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Seasonal Variation in the Accumulation of Radionuclides of the Uranium Series by Yellow Pond-Lily (*Nuphar lutea*)

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The aquatic environment is very sensitive to the pertubations which may accompany the mining of metals. Slight alterations in the loading of chemicals in freshwater systems are frequently reflected in large changes in the transfer of contaminants to aquatic species because of the potential for bioconcentration. Bioconcentration of radionuclides by the biota is a source of interest to both environmental scientists and regulatory agencies, since aquatic plants may be potential indicators for aquatic pollution and could also be significant sources of contaminants for herbivorous wildlife near mines and mine tailings systems.

The discovery of a significant uranium orebody in a region encompassing many small lakes in the Okanagan region of south-central British Columbia permitted the assessment of seasonal uptake of naturally occuring radionuclides of the uranium series by aquatic plants.

The objectives of this study were to assess the potential for bioconcentration of naturally occuring radionuclides in yellow pond-lily (Nuphar lutea subspecies polysepala (Engelmann) Beal),and to determine if seasonal variation in accumulation occured.

MATERIALS AND METHODS

Water, plant and lake sediment samples were collected from an area of high natural radioactivity in the Okanagan Highlands of south-central British Columbia . Surface water samples were acidified to 1% HNO_3 at the time of collection; subsequently they were filtered through a 0.3 um filter and digested with perchloric acid prior to analysis. Sediment samples were collected by Ekman grab, and frozen at -20C until analysis. Pond-lily samples, consisting of floating leaves and petioles were collected by hand from water at least three meters deep,and then frozen at -20C. The leaf samples represented the current years growth, since in Nuphar lutea, the floating leaves are produced annually in late spring or early summer, and do not persist throughout the winter in systems where freezing occurs (HUTCHINSON 1975).

Plant tissue samples were ground in a Wiley mill to pass through a -10 mesh. A portion of this material was dry ashed at 550C, digested in fuming perchloric acid and analysed for U_{nat}, ^{210}Pb and ^{226}Ra. A second portion of the material was wet digested in fuming perchloric acid and analysed for ^{210}Po.

Sediment samples were dried by forced air draught at 60C, and sieved through a -10 mesh. The material was weighed, compressed into a disc and analysed by gamma spectroscopy. The spectroscope used a Ge(Li) detector with a resolution of 1.95 Kev at 1.33 Mev, a peak to Compton ratio of 45:1 with an efficiency of 17%. Peaks were analysed with a multichannel analyser (Ortec Model 044, Ortec Ltd., Ontario), with a 100 MHz 4K ADC live time clock, data storage system (Plessy Model PM-DD/11B, Plessy Ltd, Scarborough Ontario) with hard cartridge discs and computer analysis system (DEC Model PDP 11/34, Digital Equipment Corp., Chicago, Ill.).

Of the naturally occuring radioisotopes of uranium, ^{238}U has a natural abundance of 99.28%, therefore only the decay products of this isotope were considered in the analysis. In the analysis there is no differentiation between uranium isotopes, so uranium content is referred to as U_{nat}. Of the decay products, only those with a long enough halflife compared to the growing season of the plants are considered, namely ^{226}Ra, ^{210}Pb and ^{210}Po.

Uranium was measured by fluorescence on a Turner Model 111 fluorimeter, with a detection limit of 0.05 ppb (A.S.T.M. 1973). ^{226}Ra was separated by coprecipitation with barium sulphate. The radium-barium sulphate was stored for one week to allow ingrowth of ^{222}Rn and daughters. The precipitate was analysed on a Canberra Model 220 alpha- beta analyser (A.P.H.A. 1975). ^{210}Pb was measured indirectly by measurement of the beta activity of the daughter ^{210}Bi, after allowing 30 days for equilibration. ^{210}Bi was extracted and counted as for ^{226}Ra, with a counting time of 100 min and a detection limit of 1 pCi/L. ^{210}Po was measured after electrodeposition on silver discs and alpha counting for 100 min, with a detection limit of 0.2 pCi/L (DOUGLAS 1967).

RESULTS AND DISCUSSION

The water chemistry of the seven sample sites during both seasons is presented in Table 1. The only significant change in water chemistry from spring to summer was the increased concentration of dissolved U_{nat} ($p > 0.5$) in the spring. There may also have been a slight increase in the ^{210}Po concentration, but this was not verifiable statistically. The pH of the water in several lakes did change with the season, but the mean values by season did not alter significantly. Both ^{226}Ra and ^{210}Pb stayed effectively below the limits of detection in the surface waters (Table 1).

Table 1. Seasonal water chemistry for surface waters in the sample study area. Mean$\pm$Std. dev., (n) = sample size.

Season	pH	U_{nat} mg/l	^{226}Ra pCi/g	^{210}Pb pCi/g	^{210}Po pCi/g
Spring (7)	6.88 ± 0.38	0.34 ± 0.11	<0.2	<0.5	<0.2
Summer (7)	6.90 ± 0.24	0.21 ± 0.11	<0.2	<1.0	0.32 ± 0.08

Radionuclide concentrations in the sediments from each location did not differ significantly ($p > 0.5$) by season, though there was seasonal variation at each sample location. These local variations probably reflect seasonal differences in the water table, surface run -off patterns and degree of saturation of the soil in the environs of the ore body (Table 2). Locations 2 and 3 are in direct communication with location 2 receiving drainage from the ore body, and draining

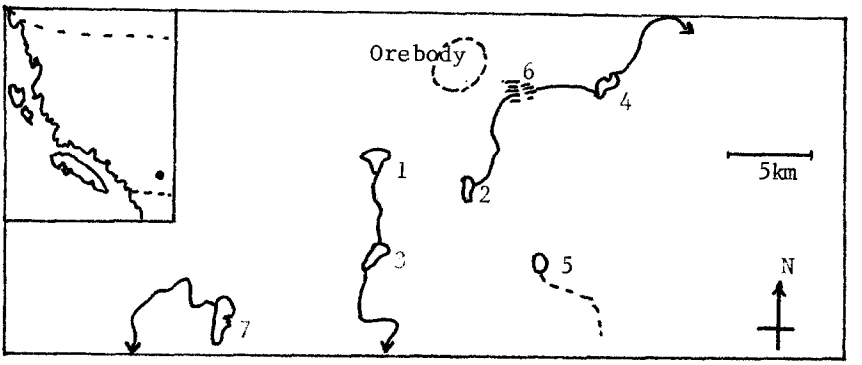

Fig.1. Location of the study area (inset), and the locations of the aquatic plant sampling sites, relative to the ore-body.

into location 3 via a creek (Fig. 1). Sample locations 1, 6 and 4 are also connected via another creek. Drainage of surface water, and possibly groundwater with high concentrations of dissolved U_{nat} off the ore body and into location 6, and then into location 4 can be seen in Fig. 1. Sample locations 5 and 7 have no direct surface water connection with the ore body. In five of the sample stations the surface water pH increases from spring to summer, (Stations 2,3,4,5,6). In spring there was a high negative correlation between pH and dissolved U_{nat} ($r = -0.67$), but no correlation between surface water pH and the sediment burden of U_{nat} ($r = 0.372$).

Table 2. Concentration of radionuclides of the U series in sediments, collected from aquatic plant sampling sites. Mean$\pm$Std. dev. (n) = sample size.

Season	U_{nat} ppm	^{226}Ra pCi/g	^{210}Pb pCi/g	^{210}Po pCi/g
Spring (7)	14.8 ± 4.28	2.2 ± 0.87	6.13 ± 2.79	4.7 ± 1.34
Summer (7)	13.8 ± 5.80	2.5 ± 1.4	6.38 ± 5.26	-

In autumn there was no correlation between the surface water pH and dissolved U_{nat} ($r = -0.28$), but a high negative correlation between surface water pH and sediment burden of U_{nat} ($r = -0.74$). The data indicate that as the pH rises the aquatic transport of U_{nat} decreases. U_{nat} apparently moves from the ore body in the spring and is accumulated in the sediments in the summer. The U_{nat} content of Nuphar displays a seasonal character, possibly due to two separate physiological processes. Nuphar accumulated

significantly ($p = 0.05$) higher levels of U_{nat} (on a weight basis) in spring (Table 3), with a high correlation between the U_{nat}

Table 3. Concentration of radionuclides of the U series in pond-lily (Nuphar lutea) by season. Mean±Std. dev., (n) = sample size

	Season	U_{nat} ppm	^{226}Ra pCi/g	^{210}Pb pCi/g	^{210}Po pCi/g
(5)	Spring	0.71±0.84	0.32±0.14	0.18±0.11	0.42±0.53
(7)	Summer	0.08±0.07	0.42±0.04	0.44±0.13	0.32±0.12

content of Nuphar and that of sediment ($r = -0.755$). There was no correlation between the Nuphar U_{nat} and that of surface waters ($r = 0.24$) or water pH ($r = -0.22$) (Table 4). In summer the reverse was true, with the Nuphar U_{nat} levels positively correlated with the surface water dissolved U_{nat} ($r = 0.85$), but not with either the sediment U_{nat} or with the pH (Table 4). In terrestrial plants, the accumulation of U_{nat} is positively correlated with the soil U_{nat} concentration (VAN NETTEN & MORELY 1982; MAHON & MATHEWES 1983). In considering the accumulation of U_{nat} in the summer, the high negative correlation with sediment U_{nat} disappeared and is replaced with a high positive correlation with the dissolved U_{nat} in surface water.

Table 4. Seasonal correlation between concentration of radionuclides of the U series in Nuphar lutea and sediment concentration, water concentration and water pH.

Season		Correlation with radionuclide content of Nuphar U_{nat}	^{226}Ra	^{210}Pb	^{210}Po
Spring	$Sediment_X$	-0.76	-0.52	-0.63	-0.43
	$Water_X$	0.24	-	-	-
	Water pH	-0.22	-0.81	0.45	-0.77
Summer	$Sediment_X$	0.41	0.23	-	0.56
	$Water_X$	0.85	-	-	-
	Water pH	-0.13	0.68	0.22	0.21

The ^{226}Ra content of the surface waters was consistantly below the detection limit of 0.2 pCi/L (Table 1). In the sediments ^{226}Ra averaged 2.3 pCi/g in both seasons, approximately the same as for soils in the region (MAHON & MATHEWES 1983), as was noted by TSIVOGLOU et al. (1967) for sediments and soils of the Animas River valley. There was a significant ($p = 0.05$) decrease in the ^{226}Ra content of Nuphar from spring to summer, paralleling that of U_{nat}, and of about the same relative magnitude. In contrast to the accumulation of U_{nat} there was a strong negative correlation between the pH of the surface waters in spring ($r = -0.81$), and a strong positive correlation in the summer ($r = 0.68$). As for U_{nat}, there was a significant negative correlation between the sediment ^{226}Ra and the Nuphar ^{226}Ra content in spring ($r = -0.52$), which disappeared in the summer. The data would suggest that there are two mechanisms in operation for the accumulation of dissolved metals by pond-lily, determined by the physiological state

of the plant. Early in spring when the plant is growing rapidly,

Table 5: Concentration factors (CF_x) for radionuclides from surface waters and sediments into Nuphar lutea. Mean±Std.dev., Range, (n)= sample size.

		CF_x Radionuclide			
		U_{nat}	^{226}Ra	^{210}Pb	^{210}Po
Water	Spring (5)	2052±2232	1590±677	352±210	2110±2634
		300-5250	900-2600	100-640	450±6750
	Summer (7)	377±196	240±187	512±292	1227±621
		180-733	50-500	120-620	575-2450
Sediment	Spring (5)	0.058±0.082	0.138±0.085	0.049±0.051	0.127±0.199
		0.005-0.20	0.062-0.274	0.006-0.133	0.022-0.482
	Summer (7)	0.006±0.004	0.023±0.023	0.089±0.038	-
		0.002-0.013	0.003-0.023	0.035-0.145	-

there appears to be a rapid accumulation of both U_{nat} and ^{226}Ra; but this is not controlled by the available radionuclide in either the surface water or sediment. It is probably a reflection of the active metabolic state of the plant.

It is also possible that there are two separate systems for the accumulation of each element, in that the accumulation of U_{nat} does not appear to be pH dependant during either season, over the pH range determined, whereas the accumulation of ^{226}Ra is strongly pH dependant during both seasons. The total reversal of pH dependancy for ^{226}Ra uptake is unusual if the small range of pH change is considered. Also the total range of pH change is similar during both seasons, yet with increasing pH in spring ^{226}Ra uptake decreases, but the reverse is true in summer. The ^{226}Ra content of the sediments and water did not change significantly during the sampling period, therefore, there is an undetermined factor in either the water chemistry or plant physiology.

Radium is an alkaline earth, and its behaviour, in general, mimics that of strontium and calcium. However, the close relationship between accumulation of calcium and strontium in aquatic plants, is not seen for calcium and radium. Evidence indicates that increasing concentrations of calcium inhibit the absorption of radium (MISTRY 1963). BRUNOVSKII & KUNASHEVA (1935) reported on the radium content of aquatic plants, specifically duckweed (Lemna) species, which were found to concentrate radium. The maximum concentration was found during periods of maximum flowering in spring, similar to the results we present for Nuphar. The ability of Nuphar lutea to concentrate U_{nat} and ^{226}Ra from water is significant in that, although the concentration of U_{nat} and ^{226}Ra in both surface water and sediments did not alter significantly from spring to summer (Tables 1,2) the concentration factors for each radionuclide from each medium into Nuphar decreased by an order of magnitude from spring to summer (Table 5). This is reflected in the concentration of each radionuclide in the plants for each season (Table 3), which

also dropped by an order of magnitude from spring to summer. This would suggest that the accumulation process is strongly associated with the growth phase in the annual cycle. This seasonality is not evident for the accumulation of either ^{210}Pb or ^{210}Po, and is indicative that the mechanism of accumulation of these radionuclides is not the same as for either U_{nat} or ^{226}Ra.

The ^{210}Pb concentration in the surface water did not rise above the detection limit during the course of the study, and the ^{210}Po concentration was only at the limit of detection during the summer season (Table 1). Considering that the levels of ^{226}Ra were below the detection limits for the whole period, and that both ^{210}Pb and ^{210}Po are decay products of ^{226}Ra, through ^{222}Rn, this was not unexpected.

The concentration factors for ^{210}Pb (Table 5) are of the same order as those reported by HUTCHINSON (1975) for lead in water hyacinth (Eichornia crassipes), but it should be noted that our values were derived from water concentrations at, or below, the limit of detection for the method (0.5 pCi/L), and thus may be well below the actual values. MATHIS & KEVERN (1973) reported the distribution of lead in a eutrophic lake system, including the lead content of water, sediment and Nuphar lutea. Using their data, relevant concentration factors were calculated, with the following results; CF_{Pb} water:Nuphar = 70, CF_{Pb} sediment:Nuphar = 0.036. The water to Nuphar coefficient was lower than our result, but by less than an order of magnitude, and the sediment:Nuphar result agrees closely with our reported values (Table 5).

The data show a significant seasonality in the accumulation of U_{nat} and ^{226}Ra by the aquatic macrophyte Nuphar lutea, and provide evidence that suggest the mechanism of accumulation is independant of the common external factors associated with the accumulation of heavy metal residues such as the water concentration or pH. The differences are thus probably controlled by changes in the physiological state of the plant. The data suggest that aquatic macrophytes would constitute a significant factor in the recycling of radionuclides and, or, heavy metals through the ecosystem by a process of seasonal accumulation followed by detrital deposition in organic sediments. Aquatic macrophytes form an important portion of the spring diet of herbivorous mammals, especially moose (Alces alces) (SINGLETON 1976), thus the seasonal aspects of the bioconcentration of U_{nat} and ^{226}Ra is of importance in assessing possible accumulation of radionuclides or heavy metals in foodchains. In addition, the data identify the critical nature of the sample collection time in the investigation of heavy metal accumulation or transport in aquatic systems.

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