The determination of Pb-210 and Ra-226 in lake sediments and dating applications by M. Farid A.F. El-Daoushy Institute of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden

Abstra 7.
The natural radioactive isotopes Pb-210 and Ra-226 were measured in two sediment cores. The Pb-210 was determined by α- detection of its grand-daughter product Po-210, using the isotope dilution technique and a surface barrier detector. Some technical improvements in the polonium extraction were achieved. The radon emanation technique was used for the determination of Ra-226. The α-activity of Rn-222 was measured using an ionization chamber with an improved filling system, which allows both low level measurements and counter calibration with standard active samples. The memory effect due to adsorption of Rn-222 on the counter walls is studied.

The accumulation rates are calculated from the unsupported Pb-210. The results from one core, Gillfjärden, are in good agreement with some studies of the reservoir effect using C-14. The data from the other core, Lake Växjösjön, indicated an irregularity in the Pb-210 profile. Results from other studies on Lake Växjösjön showed a similar propensity.
Introduction

General — Ra-226 which belongs to the naturally occurring U-238 decay series gives rise to Rn-222, which escapes from the ground surface of the land at an average rate of 42 atoms/min/cm² (Israel, 1951) into the atmosphere. Radon concentrations vary by a factor of a hundred or more between the ocean bodies and land areas (Junge, 1963).

The Rn-222 (3.8 d) remains in the atmosphere until it decays through a series of short-lived daughters to Pb-210 which, despite its long half-life (22.26±0.22 yrs), does not fuse uniformly with the atmosphere because of its short period of residence. Poet et al. (1972) and Rangarajan et al. (1975) estimated a mean atmospheric residence of about one week. The seasonal variations in activity of the short-lived radon daughters and Pb-210 in the surface air are mainly due to the seasonal changes in the stability of the atmospheric surface air (Gopalakrishnan, 1970). No significant change in the source and composition of the air mass in areas like Moscow and Finland (Rangarajan et al., 1975) were observed.

After this short residence, Pb-210 is first locally scavenged either by dry fallout or precipitation, then merges into the geochemical and biological cycles taking place in lakes, oceans and soils. This part of Pb-210 which permeates the atmosphere is called unsupported Pb-210.

Persson (1970, 1974), who studied the deposition of Pb-210 on the lichen-moors of northern Sweden in 1961-1969 and Central Sweden in 1961-1972, estimated a value of about 1.7±0.3 nCi/m² y. He stated that he found a systematic error due to Pb-210 which is produced from the Ra-226 content in the lichen. He claims that this error is negligible because Pb-210 takes some 80 years to reach radioactive equilibrium with Ra-226. Ramzaev et al. (1969) and Blanchard & Moore (1970) estimated that the Ra-226/Pb-210 activity ratio in lichens
is only about 0.01-0.08. Results from northern and southern Finland concerning Po-210 and Pb-210 in the arctic food chain of the Lapps (Kauranen and Miettinen, 1969) are in good agreement with those from Sweden.

Pb-210 is also derived from the Ra-226 (1620 yrs) which either originally exists in the soils, rocks and waters (ground water, standing water and streams) or is introduced (as well as its daughter Rn-222) into soil and water reservoirs through geochemical, geophysical or biochemical processes such as solubility, ionic exchange, chemical precipitation or coprecipitation, leaching, oxidation/reduction, scavenging by particulates, weathering, drainage and biological activities of organisms. This part of Pb-210 is called supported Pb-210. Supported Pb-210 may or may not be in secular equilibrium with Ra-226.

Studies of Pb-210 and Ra-226 in different reservoirs yield some important results. Pb-210 is sequestered by organic material and rapidly homogenized within organic rich layers of soils (Lewis, 1977). Lewis estimated a mean residence of 2000 yr for metals similar to Pb-210 in soil profiles, and also indicated that stream sediments directly reflect the metal content of soils. In addition, Lewis found that iron and manganese hydroxides cause Pb-210 to be rapidly scavenged from water river systems onto suspended particles. Megumi and Mamuro (1977) found that the concentrations of uranium series nuclides increase with the decrease in particle size for a soil particle size below 0.15 mm.

Moore and Poet (1976) who found that Pb-210/Ra-226 activity ratios in different surface soil profiles are generally greater than unity, but decrease with depth to less than unity, claimed that the activity ratios would undoubtedly increase to unity at greater depths, where the Ra-226, Rn-222 and Pb-210 reach equilibrium. They refer to Eakins' and
Morrison's calculation that the depth at which Pb-210/Ra-226 activity ratio becomes unity is 128 yrs for an undisturbed sediment.

Lead-210 dating and applications — The Pb-210 dating method was originally introduced by Goldberg (1962).

Picciotto et al. (1968) used Pb-210 for determination of the rate of snow accumulation at the pole of relative inaccessibility (eastern Antarctic plateau). In environments polluted by Pb injection from combustion of leaded gasoline (in internal combustion engines) the Pb-210 dating method is hazardous (Picciotto, private communication 1976). Crozaz (1967) showed that in polar regions the névé (taken in the Antarctic, in Greenland and on an alpine glacier) behaves as a closed system from the moment of precipitation, and the accumulation rates deduced from the Pb-210 method are in excellent agreement with those of other methods.

Petit (1974) studied the stable lead content and the lead isotopic composition in sediment cores from a small Belgian pond and used Pb-210 to construct a time scale. He found that the stable lead content steeply increases with decreasing depth, whereas the lead isotopic composition becomes progressively less radiogenic (the Pb-210 activities were normalized for the decay since the time of deposition). The lead isotopic composition of the top sediment was identical to that in the atmosphere. Krishnawamy et al. (1971) described some successful attempts to use radiometric techniques which included Fe-55 (2.7 yrs), Cs-137 (30 yrs), Si-32 (>300 yrs) and Pb-210 to date lake sediments. Cs-137 and Fe-55 are derived primarily from testing of nuclear weapons, while Si-32 is produced naturally through the interaction of cosmic rays with atmospheric argon.
Pennington et al. (1976) reviewed the dating methods of recent sediments and included results from Blelham Tarn which is a small lake near Windermere.

Nozaki et al. (1976) examined two sediment cores from the Mid-Atlantic Ridge. Both cores were taken at a depth of about 2500 m, for the top sediment layers of one core, they obtained C-14 ages which were constant and earlier than expected. This was attributed to biogenic mixing, and the mixing coefficient at the surface was calculated from the Pb-210 pattern. The data for the second core indicated physical disruption of the section.

Krishnawamy et al. (1975) also studied Pb-210/Ra-226 disequilibrium in the Santa Barbara Basin, and concluded that the fate of lead (and Pb-210) is rigidly controlled by the settling particles.

Robbins and Edgington (1975) determined the sedimentation rates in Lake Michigan using Pb-210 and Cs-137. They concluded that Pb-210 dating is a major technique for establishing the age of recently deposited sediments in the Great Lakes, and their results are in agreement with those derived from more laborious and less exact methods. Their Pb-210 profiles were normalized for sediment compaction. They also found secular equilibrium between supported Pb-210 and Ra-226 in about two-thirds of the stations studied. They used Cs-137 to check the recovery of the uppermost levels of the sediment cores as suggested by Koide et al. (1973), since they claim that there is a possibility of losing the top portions of the sediment in normal coring devices. Robbins et al. (1977) correlated the post-depositional redistribution in the Great Lakes (as indicated from Pb-210 and Cs-137 profiles) with deposit-feeding organisms such as benthic macro-invertebrates (oligochaetes and amphipods) which are present in the top layers.
Oldfield et al. (1978) examined some Pb-210 (unsupported) profiles from Lough Erne, Northern Ireland and Lake Ipea, Papua New Guinea. These Pb-210 profiles were "kinked" and showed that the concentration of the unsupported Pb-210 increases markedly with depth, such a character being inconsistent with the basic dating assumption of constant initial concentration (c.i.c.) of the unsupported Pb-210 per unit dry weight in the sediment cores at each depth. Moreover the profiles, as judged from results of other studies, have not been significantly disturbed. Oldfield et al. explained that a dilution of unsupported Pb-210 occurred by accelerated sediment accumulation. They further adopted an alternative approach for Pb-210 dating, assuming a constant rate of supply (c.r.s.), and used the integrated Pb-210 activity for deriving dates. They tested the validity of the alternative approach by making use of the presence of some synchronous events in the sediment cores as a scale of reference. They concluded that both the c.i.c. and c.r.s. models will give identical results, and possibly reliable dates, in cases where the accumulation rates have been constant.

Koide et al. (1973) discussed Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. They found that reducing environments can alter the distribution of lead isotopes and thus limit the Pb-210 geochronologies, while the immobility of thorium isotopes in the deposits makes the Th-228/Th-232 technique of special value. Koide et al. (1976) further applied the Ra-226 chronology in coastal marine sediments.

Chemical treatment of samples

Determination of Pb-210

General — Several chemical methods were used, which are practically based on either \( \beta \)-detection of Bi-210 (the daughter product of Pb-210) or \( \alpha \)-detection of Po-210 (the grand-daughter product of Pb-210). The latter technique (the isotopic dilution)
which includes an internal yield tracer, shows many advantages over the former (Eakins and Morrison, 1976). Eakins et al. (1976), who checked the mobility of polonium in one core, found it to be non-existent. The Po-210 was extracted according to a procedure which is essentially developed by Eakins and Morrison (1976), but with further modifications. Figure 1, gives a short description of the chemical treatment, the details being given in Appendix I.

Technique used — A quartz extraction apparatus, Fig. 2, was used. The quartz allows the extraction to be carried out at a higher temperature than could be attained using glass ware. Complete recovery of the organic material from the sediment is achieved at such temperatures.

The thin polonium α-source for the spectral analysis was prepared using the self-deposition cell, Fig. 3. The principles of the process are defined by Flynn (1968).

The glass ware was invariably washed with conc. HNO₃, which effectively removed any remains from the chemical treatment of sediment samples. All the chemicals used apart from the nitric acid (used for washing) are of analytical grade and the water is doubly distilled.

**Determination of Ra-226**

General — Two methods are in current use, namely isotopic dilution (Koide and Bruland, 1975) and radon emanation (Lucas (1957), Högberg and Gustavsson (1973), Li et al. (1977)).

Technique used — Ra-226 is separated as chloride (melts at 1000°C) from the sediment residue after polonium distillation using a barium carrier.

The details of the chemical treatment for Ra-226 are also given in Appendix I.
Dry grounded sediment.

Carefully add conc. HCl
until no CO₂ or H₂S is evolved.

Add 3–10 pCi Po-208 spike and
10 mg Ba-carrier for each 1 g dry
sediment. Stir for complete blending
of the mixture.

Dry at 110°C overnight.

Distill at 550–600°C for ~20 min,
use the quartz distillation apparatus.

Treat the residual sediment
with conc. HCl until no
H₂S is evolved.

Dry at 110°C overnight

Extract the radium,
barium, and other metallic
chlorides, using hot, double-
distilled water and ultra-sonic
agitation. Filter into the radon
bottle.

Further extract with double-
distilled water and ultra-sonic
agitation. Filter into the radon
bottle.

Wash any remains by shaking in
double-distilled water. Filter
to the radon bottle.

Clean the conical joint and
glass valves of the bottle.
Grease them.

Remove any trapped Ra-gas
and fill the bottle with N₂.
Close the valves and store
the bottle.

Condense the polonium vapour
and the organic material on wet-
ted glass wool in a quartz tube.

Treat the condensed material
with conc. HNO₃ under reflux.
Complete oxidation of the organic
condensation is recommended.

Allow the extract to cool and
filter using a glass funnel,
porosity 2.

Treat the filtrate with conc. HCl
until complete removal of HNO₃.
Never let the solution dry.

Allow the final solution to cool
(~10°C) and filter to the assembled
deposition cell with its silver disk.

Adjust the final normality of the
solution to 1.5–2 N and the total
volume to ~40 ml.

Plate the silver disk at
85–90°C for ~3 hr.

Disassemble the deposition
cell and wash the silver disk
with acetone, ethylated alcohol
and double-distilled water.
Dry with IR-lamp.

Fig. 1. A short description of the chemical treatment.
Fig. 2. The quartz extraction apparatus. \( Q_2 T_2 \) is a quartz tube equipped with a conical joint, used for handling the sediment. \( Q_1 T_1 \) is also a quartz tube but both ends have conical joints. One end is fitted to \( Q_2 T_2 \), and the other to a conical joint of a glass tube \( GT \), which is connected to some outlet. \( Q_1 T_1 \) serves as a trap for the evolved vapors which pass through the wetted glass-wool plug, \( GW \). During the distillation of the polonium chloride, \( Q_2 T_2 \) and \( Q_1 F \) are placed in a furnace at 600\(^\circ\)C.
Fig. 3. FJ is a flat joint, "Quickfit FG25". A1 is an aluminium base supporting the silver disk S. The aluminium base and the silver disk fit into a teflon flange, T. The teflon flange allows the glass/metal joint to be a waterproof seal, once the cell units are screwed tight using the teflon-tipped screws Q and the aluminium cramps A2.
Preliminary tests showed that radium is strongly adsorbed on glass ware unless a suitable amount of Ba-carrier is added.

Four bottles which contained a standard Ra-226 solution (0.01 μg Ra-226 and 0.07 mg Ba-carrier) were used, partly for calibration of the ionization chamber (during a seven-month period) and partly to estimate the amount of the barium required as a carrier for the radium separation. After a seven months in storage, the bottles were washed five times with tap water and a further five times with distilled water (radium chloride is soluble in both cold and hot water). About 45±5 % of the initial Ra-226 activity still remained in each bottle, indicating that the amount of Ba-carrier was not sufficient. The amount of Ba-carrier was increased to 2 mg for each 1 pCi Ra-226, this amount sufficing for complete recovery of radium. The use of barium as a carrier allows not only a complete radium extraction from the sediment residue but also prepares the bottles for background routine work.

Up to 92±2 % of the remaining Ra-226 activity in the bottles is removed when the recommended chemical procedure, Appendix II, is used.

**Activity measurements**

The thin α-sources are mounted externally, and then introduced to the counting chamber, Fig. 4. The details of the electronics used, together with the silicon surface barrier detector, are given in Fig. 5. A resolution of 25 to 45 keV, for the Po-208 peak (5.114 MeV) which is well differentiated from the Po-210 peak (5.305 MeV), is a partial consequence of the chemical treatment.

An ionization chamber (Högberg and Gustavsson, 1973) is used for the measurement of the Rn-222 activity. The extracted Ra-226 sample is stored in a glass bottle (gas washing bottle, equipped with a glass filter) for a known period, then the emanated
Fig. 4. The counting chamber. CH1 is the chamber body. H is a horizontally moving rod which transports the sample after external mounting into the chamber, while F1 and F2 are used to guide the rod into a predetermined position. The sample can be moved vertically by means of square-threaded screw, V2/V3, which is connected by the screw, I1, with a handle, V1. The square-threaded screw is fixed to the chamber body by a sheath, V4 and the screws I2. HV supports the aluminium tray with the plated silver disk. D is the surface barrier detector, which is shielded by a pure copper shield P. The detector D is connected to its electronic system by a vacuum feedthrough M (BNC to Microdot, ORTEC-C13). The copper shield, P, is screwed to the chamber cover, CH2. The chamber is made vacuum-tight with the help of viton O-rings R1, R2, R3, R4, R5, R6, R7, R8, R9 and R10. The parts of the chamber are screwed together, with the screws I3, I4 and I5. The chamber is held in position by insulated bakelite legs L2. T1-T2 is a copper tube for cooling the detector.
Fig. 5. A schematic diagram of the electronics used with the silicon surface barrier detector.
Rn-222 is swept to the chamber by a nitrogen gas. The filling system is improved to allow not only low level counting but also calibration of the chamber by standard Ra-226 samples, the details of the modifications being given in Fig. 6.

Results and discussion

The ionization chamber

Efficiency — The efficiency of the counter, including the filling system, was determined using a Ra-226 standard (Amersham). A value of 1.33±0.05 was obtained, with application of a chamber voltage of 3000 V, and a discriminator level somewhat higher than that used by Högberg and Gustavsson (1973). The uncertainties in all the physical measurements are included in the final uncertainty. The Rn-222 needs about three hours to reach secular equilibrium with the daughters Po-214 and Po-218. No determination of the individual efficiencies was made.

Slope of the plateau — Since the ionization chamber is fairly sensitive to electro-negative impurities, special care is taken during the counter filling. For a pure Rn/N₂ sample, the slope of the plateau is 0.001%/100 V (Fig. 7).

Background — The background of the ionization chamber (Högberg and Gustavsson, 1973) was studied from June 77 onwards. It was first determined as 2.2 cpm with a long term variation of about 0.7 cpm. This variation was attributed to mechanical vibrations of the ionization chamber and its tube electronical system. However, recent experiments show that the Rn-222 undergoes adsorption to the counter walls. Taking this factor into consideration the value of the background is determined as 2.35±0.15 cpm. Li et al. (1977) improved the reproducibility of their counting chamber by using quartz material instead of perspex. About 0.15% of the standard activity is adsorbed in the course of c. four hours. In one
Fig. 6. The gas-washing bottle (sample bottle) used for the collection of the emanated Rn together with the modified filling system.
BOTTLE 300/341, Ra-STANDARD, MEASURED ON 77-09-28.
- BOTTLE 300/341, Ra-STANDARD, MEASURED ON 78-03-08.
• BOTTLE 282/397, Ra-STANDARD, MEASURED ON 78-03-09.
× BOTTLE 165/279, Ra-STANDARD, MEASURED ON 78-03-11.
○ BOTTLE 288/251, Ra-STANDARD, MEASURED ON 78-03-12.

Fig. 7. Characteristics of the used ionization chamber. The Ra-226 standard in each bottle is 8.0±0.3 nCi. The discriminator level was changed slightly on October 14th, 1977. The Ca-furnace was charged with fresh calcium on March 8th, 1978. The furnace was the baked at 350°C until the degassing ceased.
experiment the adsorbed activity needed about three days for recovery (to about 98%) from the counter surfaces, even if the counter was refilled three times. The results from another experiment are given in Fig. 8.

**The surface barrier detector**

Efficiency — The efficiency of the detector is estimated to be 1.16\% when the distance between the sample and the detector is ~4 mm. The detector has an effective surface area of 450 mm$^2$, while that of the sample is ~40C mm$^2$. The Po-208 sample was supplied by Eakins and, according to him, checked against standardized material (private communication, 1977).

Background and blank runs — In the preliminary tests of the detector and the electronics, a Po-210 source was used which contaminated the detector. The contamination was so low as to allow the measurement to be carried out, but corrections for the background are needed. Table 1 and Fig. 9 summarize the background history of the detector, and also provide information on the blank runs and the spikes. Background runs 1 and 2 show that the background is almost exclusively due to the active polonium diffused in the thin gold front electrode of the detector. The level of the background is partly a function of the radiation dose received by the detector. Poet et al. (1972) used different detectors to measure samples with high and low activities in order to minimize the difficulty arising from the contamination of the detector from recoiled polonium atoms and volatility of some Po-atoms. The blank runs 10 and 11 show the suitability of the chemicals used, and indicate the absence of memory effects on the quartz and the glass ware when well washed. Blank 1 and blank 2 refer to two different runs, which were carried out using two different sets of glass ware, together with two different quartz extraction apparatus. Runs 3 and 12 show the purity of two different spikes, namely spike 1 (supplied by Eakins) and spike 2 (prepared in Finland). Appendix III gives some information on
Fig. 8. The recovery of the adsorbed Rn-222 from the counter walls, accompanied by a change in the counting efficiency from $2\pi$ to $4\pi$. At time zero the standard was in secular equilibrium (about three hours after charging the ionization chamber with the standard), one hour later the standard was pumped out and the ionization chamber charged with pure nitrogen.
Table 1. A summary of a) The background of the used Si-detector. b) The blank runs of the glass ware, quartz and the used chemicals. c) spike purity.

<table>
<thead>
<tr>
<th>Date</th>
<th>Run No.</th>
<th>Specification</th>
<th>Electronic Settings</th>
<th>Integrated counting rate, cpm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Po-208 peak</td>
</tr>
<tr>
<td>77-08-16</td>
<td>1</td>
<td>Background *</td>
<td>A.G. 170, L.L.D. 2.5% C.G. 1024 channels</td>
<td>0.078±0.009</td>
</tr>
<tr>
<td>77-08-18</td>
<td>2</td>
<td>Background *</td>
<td></td>
<td>0.079±0.009</td>
</tr>
<tr>
<td>77-10-27</td>
<td>3</td>
<td>Background + 4.7 pCi Po-208, spike No. 2</td>
<td>A.G. 250, L.L.D. 7% C.G. 1024 channels</td>
<td></td>
</tr>
<tr>
<td>77-10-25</td>
<td>4</td>
<td>Background</td>
<td></td>
<td>0.067±0.003</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Background</td>
<td>A.G. 250, L.L.D. 7% C.G. 256 channels</td>
<td>0.049±0.005</td>
</tr>
<tr>
<td>77-12-12</td>
<td>6</td>
<td>Background + blank + 3.2 pCi Po-208, spike No. 1</td>
<td></td>
<td>1.020±0.020</td>
</tr>
<tr>
<td>78-01-06</td>
<td>7</td>
<td>Background + blank + 20 mg Ba-carrier</td>
<td></td>
<td>0.270±0.012</td>
</tr>
<tr>
<td>78-01-08</td>
<td>8</td>
<td>Background</td>
<td></td>
<td>0.053±0.005</td>
</tr>
<tr>
<td>78-02-06</td>
<td>9</td>
<td>Background</td>
<td></td>
<td>0.042±0.003</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Background + blank 1</td>
<td></td>
<td>0.051±0.004</td>
</tr>
<tr>
<td>78-02-12</td>
<td>11</td>
<td>Background + blank 2</td>
<td></td>
<td>0.053±0.004</td>
</tr>
<tr>
<td>78-02-15</td>
<td>12</td>
<td>Background + 4.7 pCi Po-208, spike No. 1</td>
<td></td>
<td>0.680±0.020</td>
</tr>
</tbody>
</table>

a) Sample holder is 50 cm away from the detector surface. All other runs are carried out at a distance of approximately 4 cm between the sample holder and the detector surface.

b) The copper shielding tube of the detector is cleaned by acid.

A.G. = amplifier gain, L.L.D. = low level discriminator, C.G. = conversion gain.
Fig. 9. Illustrates the summary given in Table 1.
spike 1 and spike 2. Figure 10 shows a spectrum of spike 1. Blank runs 6 and 7 demonstrate memory effects of inefficient washing of the glass ware. Background runs 5 and 8 indicate a decaying activity with the expected half-life for Po-210. There seems to be a tendency to stability of the background (value) at the beginning of February 1978, which implies that the activity registered by the detector compensates the decay.

The Gillfjärden sample — A sediment core from Gillfjärden was originally collected for the study of the reservoir effect, using C-14 as a tracer.

The Po-210 was extracted according to the chemical treatment given in appendix I. The samples were dried at 110±2°C, and it was difficult to grind them. No Ba-carrier was used for the extraction of radium, but the final radium extracts were filtered directly to the gas-washing bottles for the radon collection. The metallic contaminants in the sediment may have acted as carriers. Thus the received radium content may be considered as a lower limit. Table 2 gives a summary of the total Pb-210 activity in the measured slices. Figure 11 shows a spectrum of the Po-210 and Po-208 separated from a slice.

The preliminary results of the unsupported Pb-210 profile are given in Fig. 12. The estimated accumulation rate is \( \leq 1.35 \text{ cm/yr} \). This value is in good agreement with the studies made by Olsson and Ingmar (in preparation).

The Lake Växjösjön samples — This core was collected by Digerfeldt using two different samplers. The upper part of the core, from zero to 70 cm depth was collected with one and the same sampler, while the lower part, deeper than 70 cm, was collected with another one.
I  Po-208 SPIKE (10 ml), 78-02-15.
II  BLANK 1, 78-02-10.
COUNTING TIME IS 10 ksec.

Fig. 10. A spectrum from the spike 1 (4.7 pCi).
Table 2

Total lead-210 activity, measured in Oct./Nov. 77 in a sediment core from Gillfjärden. The core was originally sampled (April 1971) for a determination of the carbon-14 apparent age of the top sediment. The activities are given with 1σ uncertainty. The uncertainty includes not only the statistical uncertainty due to the counting rates (the total counting rate and the background counting rate) but also the errors in the physical measurements such as the sediment weight, the amount of spike used and the decay of the spike.

<table>
<thead>
<tr>
<th>No.</th>
<th>Depth, cm</th>
<th>Total Pb-210 activity&lt;sup&gt;a)&lt;/sup&gt;, dpm/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5-9.0&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>18.8±0.6&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>7.5-9.0</td>
<td>17.5±0.3</td>
</tr>
<tr>
<td>3</td>
<td>10.5-12.0</td>
<td>13.4±0.3</td>
</tr>
<tr>
<td>4</td>
<td>12.0-13.5</td>
<td>12.8±0.3</td>
</tr>
<tr>
<td>5</td>
<td>13.5-15.0</td>
<td>12.6±0.2</td>
</tr>
<tr>
<td>6</td>
<td>15.0-21.0</td>
<td>12.1±0.2</td>
</tr>
<tr>
<td>7</td>
<td>21.5-23.0</td>
<td>11.5±0.2</td>
</tr>
</tbody>
</table>

<sup>a)</sup> Preliminary measurements of radium-226 indicate that the supported Pb-210 activity is at least 5.5±0.4 dpm/g. Radium-226 extraction was carried out without Ba-carrier.

<sup>b)</sup> The sample is measured in July 77 at a lower discriminator level. The activity is normalized for the Pb-210 decay but not for the discriminator level.
Fig. 11. A spectrum of Po-208 and Po-210 separated from the graphite core.

COUNTING RATE PER CHANNEL

CHANNEL NUMBER

COUNT TIME IS 4 KSEC.

II BACKGROUND 77-12-02.

I GILFRACTEN 15-21.5 CM SPiked with Po-208 77-11-14.
SEDIMENT CORE FROM GILLFJÄRDEN

SAMPLE No.1 (table 2).

PRELIMINARY ESTIMATED ACCUMULATION RATE \leq 1.35 \text{cm/yr.}

Fig. 12. The accumulation rate in the Gillfjärden core.
The total Pb-210 in some slices is given in Table 3. All the slices were treated according to the chemical procedure given in appendix I. The time for the nitric-acid treatment (step No. 10 in the chemical treatment) is also given in Table 3. The prolonged period of treatment with nitric acid does not appear to affect the Po-210 yield. One hour, or even less, is sufficient. Figures 13, 14, 15 and 16 illustrate various Po-210 and Po-208 spectra obtained from the polonium extracts of some slices. The influence of some metallic contaminations on the final spectrum is seen in Fig. 16. The total Pb-210 is given in Fig. 17, and the Ra-226 content in Table 4. An irregularity is seen in the profile.

The unsupported Pb-210 in the investigated slices of the core is given in Table 5. The calculated sedimentation rate is given in Fig. 18, using the least square fitting. A value of 0.82±0.03 cm/yr was obtained, based on the measured Ra-content at three levels, and the weighted average content for the others, while the uncertainty increases to ±0.10 if a common value, the weighted average, for the Ra-content is used. The Ra-226 activity of the deepest slice is so low that a disturbance may be suspected; consequently the accumulation rate was calculated with and without this slice and a mean value chosen yielding a value 0.80±0.10 cm/yr.

Conclusions — The present study shows that adsorption is a serious problem and precautions should be considered to avoid the risks of memory effects. The results of the Pb-210 dating method are promising, especially if the amount of the supported Pb-210 is carefully determined in the different parts of the investigated cores.
Table 3

Total lead-210 activity (dpm/g) in the sediment core A, from Lake Växjösjön collected June 76, and measured in Dec. 77/Jan. 78. The time for the nitric-acid treatment (step No.10 in the chemical treatment) of each sediment slice is also given. The activities are given with 1σ uncertainty, which is only due to the uncertainty in the counting rates (total counting rate and background counting rate), since the incidence of other physical uncertainties in weight, amount of spike etc. falls below 10%.

<table>
<thead>
<tr>
<th>No.</th>
<th>Depth, cm</th>
<th>Total Pb-210 activity, dpm/g</th>
<th>Treatment time with HNO₃, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5-10</td>
<td>20.75±0.30</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>10-15</td>
<td>21.15±0.20</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>15-20</td>
<td>22.60±0.40</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>20-25</td>
<td>18.70±0.20</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>25-30</td>
<td>18.10±0.20</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>30-35</td>
<td>15.85±0.25</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>40-45</td>
<td>14.30±0.20</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>60-65</td>
<td>10.40±0.20</td>
<td>18</td>
</tr>
<tr>
<td>9a)</td>
<td>60-65</td>
<td>12.70±0.45a)</td>
<td>21a)</td>
</tr>
<tr>
<td>10</td>
<td>80-85</td>
<td>8.25±0.15</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>100-105</td>
<td>6.30±0.10</td>
<td>5.5</td>
</tr>
<tr>
<td>12</td>
<td>115-120</td>
<td>7.00±0.15</td>
<td>4.5</td>
</tr>
<tr>
<td>13</td>
<td>130-135</td>
<td>5.25±0.10</td>
<td>12</td>
</tr>
<tr>
<td>14</td>
<td>150-155</td>
<td>3.55±0.10</td>
<td>1</td>
</tr>
</tbody>
</table>

a) The solution was contaminated by metallic iron during its evaporation (step No.12 in the chemical treatment).
Fig. 13. A spectrum of Po-208 and Po-210 separated from the Lake Växjösjön core.
Fig. 14. A spectrum of Po-208 and Po-210 separated from the Lake Växjösjön core.
Fig. 15. A spectrum of PO-208 and PO-210 separated from the Lake Vrksjöbron core.

Counting rate per channel

Channel number

Counting time is 4 ksec.

I Background, 77-12-03

1 Vrksjöbron 150-155 cm spiked with PO-208, 77-12-05.
Fig. 16. The influence of metallic contamination on the spectrum of Po-208 and Po-210 separated from Lake Växjösjön. The metallic contaminant was introduced during the chemical treatment (step No. 12).
**Fig. 17. The total Pb-210 profile in Lake Växjösjön.**
Table 4

The radium-226 activity (dpm/g) in some slices of the sediment core A, from Lake Växjösjön, collected in June 76 and measured in Dec. 77/Jan. 78. The activities are given with 1σ uncertainty, which includes the uncertainties in the counting rates (total counting rate and blank counting rate) and the uncertainty in the efficiency of the counting system.

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>Ra-226 activity, dpm/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-65a)</td>
<td>1.45±0.15a)</td>
</tr>
<tr>
<td>40-45</td>
<td>7.60±0.30</td>
</tr>
<tr>
<td>60-65</td>
<td>7.80±0.30</td>
</tr>
<tr>
<td>80-85</td>
<td>7.00±0.25</td>
</tr>
</tbody>
</table>

a) No Ba-carrier was used in the chemical extraction of the radium. The extracted radium solution was first stored in a glass bottle for about one month, and then transferred to the glass-bottle for the radon collection.

b) Weighted average, assuming that the radium content is constant in the sediment core A.

c) Arithmetic average value of the radium content in the sediment core A.
Table 5

Unsupported lead-210 activity (dpm/g) in the sediment core A, from Lake Växjösjön collected in June 76 and measured in Dec. 77/Jan. 78. The activities are given with 1σ uncertainty.

<table>
<thead>
<tr>
<th>No.</th>
<th>Depth, cm</th>
<th>Unsupported Pb-210 activity, dpm/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>using the weighted average</td>
</tr>
<tr>
<td>1</td>
<td>5-10</td>
<td>13.35±0.35</td>
</tr>
<tr>
<td>2</td>
<td>10-15</td>
<td>13.75±0.25</td>
</tr>
<tr>
<td>3</td>
<td>15-20</td>
<td>15.20±0.45</td>
</tr>
<tr>
<td>4</td>
<td>20-25</td>
<td>11.30±0.25</td>
</tr>
<tr>
<td>5</td>
<td>25-30</td>
<td>10.70±0.25</td>
</tr>
<tr>
<td>6</td>
<td>30-35</td>
<td>8.45±0.30</td>
</tr>
<tr>
<td>7</td>
<td>40-45</td>
<td>6.90±0.25</td>
</tr>
<tr>
<td>8</td>
<td>60-65</td>
<td>3.00±0.25</td>
</tr>
<tr>
<td>10</td>
<td>80-85</td>
<td>0.85±0.20</td>
</tr>
<tr>
<td>11</td>
<td>100-105</td>
<td>-1.10±0.20</td>
</tr>
<tr>
<td>12</td>
<td>115-120</td>
<td>-0.40±0.20</td>
</tr>
<tr>
<td>13</td>
<td>130-135</td>
<td>-2.15±0.20</td>
</tr>
<tr>
<td>14</td>
<td>150-155</td>
<td>-3.85±0.20</td>
</tr>
</tbody>
</table>
LAKE VÄXJÖSJÖN, CORE A.

+ CALCULATED USING THE WEIGHTED AVERAGE FOR Ra-226.
+ CALCULATED USING THE MEASURED VALUE FOR Ra-226 AT THE ACTUAL LEVEL.

Fig. 18. The accumulation rate in the Lake Växjösjön.
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Appendix I

Chemical treatment of sediment samples for polonium and radium separation:

1) Freeze-dry the sediment. Further drying at 110°C overnight.

2) Grind to a fine powder. This step is fairly difficult unless the sample is freeze dried to give a rather fine powder. Freeze-drying is a recommended laboratory routine. (Cato, 1977).

3) Weigh a suitable aliquot (1 to 4 g) in quartz tube Q,T2 (avoid adhesion of sediment grains to the conical joint), add 2 to 4 ml distilled water and 5 to 15 ml conc. HCl. Cease addition of HCl when the evolution of the gases ends. CO₂ and H₂S are likely to be evolved.

4) For each gramme of dried sediment sample, add a suitable amount 3 to 10 pCi of polonium-208 spike, then add 10 mg Ba-carrier. The polonium spike is stored in 5.5 N HCl solution to avoid adsorption to the walls of the glass container, since polonium is known to be strongly adsorbed on glassware. Stir with a glass rod for complete mixing. Remove any sediment from the glass rod by washing with a little distilled water. The conical joint of the quartz tube should always be washed and kept clean from possible sediment.

5) Let the mixture dry at 110°C overnight. Carefully examine the conical joint of the quartz tube. It should be free from any dried material, otherwise wash and allow to dry at 110°C. However, it is essential to prevent the final mixture from reaching the conical joint.

6) Remove quartz tube Q,T2 from the oven and allow to cool. Insert a suitable plug of a wetted glass wool into the mid-section of the tube Q,T1 (the glass wool should not be dripping wet — if so: wring out any excess water).

7) Assemble the polonium distillation apparatus in a horizontal position Fig. 2. No water should drip onto the quartz tube Q,T2. The distillation time depends on the temperature.
On average the sediment samples are left for about 20 min at 550-600°C. Ten min is sufficient to allow the sediment sample to heat.

8) Remove the distillation apparatus from the oven horizontally. Allow the distillation apparatus to cool to room temperature and meanwhile disconnect at GT. Watch carefully to prevent possible flow back of liquid drops from the tube Q1T1 to the tube Q2T2.

9) Detach the quartz tubes Q1T1 and Q2T2.

10) Carefully remove the glass wool, and place it together with the quartz tube Q1T1 in a 3-1 beaker, add ~150 ml conc. HNO3, cover with a watch glass. Boil under reflux on a hot plate until the organic condensation on the glass wool and/or the walls of the quartz tube Q1T1 disappears (complete oxidation of the accompanying organic extract). Agitate intermittently to stir the glass wool and promote acid circulation. A period of one hour is sufficient for complete oxidation. Strong boiling should be avoided.

11) Cool and wash the quartz tube Q1T1 with distilled water, then remove it. Decant the liquid through a glass filter funnel (No. 2 porosity) into a 400-ml beaker. Wash away any extract from the glass wool, stir to allow for some circulation, decant again. The filtrate together with the washings are kept in the 400-ml beaker.

12) Evaporate the filtrate and the collected washings to ~5 ml.

13) Add carefully ~20 ml conc. HCl (evolution of some oxides of nitrogen with a characteristic red colour) and evaporate to ~3 ml but never to dryness. Elimination of any remaining HNO3 is necessary for proper deposition (step 17). Further treatment with 2 to 4 ml conc. HCl is recommended. Evaporate to ~3 ml but never allow to dry. Gentle heating is required to avoid loss of polonium. Polonium, which is a low melting metal (254°C), becomes volatile even at moderate temperatures — already at 55°C about 50% of polonium evaporates in air in 45 hours (Handbook of
Chemistry and Physics, 55th edition B-25). Eakins studied the volatility of polonium chloride and polonium nitrate and found that the recovery of the chloride is quantitative above 330°C, whereas about 2% of the nitrate recovers even at 800°C. Most organic and inorganic polonium compounds are either volatile or sublime at temperatures well below 900°C, but some of them decompose. PoCl₂ sublimes at 190°C while PoCl₄ melts at 300°C (in Cl atm.) and boils at 390°C.

14) Add ~5 ml HCl (5-6 N) and cool to ~10°C.
15) Polish the silver disk with a fine grade emery paper, wash with acetone, ethylated spirit and finally with distilled water.
16) Assemble the deposition cell and filter the acidic polonium solution into it. Wash the residue in the beaker with some 2 N HCl. The final volume is about 40 ml, and the final normality 1.5-2 N. Use distilled water to adjust the final normality. Flynn reported that for most effective deposition, the normality of the final hydrochloric acid solution should be 1 to 2 N, while the best yield for self-deposition was obtained by plating for 3 hrs in a water bath at 85-90°C with continuous stirring by air bubbling.
17) Plate at 85-90°C for ~3 hrs with continuous stirring by air bubbling.
18) Disassemble the deposition cell. Wash the silver disk with acetone, ethylated spirit and distilled water. Dry carefully using an infra-red lamp.
19) An aluminium tray is used to hold the plated silver disk and introduce it into the counting chamber.
20) Add ~10 ml conc. HCl to the residual sediment in the quartz tube Q₂T₂. Allow to dry over night. Check complete reaction of the residual sediment with HCl by the cessation of the evolved H₂S.
21) Pre-soak the bulk sediment material with ~40 ml warm double-distilled H₂O, and break it up gently using a rod. Immerse in the ultra-sonic bath for ~2 min. at ~50°C for complete dissolution of the chlorides by agitation on the treated sediment particles. Filter using a membrane filter in a well cleaned gas-washing bottle for radon collection (Rn-bottle).
22) Add 40 ml double distilled water and treat again for ~2 min in the ultra-sonic bath (at room temperature), filter into the Rn-bottle.

23) Finally wash with 20 ml double-distilled water. Shake for complete cleaning of the sediment grains.

24) Carefully clean the conical joint and the glass valves of the bottle and regrease them with Apiezon grease, type L.

25) With the valves open, warm the bottle container and then allow a slow N₂ stream to bubble through the liquid for ~2 minutes.

26) Close the valves and store the bottle to collect the radon.
Appendix II

The chemical procedure used for the recovery of the adsorbed radium-226 from the glass surfaces of the radon collection bottle:

1) Slow and gentle etching of the glass surfaces by rinsing with 37% HCl for about three days, while the bottles which were not highly contaminated were rinsed with 5.5 N HCl.

2) Cleansing of the acidic solution with normal tap water. Radium chloride is known to be soluble in both cold and hot water, and slightly soluble in HCl.

3) A second rinse with 37% HCl. The solution is boiled gently, with suitable thermal agitation, for about five hours.

4) Final agitation in an ultra-sonic bath (usually for 2 wk). Wash with ~50 ml Ba-solution (10 mg Ba/ml sol.).

5) A rinse with 100 ml Ba-solution, and gentle boiling for about one day.

6) Washing with ~50 ml Ba-solution, followed by agitation in ultra-sonic bath.

7) Immersion in 100 ml Ba-solution overnight. Removal of the solution.
Appendix III

Information on the Po-208 spikes.
Spike 1: prepared from natural lead which has been irradiated with He-3 ions. At the end of the irradiation there are ~0.5% Po-209 and ~10% Po-210 (Amersham, private communication, 1977) in the Po-208 produced.
Spike 2: prepared from natural Bi-209 which is bombarded with 19 MeV protons. The Po-208 contains ~0.12% Po-209 and 0.52% Po-210. These values were calculated on the following data:

A) Bi-209 (p,2n) Po-208 with $\sigma = 0.7$ barns at 19 MeV.\(^a\)
B) Bi-209 (p,n) Po-209 with $\sigma = 0.03$ barns at 19 MeV.\(^b\)
C) Bi-209 (p,\gamma) Po-210 with $\sigma = 0.00047$ barns at 19 MeV.\(^c\)
D) $t_{1/2}$ (Po-210) 0.38 yr.
$t_{1/2}$ (Po-208) 2.93 yrs.
$t_{1/2}$ (Po-209) 103.0 yrs.

a) and b) according to Jackson, 1956.
c) according to Cohen, 1955.

Preliminary measurements of spike 2 are in good agreement with the given calculated values.