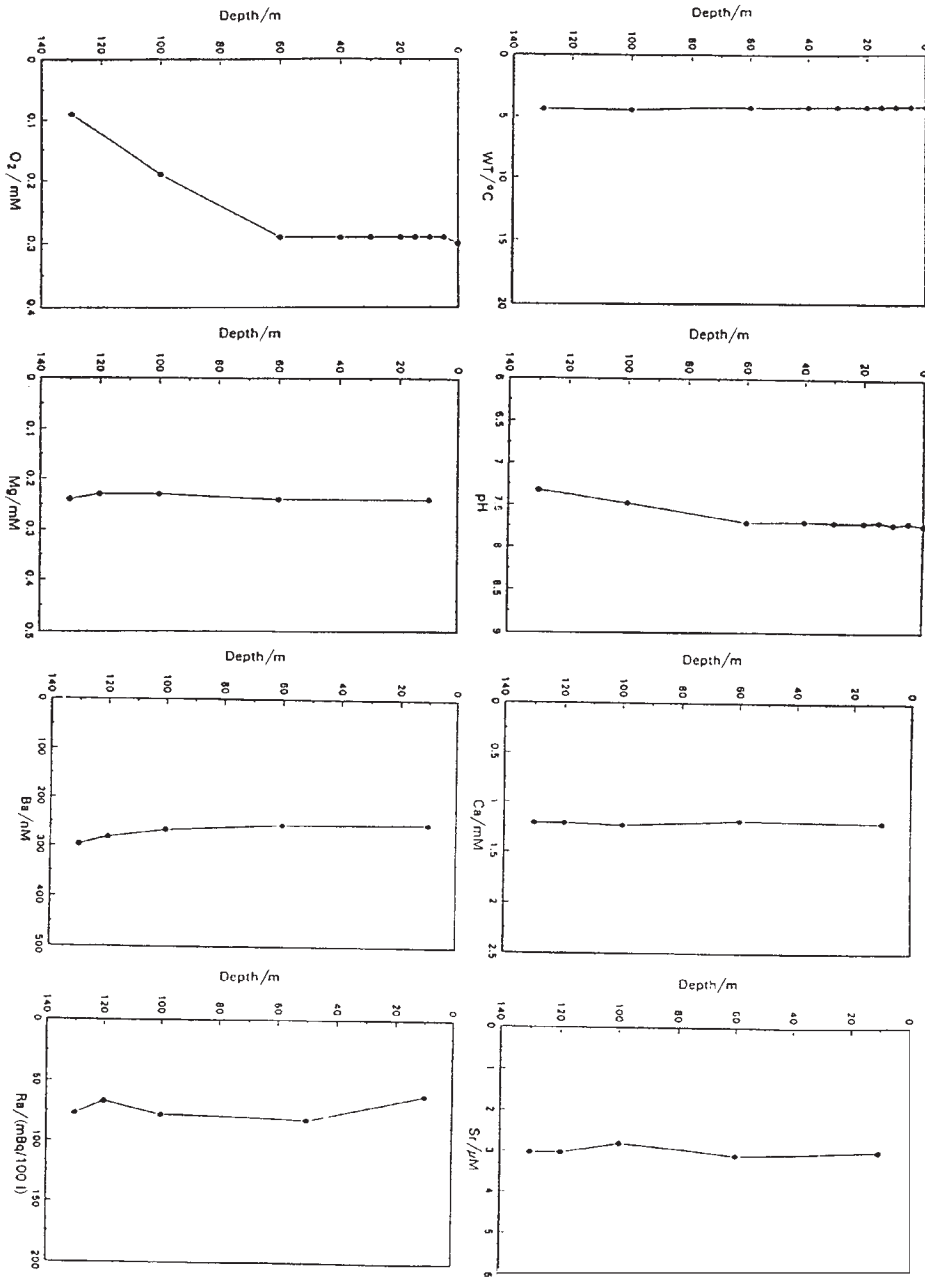


Figure 3. Vertical distribution in the water column of dissolved oxygen, water temperature (WT), pH and alkaline earth elements on 5th February 1991. Analytical errors ( $1\sigma$ ) are 5% for Mg and Ca, 5–7% for Sr and Ba. See Table I for errors of  $^{226}\text{Ra}$ . 1 Bq (1 disintegration per second) corresponds to a  $^{226}\text{Ra}$  concentration of  $\approx 1.2 \times 10^{-13}$  mol.

tically constant down to a water depth of  $\approx 60$  m and decreased steadily below. This decrease is the result of the degradation of organic matter in the deeper part of the lake. Contrary to the  $O_2$  concentrations, the vertical distributions of temperature, pH, and concentrations of all AEE's were quite uniform (Figure 3).

However, in contrast to the relatively constant and evenly distributed concentrations of Mg, Ca, Sr and Ba, large seasonal variations of the concentration and depth distribution of  $^{226}\text{Ra}$  were observed in the water column of Zürichsee. For instance, the mean concentrations in the water column of  $^{226}\text{Ra}$  in February 1992 ( $73.2 \pm 8.3$  mBq/100 L) were much lower than in October 1991 ( $116.4 \pm 30.7$  mBq/100 L). Using the concentration data of Table I, residence times for  $^{226}\text{Ra}$  can be calculated according to Ref. 20. Assuming a mean water depth of Zürichsee of 51 m, a mean sedimentation rate of  $0.14 \text{ g cm}^{-2} \text{ year}^{-1}$  (Ref. 18) and a mean  $^{226}\text{Ra}$  activity of the sediments of  $33 \text{ mBq g}^{-1}$  (Ref. 18), the following residence times for  $^{226}\text{Ra}$  are obtained (averaged for the indicated two months): August/October 1.2 years; November/December 1.0 year; February/April 0.7 years. This demonstrates that radium is removed quite efficiently from the water column during the turnover of the lake. A possible process of removal is discussed below.

Also, the  $^{226}\text{Ra}$  concentrations at the lake surface decreased from 115 mBq/100 L in August 1991 to 62 mBq/100 L in February 1992, and increased to 80 mBq/100 L in April 1992. Table I, presenting the complete set of  $^{226}\text{Ra}$  data, furthermore indicates that the Ra concentrations at the bottom of the lake were at a minimum in February and increased towards April 1992, at the beginning of the next stagnation period. Unfortunately, we did not follow this trend between April 1992 and October 1992.

The concentration changes in summer at the lake surface can be explained by an enhanced adsorption and incorporation of  $^{226}\text{Ra}$  to growing biota. Hesslein and Slavicek<sup>7</sup> reported that macrophytes can enrich  $^{226}\text{Ra}$  up to a factor of 5000. The very low activity concentrations in April 1992

TABLE I

$^{226}\text{Ra}$  concentrations in the water column of Zürichsee/(mBq/100 L)\*

Depth m	August 28.8.1991	October 9.10.1991	November 6.11.1991	December 4.12.1991	February 5.2.1992	April 8.4.1992
10	$115 \pm 3$	$107 \pm 7$	$103 \pm 7$	$82 \pm 7$	$62 \pm 5$	$80 \pm 5$
50	$98 \pm 5$	$142 \pm 7$	$88 \pm 7$	$92 \pm 5$	$82 \pm 7$	$27 \pm 5$
100	$120 \pm 7$	$93 \pm 7$	$87 \pm 5$	$77 \pm 5$	$78 \pm 7$	$17 \pm 3$
120	$125 \pm 10$	$85 \pm 5$	$98 \pm 7$	$100 \pm 7$	$67 \pm 5$	$58 \pm 5$
130	$127 \pm 7$	$155 \pm 10$	$108 \pm 8$	$145 \pm 8$	$77 \pm 7$	$108 \pm 12$

\* 1 mBq corresponds to a  $^{226}\text{Ra}$  concentration of  $\approx 1.2 \times 10^{-16}$  mol; 1 Bq = 1 disintegration/sec.

(27 mBq/100 L at 50 m, and 17 mBq/100 L at a 100 m depth) resulted probably from scavenging of  $^{226}\text{Ra}$  by manganese oxides or hydroxides that were formed and precipitated when the lake became more oxic during the turnover period. The adsorption of Ba and Ra to hydrous manganese oxides is well known and very selective, and was for instance used for a preconcentration of  $^{226}\text{Ra}$  or  $^{133}\text{Ba}$  from large volumes of lake water by Refs. 21, 22, and in the present investigation. Compared to Ra and Ba, the adsorption of Mg, Ca, and Sr to amorphous Mn (hydr)oxides is about 100 times smaller.

Manganese precipitation is manifested in Figure 4 by the much smaller manganese inventory in the water column in February 1992 than in October 1991 or April 1992. Figure 4 also shows that the total concentrations of Mn at the bottom water of the lake were always much higher than at the lake surface. These results for Mn are in agreement with the data of Sigg<sup>14</sup> who also reported elevated concentrations of  $\text{Mn}^{2+}$  near the sediment/water interface of Zürichsee. At the end of stagnation, a reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and to  $\text{NH}_4^+$  was observed in Zürichsee at a 110 m depth,<sup>16</sup> thus enabling the dissolution of manganese oxy-hydroxides. We postulate that the dissolution of manganese oxy-hydroxides from sediments during the reducing conditions in the stagnation period co-releases adsorbed Ba and Ra to the wa-

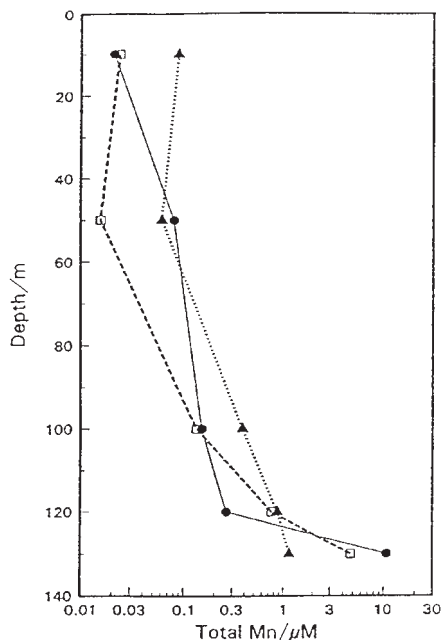


Figure 4. Total (dissolved and particulate) concentrations of Mn in the water column of Zürichsee. ● October 1991, □ February 1992, ▲ April 1992. Analytical errors ( $1\sigma$ ) 5–7%.



ter phase and thus, produces the observed higher concentrations of these elements at the bottom of the water column (see above).

The considerable differences in the behaviour of Ba and  $^{226}\text{Ra}$  in the water column of Zürichsee (Figures 2 and 3) contrast to the generally linear correlation of these elements in the saline water of oceans and estuaries.<sup>10</sup> Here, diatoms have been suggested as major carriers of both Ba and  $^{226}\text{Ra}$ .

#### *Interstitial Water (Pore Water)*

In Figure 5, we present the concentration *vs.* depth profiles of the redox sensitive elements Fe and Mn in the interstitial water of a sediment core collected in August 1991 in Zürichsee at a depth of 136 m. The concentrations of Mn in the interstitial water decreased with the sediment depth. The manganese profile in the interstitial water was similar to a profile observed by Robbins and Callender<sup>23</sup> in Lake Michigan. These authors have demonstrated that Mn particles were supplied by the ongoing sediment accumulation and have shown that rhodochrosite ( $\text{MnCO}_3$ ) formation<sup>24</sup> was responsible for a Mn consumption in deeper pore water.

Contrary to Mn, the concentrations of Fe in the interstitial water increased with the sediment depth (Figure 5). We found a strong anticorrelation ( $r = -0.97$ ) of Fe with phosphate. These conditions were quite similar to dissolved Fe and phosphate distributions in anoxic sediments of Greifensee (Lake Greifen), Switzerland.<sup>25</sup> These authors found strong evidence that the Fe concentrations in the interstitial water were controlled by authigenic

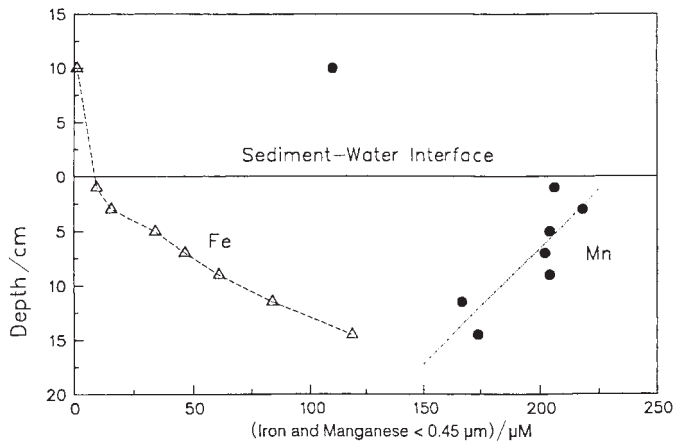


Figure 5. Fe and Mn concentrations in the interstitial water (pore water  $< 0.45 \mu\text{m}$ ) of a slightly anoxic sediment core from Zürichsee (August 1991, 136 m water depth). Values above the sediment/water interface are from lake water samples collected on the same day. Analytical errors ( $1\sigma$ ) are 5–7%.  $\Delta$  Fe,  $\bullet$  Mn.

TABLE II

Pore water concentrations (interstitial water < 0.45  $\mu\text{m}$ ) of alkaline earth elements in sediments of Zürichsee (136 m depth, August 1991)

Depth cm	Mass depth <sup>a</sup> g cm <sup>-2</sup>	Mg mM	Ca mM	Sr $\mu\text{M}$	Ba $\mu\text{M}$	<sup>226</sup> Ra (Bq/100 L) <sup>b</sup>
1	0.21	0.23	0.94	3.14	1.77	4.9 $\pm$ 0.5
3	0.63	0.24	1.07	3.39	1.77	4.3 $\pm$ 0.4
5	1.14	0.24	1.10	3.61	1.71	2.8 $\pm$ 0.3
7	1.85	0.26	1.16	3.64	1.38	2.2 $\pm$ 0.3
9	2.84	0.29	1.29	4.06	1.25	1.7 $\pm$ 0.2
11.5	4.06	0.29	1.33	4.18	1.11	1.0 $\pm$ 0.2
14.5	5.74	0.32	1.53	4.61	1.16	0.8 $\pm$ 0.1

<sup>a</sup> Mass depth is the density/cm depth.

<sup>b</sup> 1 Bq (1 disintegration/sec) corresponds to a <sup>226</sup>Ra concentration of  $\approx 1.2 \times 10^{-13}$  mol.

<sup>c</sup> Analytical errors ( $1\sigma$ ) are 5% for Mg and Ca, and 5–7% for Sr and Ba.

formation of vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ] in the sediments. Similar processes may apply to the Zürichsee sediments.

In Table II, we present the concentrations *vs.* depths of the AEE's in the interstitial water (pore water) of the sediment core collected in August 1991 (see above). The concentrations of Mg, Ca and Sr in the interstitial water were mutually strongly correlated ( $r = 0.99$ ) and increased with the sediment depth. This increase could result from the increasing sediment density with depth. On the other hand, the concentrations of Ba and <sup>226</sup>Ra decreased with the sediment depth and were anticorrelated to Sr ( $r = -0.89$ ), but correlated between themselves ( $r = 0.94$ ).

The concentration decrease of Ba and Ra with depth resembles somewhat that of Mn, but the correlations are rather weak (Mn/Ba:  $r = 0.64$ ; Mn/<sup>226</sup>Ra:  $r = 0.59$ ). The different slopes in the depth distribution of Ba and Ra may reflect a different adsorption behaviour of the two elements with respect to Mn (hydr)oxides. The decrease of the Ba and <sup>226</sup>Ra concentrations with the sediment depth is probably related to the manganese chemistry. When the redox potential decreases at the water/sediment interface due to oxidation of organic materials, a bacteria-mediated reduction<sup>26</sup> of Mn(IV/III) to Mn(II) is one of the first reactions to occur after the disappearance of oxygen.<sup>27</sup> This reduction takes place mainly in the uppermost sediment layers. From there Mn<sup>2+</sup> is released together with Ba and Ra into the interstitial water. <sup>226</sup>Ra is more strongly adsorbed by these materials than Ba, and therefore, more <sup>226</sup>Ra than Ba will be released to the interstitial water when Mn deposits are dissolved.

Concentrations of Mg, Ca, and Sr in the interstitial water are not much higher than their concentrations in the water column. In contrast, the concentrations of Ba and Ra are much higher (5 times for Ba, 33 times for Ra)

in the interstitial water than in the water column. These very large concentration gradients between the interstitial water and the lake water are the main reason for a significant diffusion of dissolved Ba and Ra species from the interstitial water of the sediments to the lake water. This mechanism explains the observed high Ba and  $^{226}\text{Ra}$  concentrations at the bottom of Zürichsee.

### *Sediment Core*

Concentrations of the AEE's in the solid phase of the sediment core of August 1991 (see above) are presented in Table III. The depth distribution of the concentrations of Mg, Ca and Sr was relatively uniform (mean of 7 values: Mg,  $6.3 \pm 0.9$  mg/g sediment; Ca,  $242 \pm 27$  mg/g; Sr,  $386 \pm 36$   $\mu\text{g/g}$ ). However, a clear concentration maximum is observed for Ca and Sr at about a 7 – 9 cm sediment depth. The 7 cm depth corresponds roughly to the year 1964.<sup>17,19</sup> The increase of the Ca and Sr concentrations between 14.5 and  $\approx 7$  cm sediment depths is an effect of the increasing eutrophication of Zürichsee due to population growth and anthropogenic activities. Increased concentrations of nutrients led to a higher biogenic calcite production. Around 1964, the operation of sewage treatment plants started a period of improved water quality in Zürichsee (*i.e.*, less nutrients) with a smaller biogenic productivity and, thereby, a decrease in the Ca (and Sr) concentrations above the sediment depth of  $\approx 7$  cm.

The activity concentration of  $^{226}\text{Ra}$  (Table III) was at a maximum in the two top layers of the sediment core, then it decreased to a minimum at a 9 cm core depth, and increased further down. A similar specific activity was

TABLE III  
Concentrations of alkaline earth elements in sediments of Zürichsee  
(136 m depth, August 1991)

Depth cm	Mass depth <sup>a</sup> g cm <sup>-2</sup>	Mg (mg/g) <sup>b</sup>	Ca (mg/g) <sup>b</sup>	Sr ( $\mu\text{g/g}$ ) <sup>b</sup>	Ba ( $\mu\text{g/g}$ ) <sup>b</sup>	$^{226}\text{Ra}$ (mBq/g) <sup>b,c</sup>
1	0.21	5.9	228	358	244	$56.0 \pm 3.6$
3	0.63	7.3	228	380	264	$57.7 \pm 3.8$
5	1.14	7.1	247	432	266	$48.5 \pm 3.7$
7	1.85	7.0	256	415	273	$44.5 \pm 2.8$
9	2.84	5.2	286	417	188	$22.3 \pm 1.8$
11.5	4.06	6.4	245	363	195	$28.5 \pm 1.8$
14.5	5.74	5.2	201	336	254	$32.8 \pm 1.7$

<sup>a</sup> Mass depth is the density/cm depth.

<sup>b</sup> Per g of dry sediment.

<sup>c</sup> 1 mBq corresponds to a  $^{226}\text{Ra}$  concentration of  $\approx 1.2 \times 10^{-16}$  mol; 1 Bq = 1 disintegration/sec.

<sup>d</sup> Analytical errors ( $1\sigma$ ) are 5% for Mg and Ca, and 5–7% for Sr and Ba.

also found in samples from core depths  $> 15 \text{ g/cm}^2$ .<sup>18</sup> Concentrations of Ba showed, like these of  $^{226}\text{Ra}$ , also a minimum at a 9 cm core depth and were slightly correlated ( $r = 0.76$ ) with the latter.

Concentration changes of Ba and  $^{226}\text{Ra}$  in the sediment core (Table III) may reflect the changes in the water quality of Zürichsee before and after the installation of sewage treatment plants around 1964. The increasing eutrophication before that date led to a decrease in the redox potential at the bottom of the lake and an associated accelerated dissolution of Mn (hydr)oxides and Ba/ $^{226}\text{Ra}$ . Due to the operation of sewage treatment plants, smaller amounts of the Mn and related Ba/ $^{226}\text{Ra}$  compounds dissolved, resulting in higher concentrations of these elements in the upper sediment core (see also Figure 5).

Sequential leach experiments [*i.e.*, 24 hours exchange with 1 M NaCl at pH = 7.4, then 4 hours extraction in the dark with Tamm's<sup>28</sup> oxalic acid (10.9 g/L) / ammonium oxalate (16.1 g/L) to attack amorphous Fe/Mn (hydr)oxides, followed by a 24 hours treatment with 2 M NaOH / 0.05 M Na<sub>2</sub>EDTA]<sup>29,30</sup> performed with the sediment samples showed that  $\approx 20\%$  of  $^{226}\text{Ra}$  was present as ionic species (exchangeable),  $\approx 10\%$  was related to oxide phases,  $\approx 15\%$  was found in the Na<sub>2</sub>EDTA extract, and the rest remained in the solid residue [dissolved with acids (see experimental)].

Even though the results of sequential leach experiments may depend on the chosen conditions and do not, therefore, unambiguously represent reality in nature, our data indicate that about half of the  $^{226}\text{Ra}$  of the solid sediments is available to dissolution by ion exchange, reduction of (hydr)oxidic Fe/Mn phases and/or decomposition of organic matter. Ion exchange and redox reactions are very common in the environmental chemistry and have been thoroughly documented by Werner Stumm and James J. Morgan.<sup>27</sup> These processes can be used to explain the high concentrations of  $^{226}\text{Ra}$  in the interstitial water of the lake sediments of Zürichsee (see above).

The data for the AEE's in the interstitial water and in the solid phase of lake sediments (Tables II and III) confirm the general geochemical behaviour of these elements. For instance, the behaviour of Sr is different from that of Ba and Ra. Sr<sup>2+</sup> can, for instance, be incorporated into calcite nodules,<sup>15</sup> whereas the ionic radii of Ba<sup>2+</sup> and Ra<sup>2+</sup> are too large for a substitution of Ca<sup>2+</sup> in the crystal lattice.

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## SAŽETAK

**Radij-226 i elementi alkalijskih zemalja u vodenom stupcu, intersticijskoj vodi i sedimentima jezera Zürich (Švicarska)**

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Raspodjela elemenata iz grupe alkalijskih zemalja – Mg, Ca, Sr, Ba i  $^{226}\text{Ra}$  istraživana je u vodenom stupcu i sedimentima (u krutoj fazi i intersticijskoj vodi) jezera Zürich u Švicarskoj. S izuzetkom Ra, koncentracije alkalijskih zemalja pokazuju uglavnom jednakomjeran raspored u vodenom stupcu i ne pokazuju sezonske varijacije. Naši rezultati pretpostavljaju uklanjanje Ra iz vodenog stupca tijekom zime, vjerojatno kao posljedice sorpcijskih efekata u periodu zamjene vodene mase u jezeru. Nadalje, pri stagnaciji jezera tijekom ljeta, koncentracije Ra (te u nešto manjoj mjeri Ba) rastu u pridnenom dijelu vodenog stupca. Držimo da je porast koncentracija ovih elemenata tijekom razdoblja stagnacije jezera posljedica njihova otpuštanja iz sedimenata, zajedno sa Mn, kad se poveća anoksija intersticijskih voda. Te su intersticijske vode obogaćene radijem i barijem. Njihove koncentracije u krutoj fazi sedimenata smanjuju se s porastom dubine sedimenta i pokazuju raspodjelu sličnu onoj mangana.