LIQUID SCINTILLATION COUNTING MEASUREMENTS OF RADON FROM SEEPAGE GROUNDWATER IN LAKE BIWA, JAPAN

KIMIKO HORIUCHI[1], *TADASHI ISHII*[2] *and MASAO KOBAYASHI*[3]

ABSTRACT. We used toluene extraction and the integral counting technique of liquid scintillation counting (LSC) to determine radon concentrations in lake water and radium concentrations in lake-bed sediments from Lake Biwa in central Japan. We find the integral counting technique not only very sensitive to these applications, but it also yields absolute concentrations of Rn. The lower detection level of Rn was 18.5×10^{-3} Bq liter^{-1} (5×10^{-13} Ci liter^{-1}) (Horiuchi & Murakami 1977, 1978). Using a seepage meter (Lee 1977), Kobayashi (1984) established that seepage groundwater enters Lake Biwa through the lake bed. We determined Rn concentrations for *ca.* 2 yr in seepage groundwater from Lake Biwa, and in nearby mineral springs. We also determined Ra levels in the lake-bed sediment and calculated the contribution to Rn levels from this source. We observed wide spatial and seasonal variations in Rn concentrations and seepage flux in Lake Biwa. Based on the local geology of a specific sampling station, we conclude that high Rn concentrations and seasonal variations are associated with seepage flux into the lake through a permeable sandy gravel stratum (Horiuchi & Murakami 1986). This demonstrates the potential usefulness of our method in geological investigations.

INTRODUCTION

Lake Biwa, located in Shiga Prefecture in the middle of Honshu, Japan, is the largest freshwater lake in Japan and one of the oldest lakes in the world. It supplies ~275×10^8 tons of drinking water for >20 million people, and provides water for industry in the Kansai (Osaka/Kyoto) area, one of the most industrialized areas in Japan. The lake yields many marine products, including pearl culture, ranking second in this category among the Japanese lakes. Lake Biwa is also a major resort. Because of the obvious economic importance of this lake, it is important to understand all factors, such as groundwater seepage, that affect the mineral balance and quality of the water. Using seepage meters, we directly measured groundwater seepage from the bottom of the lake (Kobayashi 1985a,b). We previously developed a method for determining Rn in natural water by extracting toluene and applying integral counting using a liquid scintillation (LS) counter. Here, we discuss our method for determining Rn in water samples obtained from Lake Biwa using a modification of Lee's (1977) seepage meter.

METHODS

We selected 34 sampling stations around Lake Biwa, 21 stations on the western shore and 13 stations on the eastern shore, based on well-known geological history (Fig. 1). Previous surveys had established these stations as sites where seepage water enters the lake. Geological formations at each station were mostly gravel, sand and clay alluvium, except in a few northern points where Paleozoic rocks dominate. We constructed two types of seepage meters and installed them at 1-m depth at the stations. One type is a drum similar to Lee's (1977) meter, consisting of a top section (15–20 cm long) of a 55-gal oil drum with the lower end removed. Another is a box (50 × 50 × 15 cm) made by cutting thin (2-mm thick) metal boards. Then four perforated metal boards were attached on each side of the meter to prevent its sinking into soft and loose sediment. We inserted the meter, open end down, into the sediment until its top was ~5 cm above the sediment surface. The top hole was then fitted with a one-hole rubber bung covered with screened nylon mesh to allow ventilation, and left in place until measurement began. The collection bag, an evacuated 4-

[1]School of Social Information Studies, Otsuma Women's University, Karakida Tama, Tokyo 206 Japan
[2]Radioisotope Laboratory, Yamanashi Medical College, Tamaho-machi, Yamanashi Prefecture 409-38 Japan
[3]Division of Natural Science, Osaka Kyoiku University, Asahigaoka, Kashiwara, Osaka 582 Japan

Liquid Scintillation Spectrometry 1992, edited by
J. E. Noakes, F. Schönhofer and H. A. Polach. RADIOCARBON *1993, pp. 383–390*

liter polyethene bag, was fitted with a 0.9-cm ID stopcock and was attached by means of a rubber bung. The stopcock was then opened and the bag allowed to fill with water. After *ca.* 1 h, the stopcock was closed and the bag removed. The water volume in the bag was measured and the seepage flux (μm sec^{-1}) was calculated from the volume (cm^3), duration time (sec) and the covered area (0.25–0.255 m^2) of the meters. All meters were left in place throughout most of the study.

To determine the Rn concentration of groundwater seepage, water samples were collected two weeks later as the lake water trapped in the meter had almost flushed out, in *ca.* 10 days. This is the reason that 100–500 times the volume of water in the meter above the sediment surface was ventilated and the electric conductivity (EC) of the water trapped in the meter was different from that of lake water. After a certain time, depending on the seepage flux at a particular location, the stopcock was closed and the bag removed. We needed 1 liter of water to yield enough radioactivity for analysis.

A toluene solution (40 ml) of scintillant (PPO 4 g $liter^{-1}$, POPOP 0.1 g $liter^{-1}$) (TS) was added to 1 liter of lake water in a polyethene bottle, which was sealed and shaken for at least 1 min to allow Rn to equilibrate among TS, water and air. The temperature of the contents was measured with a thermometer. After allowing the layers to separate, 20 ml of the toluene extract was transferred from the bottle to a counting vial. The radioactivity was then determined using a Packard 3320 LS counter applying an integral counting technique, which allows us to determine Rn and calculate its concentration in the original sample of seepage water.

The aqueous layer from the original toluene extraction was purged with nitrogen to remove any remaining traces of Rn and a 40-ml aliquot of TS was added. The mixture was allowed to stand in a tightly sealed glass bottle for 10–30 days, during which the water and toluene phases separated. LSC of the toluene extract yielded the Rn content that originated from the Ra present in the original sample (Horiuchi & Murakami 1981). Thus, we can calculate the Ra concentration of the original lake-water sample.

Samples of lake-bed sediment (Ø = 3 cm) were collected with plastic or steel pipes at 10–100 cm depth. The samples were allowed to dry and were exposed to the atmosphere. The dried samples were thoroughly mixed and large stones and other large particles removed. Representative samples (5–7 g) were dissolved in HCL (0.1 M; 50 ml). The HCL solution containing extracted Ra was filtered and the acid solution added to water to give a total volume of 1 liter; 40 ml TS was added to the 1-liter acid solution and, after mixing, the sample was prepared for Ra determination by LSC as described above. EC measurements were made by standard methods using a Yokokawa Electric Company SC 51 conductivity meter.

RESULTS AND DISCUSSION

Figure 1 illustrates the geology of the area around Lake Biwa. The lakeshore is largely alluvium except in the northern reaches and west central shore where Palaeozoic sediments and granite outcrops. The western lakeshore is mountainous, whereas the eastern shore is planar. In much of the western region, especially the central area, groundwater is unconfined, whereas in the eastern region, it is largely confined. Figure 1 also shows the sampling stations and Rn concentrations. The highest Rn levels, 100–200 (× 0.37 Bq $liter^{-1}$), were found on the western shore, adjacent to the steeply sloping granitic region. Little variation in Rn concentrations was observed along the eastern shore, 0–30 (× 0.37 Bq $liter^{-1}$). To determine the amount of observed Rn produced from Ra in the lake bed sediment, we collected sediment samples from seven stations, and carried out Ra determinations on each sample. Table 1 shows the results. We also calculated the Rn concentration

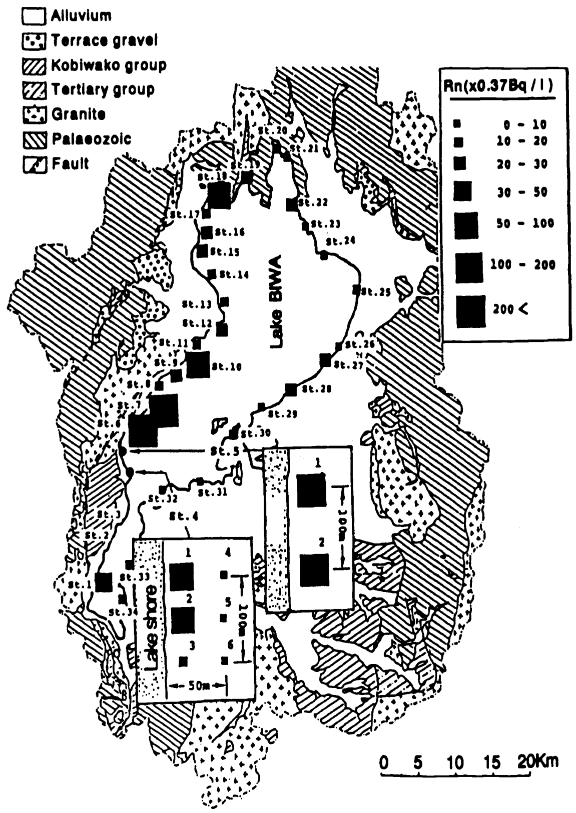

Fig. 1. ^{222}Rn concentration in seepage water at the bottom of the Lake Biwa; ■ = graduated sizes represent increasing levels of concentration.

TABLE 1. Calculation of ^{222}Rn Buildup From ^{226}Ra in Lake Bottom Soil*

Sample no. (Sta.)	^{226}Ra** (1×10^{-3} Bq liter^{-1})	Time† (min)	^{226}Rn (Cal)‡ (Bq)	^{222}Rn (Exp)§ (Bq liter^{-1})
4	4.1 ± 1.1	93.8	0.30	2.70 ± 0.04
5	8.9 ± 1.1	46.9	0.30	8.88 ± 0.08
8	8.1 ± 1.1	480.7	3.15	0.26 ± 0.04
12	5.2 ± 1.1	581.4	2.41	3.44 ± 0.04
13	5.9 ± 1.9	655.7	3.11	0.48 ± 0.04
17	5.9 ± 1.9	76.4	0.37	0.37 ± 0.04
18	4.8 ± 0.7	86.3	0.30	2.52 ± 0.04

* Seepage meter cross-section: 2500 cm^2; soil density: 2.65 g cm^{-3}
** ^{226}Rn concentration in 1 g soil of lake bottom
† Time (min) for collection of 1-liter seepage groundwater
‡ ^{222}Rn in buildup from ^{226}Ra in soil 1 cm from the surface in time t (calculated)
§ ^{222}Rn in seepage water

expected from the amount of Ra present at each site. We compared these experimental results with the Rn concentrations. In three cases, at Stations 4, 5 and 18, the measured Rn concentrations were *ca.* 10–20 times greater than the calculated levels, which at Stations 8 and 13, were very similar to those actually measured at these locations. In contrast, the concentrations found at Sites 8 and

13 were about 10% the calculated levels (Table 1). These results suggest that a source of Rn, other than Ra in the lake sediment, contributes to the levels observed at Stations 4 and 5. The reasons why lower-than-expected Rn concentrations were found at Stations 8 and 13 are unknown. However, we do know that Rn buildup from sediment Ra did not dissolve in the water that passed through the sediment. We chose Stations 4 and 5 for more detailed studies to identify the source of the high Rn concentrations observed at these sites. Station 5 was chosen because of the steep incline into the lake and associated high seepage flux. The lake-bed sediment at Station 5 did not contain high levels of organic material. Station 4 was chosen because it was adjacent to Station 5, the slope of lake bed was gentle and the average seepage flux was only about one-third of that at Station 5. In addition, the sediment at Station 4 contained considerable organic material.

In the first study, we determined the variation in Rn concentrations at Stations 4 and 5 over a 2-yr period (summer 1983 to winter 1985). Figure 2 shows the results. We also determined the variation of seepage flux at Stations 4 and 5 over the 2-yr period, using the seepage meter previously described. Figure 2 shows variations in seepage flux, along with precipitation levels and overall lake-water levels for the same period.

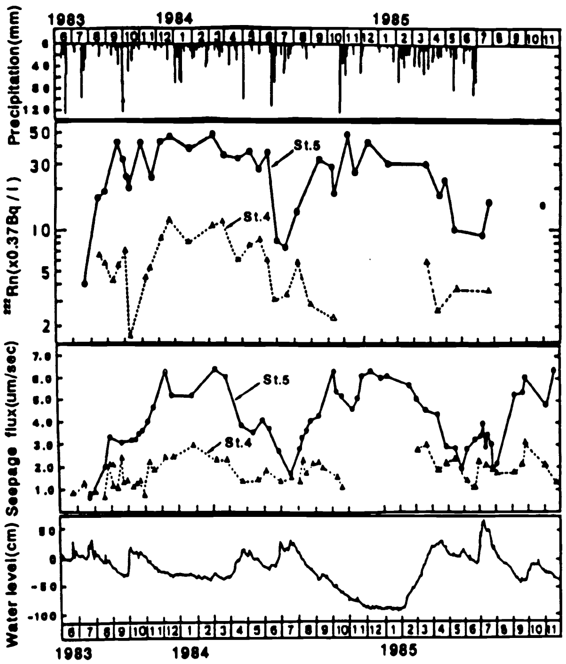

Fig. 2. Seasonal variation of Rn concentration in seepage water, seepage flux and precipitation at Station 5

Concentrations of Rn at Station 5 were generally much higher than those at Station 4. We observed wide seasonal variations in Rn concentration at both sites. At Station 5, the concentrations were generally lower in summer compared to winter, suggesting a cyclical trend. To some extent, the same pattern can be observed at Station 4 where data were available. During the last few months of 1984, however, the water level of Lake Biwa fell considerably, as shown in Figure 2. Consequently, the meter used at Station 4 was exposed, and data could not be obtained at this Station until early 1985, when the water rose to a sufficient level to cover the meter again. Figure 2 compares seepage flux measured over the same 2-yr period at Stations 4 and 5. The seepage flux at Station 5 was generally higher than that at Station 4. We observed considerable variations in seepage flux at Station 5 during the study period. Seepage flux was lower in summer than in winter;

there appears to be a similar cyclic trend in variation of Rn concentration. Smaller variations in seepage flux observed at Station 4 appear to follow a broadly similar trend.

We conducted another series of experiments in which we also measured Rn concentrations in water taken from the surface of Lake Biwa directly above each of our sampling meters at Stations 4 and 5, respectively (Fig. 3). The Rn concentration in surface water at Station 4 showed very little seasonal variation during the two years, whereas the surface water at Station 5 showed considerable variation. Although many other factors, such as currents, temperature and lake level will contribute to the distribution of Rn concentrations in surface water, it is clear from Figure 3 that Rn concentrations in surface water from Station 5 were much higher than at Station 4 throughout the study.

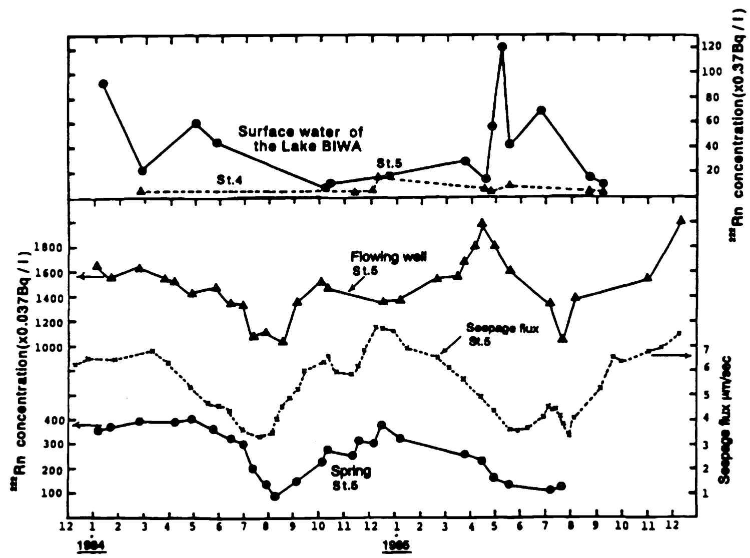

Fig. 3. Seasonal Rn variation in flowing well, seepage water, lake water and seepage flux (Station 5)

We also determined Rn concentrations in water from a flowing well in the area of Station 5 that had the same source as the seepage water entering the lake. The results in Figure 3 are compared with seepage flux and Rn concentrations in seepage water at Station 5. Rn concentrations in seepage water correlate well with those of seepage flux at Station 5, especially during the first 1.5 yr of the study. The variation in Rn concentration measured in flowing well water also seems to follow a similar pattern over the first year. A sharp rise in Rn concentration observed in the flowing well water during the spring of 1985, in the the second year of the study, is not reflected in a rise in concentration in seepage water, which actually decreases, as does seepage flux during the same period.

In a different study, we determined the Rn concentrations, seepage flux and EC as a function of distance from the lakeshore at Station 5 (Fig. 4); we placed 14 seepage meters 5–45 m from the lakeshore to measure these quantities. Figure 4 shows the positions of the seepage meters, the variations in Rn concentration, seepage flux and EC. An increase in Rn concentration was observed 30–35 m from the shoreline with little variation at 20–30 m. Seepage flux followed a broadly similar pattern with an increase over the same distance. EC showed a sharp decrease between 25

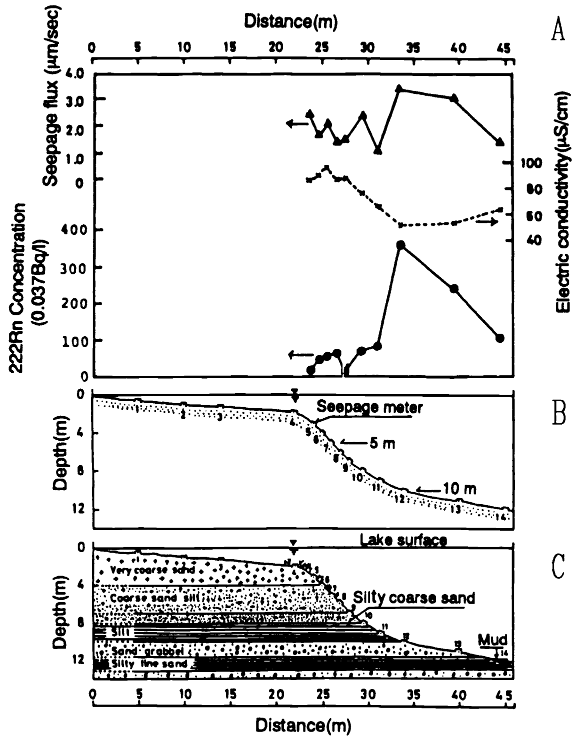

Fig. 4. A. Variation of Rn concentration, EC and seepage flux in seepage water. B. Seepage meter setting places tranced perpendicular to the shoreline of Station 5. C. Stratum profile of Station 5

and 35 m, in contrast to the increased Rn concentrations observed over the same area. A repeat study carried out one year later at the same site gave the same result, with high Rn concentrations beyond 30 m from the shoreline, again correlated with high seepage flux and reduced EC. On the basis of stratigraphy of Station 5 (Fig. 4), we deduce that seepage water entered the lake through the permeable sand gravel at ~10–12 m below the lake surface. Groundwater of this stratum is known to have low EC, and thus lends weight to the hypothesis that high Rn concentrations are associated with high seepage flux of groundwater into the lake.

To explore this further, we determined Rn concentrations and also EC in natural water originating from flowing springs (in the vicinity of Station 5), rivers (flowing into Lake Biwa) and lake water (from different Stations around Lake Biwa). Table 2 shows our results. Where possible, we collected multiple samples for each water type, for varying intervals. Rn concentrations were highest in the flowing springs (9–104 Bq liter^{-1}), lower in river water (0.1–9 Bq liter^{-1}) and lowest in lake water (0–5 Bq liter^{-1}) (Table 2).

Although there is considerable overlap in ranges of EC measured in the three types of water, the range from spring water (50–88 μS cm^{-1}) is lower than the range for lake samples (73–102 μS cm^{-1}). The range of ECs in river water (36–114 μS cm^{-1}) encompasses those for spring and lake water. Although attempts to correlate Rn concentration with EC must be treated with caution due to many contributing factors, we have observed that high Rn concentration is associated with reduced EC, at least for spring and lake waters. We also measured the Rn concentrations and ECs of lake and seepage water along the western shore of the lake (Table 3). Lower Rn concentrations (0.07–10 Bq liter^{-1}) at Station 4 are associated with higher ECs (103–254 μS cm^{-1}), whereas higher Rn concentrations (0.5–20 Bq liter^{-1}) at Station 5 are associated with lower EC values.

TABLE 2. One-Year Results from Lakeside Flowing, Spring, River and Lake Waters

Sampling site	Date	No.	Water temp. (°C)	EC (μS cm^{-1})	Rn(Bq liter^{-1})
Flowing, spring					
Kitazawa. F.	85.1.12–86.2.18	14	13.4	53–64	39.4–81.8
Kitazawa S.	85.1.12–86.2.18	14	13.0	50–66	26.3–71.5
Kido F.	85.1.12–85.10.31	10	14.1	57–62	50.2–103.9
Suizinmae S.	85.2.18–85.10.31	11	12.7–15.4	74–88	22.8–76.7
Nakata S.	85.1.12–85.7.20	9	11.4–15.2	55–70	30.3–47.8
Lake saide H.S.	85.10.31	1	13.1	51	94.8
Sugie F.	85.12.12	1	14.3	59	64.2
Nakamura S.	85.12.12	1	6.6	58	26.5
Sawai S.	85.3.15	1	13.5	110	12.9
Harie F.	85.12.12	1	14.2	77	9.36
River					
Ado	85.12.12	1	9.0	100	7.25
Sta. 5 R-1	85.3.15–85.7.20	7	8.9–21.8	36–70	0.02–0.3
Sta. 5 R-2	84.10.12	3	13.8–16.4	80–114	7.22–8.58
Wani	84.10.12	1	19.2	86	0.15
Lake water (west)					
Sta. 4	85.3.15–85.11.1	7	8.8–30.8	86–96	0.19–0.27
Sta. 5	5.2.18–86.2.18	10	5.6–27.3	73–92	0.35–4.48
Sta. 7	84.11.7	1	17.8	89	1.39
Lake water (east)					
Sta. 30	84.10.31	1	16.0	89	0.04
Sta. 32	84.10.31	1	17.0	102	0.24

TABLE 3. Rn Concentrations in Seepage Groundwater and Lake Water

Station no.	Determination no.	EC μS cm^{-1}	Rn (Bq liter^{-1})
Seepage water			
Sta. 4 SM – 1	24	110–245	0.48–4.44
2	28	103–273	0.07–10.10
5 SM – 1	37	78–91	1.52–17.98
2	19	79–84	0.48–19.54
9	6	86–100	0.74–1.78
10	6	91–103	0.02–2.33
11	6	87–192	0.02–0.81
13	6	88–96	0.32–0.59
Lake water			
Sta. 4	14	84–102	0.02–0.53
5	9	73–94	0.19–4.48
7	2	89	1.41

The sediment from Station 4 contains more organic material than Station 5. However, a summary of all statistics (excluding Station 4, which shows anomalously high conductivity) shows Rn concentrations of 0–20 Bq liter^{-1} seepage and surface water samples (0–5 Bq liter^{-1}) have similar ECs, in the ranges 78–91 μS cm^{-1} (seepage) and 73–102 μS cm^{-1} (surface water). Interpretation of these data is difficult; it does not seem possible to correlate high Rn concentration with low EC in this study, as we had hoped. Fellows and Brezonik (1980) measured seepage flux as a function of distance from the shoreline of two lakes in Florida, and concluded not contribute Rn significantly to the lake water beyond 30 m from the shoreline. In contrast, we observed a considerable increase in seepage flux between 30 and 45 m from the shore in Lake Biwa, which was associated with increased Rn concentration. This may merely reflect local geological differences at the different lakes.

Conclusions

Our samples represent the true influx of Rn into Lake Biwa because seepage water entering the lake is allowed to equilibrate in the sampling meter. The technique described for measuring Rn concentrations is sensitive enough to allow such determinations at other sites. We have been able to determine groundwater seepage Rn concentrations in seepage water from the lake bed, and to establish a correlation between high Rn concentration in seepage water and high seepage water flux with seasonal variations. Variations are cyclical, generally high in winter and low in summer. We have also applied our method to determining Ra concentrations in lake-bed sediment, and we calculated the amount of Rn in seepage water that arose from Ra in sediment. We also attempted to establish a link between Rn concentration and EC. Although high Rn concentrations may be associated with low EC, we could not establish an unequivocal link. However, we can conclude that, at one site, Station 5, seepage water enters the lake through a permeable sandy gravel stratum at 10–12 m below the lake surface, and at about 30–35 m from the lakeshore. This demonstrates the potential usefulness of our method in hydrogeological investigations.

References

Fellows, C. R. and Brezonik, P. L. 1980 Seepage flow into Florida lakes. *Water Resources Bulletin* 16: 635–641.

Horiuchi, K. and Murakami, Y. 1977 Basic studies on the new determination method of radon in mineral springs with a liquid scintillation counter *Journal of the Balneological Society of Japan* 28: 39–47 (in Japanese).

_____1978 Some remarks on the new determination method of Rn in hot springs by extraction liquid scintillation counting. *Journal of the Society of Engineers for Mineral Springs, Japan* 13: 95–103 (in Japanese).

_____1981 A new procedure for the determination of radium in water by extraction of radon and application of integral counting with a liquid scintillation counter. *International Journal of Applied Radiation and Isotopes.* 32(5): 291–294.

Horiuchi, K. and Murakami, Y. 1986 Lake-shore groundwater seepage is characterized by its radon concentration, at Lake Biwa. *Environmental Science, Report of Research* B289–R12–2: 91–106 (in Japanese).

Kobayashi, M. 1984 Groundwater seepage into Lake Biwa. *Environmental Science, Report of Research* B225–R12–2: 89–97, 107–117 (in Japanese).

_____1985a Some aspects on the groundwater seepage from the bottom of Lake Biwa observed at Matsunoura Beach. *Hydrology* 15(1): 33–41 (in Japanese).

_____1985b Groundwater seepage into Lake Biwa. *Environmental Science, Report of Research* B262–R-12–2: 93–103 (in Japanese).

Lee, D. R., 1977 A device for measuring seepage flux in lakes and estuaries. *Limnology and Oceanography* 22(1): 140–147.