Geochimica et Cosmochimica Acta, 1977, Vol. 41, pp. 1557 to 1564. Pergamon Press. Printed in Great Britain

The use of ^{210}Pb as a heavy metal tracer in the Susquehanna River system

DALE M. LEWIS*
Department of Geology and Geophysics, Yale University,
New Haven, CT 06520, U.S.A.

(*Received* 21 *June* 1976; *accepted in revised form* 15 *June* 1977)

Abstract—Analysis of soil profiles and shallow ground water in the Susquehanna River basin, northeastern U.S.A., indicates that the atmospheric flux of ^{210}Pb is efficiently scavenged by the organic-rich horizons of the soils. This atmospherically supplied ^{210}Pb in soil profiles can only be lost from the system by soil erosion. Based on the annual sediment yield of the Susquehanna River and the excess ^{210}Pb concentration in particulate matter, a mean residence time of 2000 yr is calculated for metals similar to Pb in soil profiles.

The West Branch of the Susquehanna River (WBSR) is strongly affected by acid mine drainage and is low in pH and high in dissolved ($<0.4\ \mu$m) ^{210}Pb, Fe and Mn. Along its course iron hydroxide is precipitating at a pH of between 4 and 4.5, and the ^{210}Pb supplied by the acid mine water is diminished by about 25% as a result of dilution. As the WBSR enters the Valley and Ridge Province of the Appalachians it has a ^{210}Pb concentration of ~ 0.2 dpm/l. At this juncture it receives a considerable influx of alkalinity from tributaries draining carbonate terranes, resulting in neutralization of the sulfuric acid and increase of the river pH to around 6.5–7. This pH adjustment is accompanied by the precipitation of Fe and Mn. Due to the slow rate of Mn removal from solution, the Mn precipitation extends a considerable distance down river from the point of acid neutralization. Analyses for ^{210}Pb in the river at points in or below the region of Mn precipitation show that ^{210}Pb is rapidly scavenged from solution onto suspended particles. From the data it is possible to calculate the removal rate of Pb from water in the presence of Fe and Mn hydroxides and other particles. At a pH of 4–4.5 Pb removal is nonexistent relative to the river flow rate, but at a pH of 6.5–7 the ^{210}Pb data indicate a residence time of <0.7 day for dissolved Pb.

INTRODUCTION

THE WIDESPREAD introduction of heavy metals into the environment from anthropogenic sources often makes the study of the behavior of these elements ambiguous. Furthermore, contamination during sample processing and analysis, especially for stable Pb, is common, again bringing the results of such studies into question. Lead-210, a naturally occurring radioactive isotope of Pb, is not subject to the same problems as stable Pb.

The most abundant naturally occurring isotope of uranium, ^{238}U, decays through a long chain of radioactive daughter nuclides to stable ^{206}Pb. One of these, ^{222}Rn ($t_{1/2} = 3.8$ d) produced from ^{226}Ra ($t_{1/2} = 1620$ yr), is a noble gas. The emanation of ^{222}Rn from soils is a widespread, well documented phenomenon (WILKENING *et al.*, 1975). Radon-222 decays through a series of short-lived nuclides (^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po) to ^{210}Pb ($t_{1/2} = 22$ yr). As a nonreactive gas ^{222}Rn remains in the atmosphere until it decays. Lead-210 and precursing short-lived nuclides, on the other hand, become attached to aerosols and are swept out of the atmosphere by precipitation and dry fallout with an atmospheric residence time of less than a week (POET *et al.*, 1972). This flux of ^{210}Pb provides a widespread, measurable flux to the land surface. There are other sources of ^{210}Pb in the system. The ^{226}Ra in the soil and rock decays to ^{210}Pb which could be leached into the ground water that feeds streams. Also, the ^{226}Ra and ^{222}Rn dissolved in ground water produce ^{210}Pb, although removal of intermediate decay products is likely.

The behavior of ^{210}Pb from these sources in the soil–ground water–stream systems provides the most direct information on the kinetics of processes involving heavy metals from natural or man-made sources. In this paper ^{210}Pb and related data in representative soil, ground water and river water are presented and the implications for heavy metal mobility in soils and removal from solution in streams are discussed. Most of the surface and ground water samples were collected in the basin of the West Branch of the Susquehanna River in Pennsylvania. (See Fig. 1.)

SAMPLING AND ANALYSIS

River and stream water samples were filtered in the field within 1–2 hr of sample collection. The filtration system was operated by pressurizing (with N_2 gas filtered through a 0.4 μm membrane filter) a jerrican containing the water and suspended sediment. The water, a bucket surface sample, was forced through plastic tubing and an in-line 142 mm, 0.4 μm pore diameter membrane filter (Nuclepore). The filtered water leaving the in-line filter holder was collected in pre-weighed, pre-washed (8 N HCl and 6 N HNO_3) polyethylene bottles containing 5–10 ml of redistilled HCl. The amount of water filtered was determined by reweighing the full bottle. Separate unacidified

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* Present address: RD No. 1 Box 380, Emporium, PA 15834, U.S.A.

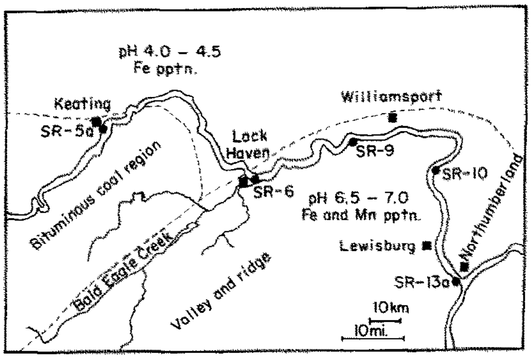

Fig. 1. Sample site locations and chemical conditions in the West Branch of the Susquehanna River, PA.

samples were collected at each site for major ion analyses. Spring water samples were not filtered.

At the time of sampling *in situ* pH measurements were made with a portable pH meter.

Soil samples were obtained by digging a pit and carefully removing a column of soil from the undisturbed rear wall.

After adding a Pb carrier solution to the water samples ^{210}Pb is extracted from solution by coprecipitation of $PbCrO_4$ and ferric hydroxide at a pH of ~6.5. The ^{210}Pb is separated from other radionuclides by ion exchange columns and is later determined by alpha counting its daughter, ^{210}Po, after ingrowth from the purified state. Details of the radionuclide analytical methods used are discussed fully by BENNINGER (1976).

Particulate ^{210}Pb analyses were performed as above, except that first the samples were totally dissolved in HNO_3–HF (Pb carrier added before dissolution). Particulate ^{226}Ra was determined by the ^{222}Rn emanation technique of TUREKIAN *et al.* (1973).

It should be noted, especially for ^{210}Pb, that concentrations of the dissolved element represent the material in the water after filtration through a 0.4 μm pore diameter membrane filter. The element may be in true solution or could be attached to particles smaller than 0.4 μm in diameter.

ATMOSPHERIC FLUX OF ^{210}Pb

The use of ^{210}Pb as a tracer entails determination of the primary sources of the element as well as its mobility in different parts of the environment. From the considerations discussed in the introduction it is apparent that the atmospheric flux of ^{210}Pb in dry fallout and precipitation is the dominant source. This section discusses three types of data that taken together illustrate the behavior of ^{210}Pb in the soil–ground water system. First, because of the pronounced positive correlation of heavy metals with organic material in soils (MITCHELL, 1964) and sediments (CALVERT and PRICE, 1970), it is proposed that soils trap the ^{210}Pb deposited on the land surface. In a soil left undisturbed for about 100 yr, the standing crop of ^{210}Pb in excess of the background ^{226}Ra can be converted to a steady-state flux and compared with BENNINGER's (1976) direct measurements of the flux. The degree of agreement between the ^{210}Pb fluxes calculated by the different methods indicates the efficiency of the soil for trapping ^{210}Pb. Second, the concentration of ^{210}Pb in young (residence time of a few years at most in the shallow aquifers in the Appalachian Plateau region of Pennsylvania) ground waters compared with expected concentrations calculated for ground waters derived from net precipitation further tests the soil scavenging efficiency. Third, using HOLTZMAN's (1964) data for old ground waters, residence times for ^{210}Pb can be calculated in the aquifers.

The atmospheric flux of ^{210}Pb in precipitation and dry fallout has been directly measured for New Haven, Connecticut, at Kline Geology Laboratory, Yale University. The results from monthly samples collected for more than a year indicate a flux of 0.9 ± 0.1 dpm $^{210}Pb/cm^2/yr$ (BENNINGER, 1976). It can be shown that this flux is approximately the same over the northeastern U.S. and probably from the Rockies eastward (BENNINGER *et al.*, 1975; MOORE and POET, 1976). The methods employed to establish this are based on the analysis of soil profiles and atmospheric measurements and, although these are less direct than the precipitation techniques, they provide more easily obtained data.

The A_1 horizon of soils, known to be rich in heavy metals and organics, can be expected to retain some, if not all, of the atmospheric flux of ^{210}Pb delivered to the site. Soil profiles are also a source of ^{222}Rn to the atmosphere which would appear as a deficiency of ^{210}Pb relative to ^{226}Ra. A radiochemical analysis for ^{210}Pb and ^{226}Ra down a soil profile permits modeling of the concentrations of ^{210}Pb and ^{226}Ra to determine the loss of ^{222}Rn to the atmosphere and the contribution of ^{210}Pb to the profile from the atmosphere (MOORE and POET, 1976). Soil profiles from several northeastern sites have been analyzed for ^{226}Ra and ^{210}Pb. MCCAFFREY (in preparation) has sampled a salt marsh soil and the soil from an adjacent upland island from the Farm River salt marsh in East Haven, Connecticut. This site is within 10 miles of the site for direct atmospheric flux sampling reported by BENNINGER (1976). FISENNE (1968) reports data for a soil profile from a tobacco-growing region of Maryland that is within 50 miles south of the mouth of the Susquehanna River.

A soil profile was collected in Pennsylvania for analysis to enable comparison with the other data. It was taken in the Cook Forest State Park, which lies just outside of the western boundary of the Susquehanna River basin at about its north–south midpoint (Table 1). The total excess ^{210}Pb (in a system with no ^{222}Rn loss excess ^{210}Pb = total ^{210}Pb − ^{226}Ra) in each site and the calculated steady-state flux are shown in Table 2. It can be seen that they all agree with the flux measured directly in New Haven, hence indicating no major variation in regional flux of ^{210}Pb for the Northeast and that the soils seem to retain the entire atmospheric flux.

The ground water and stream water data further indicate scavenging of ^{210}Pb by soils. Using the average annual rainfall (~100 cm), the evapotranspiration rate of 50% (USGS, 1975) and the atmospheric flux of ^{210}Pb (1 dpm/cm^2/yr), the concentration of

Table 1. Cook Forest soil profile radionuclide and physical data required to calculate the ^{210}Pb atmospheric flux*

	Depth cm	ρ gm/cm^3	^{226}Ra dpm/gm	^{210}Pb dpm/gm
CF-1	0-2.9	0.11	0.51 ± 0.08	45.49 ± 1.46
CF-2	2.9-5.9	0.18	0.69 ± 0.03	26.54 ± 0.13**
CF-3	5.9-6.2	0.57	0.84 ± 0.07	7.71 ± 0.33
CF-4	6.2-11.3	1.23	1.01 ± 0.25	1.92 ± 0.08
CF-5	11.3-15.7	1.17	1.06 ± 0.05	1.37 ± 0.06
CF-6	15.7-30.9	1.05	1.37 ± 0.05	1.07 ± 0.03**
CF-7	30.9-40.8	1.28	1.36 ± 0.16	1.18 ± 0.09
CF-8	40.8-62.1	1.26	1.35 ± 0.07	1.06 ± 0.05
CF-9	62.1-73.2		1.82 ± 0.30	1.20 ± 0.10

* Masses are unashed, dried samples (105°C).

Errors are the standard deviation of repeated counts for the same sample of ^{210}Pb or repeated emanation and counting of ^{222}Rn for a ^{226}Ra sample.

** 1 σ counting error only.

Table 2. Comparison of the measured atmospheric ^{210}Pb flux with fluxes calculated from the soil standing crop of ^{210}Pb

Soil	Soil ^{210}Pb Standing Crop dpm cm^{-2}	^{210}Pb Flux dpm cm^{-2} yr^{-1}	Source
Cook Forest	30	1.0	this study
Maryland	36	1.2	Fisenne, 1968
Salt Marsh, Conn.	30	1.0	McCaffrey, in preparation
Island, Conn.	24	0.8	McCaffrey, in preparation
Rain Collection New Haven, Conn.		1.0	Benninger, 1976

^{210}Pb in waters recharging ground water systems should be ~20 dpm/l. The water from three springs analyzed for ^{210}Pb shows concentrations more than an order of magnitude lower (Table 3). Two of the springs, RV-5 and SM-spring, are thought to be fed by waters with shorter residence times than the well and the other springs sampled because of the significantly lower concentrations of rock-derived major ions in these two springs compared with the others.

It has been shown that at all times (except, perhaps, for extraordinary flood conditions) the water flowing in the streams of the Susquehanna basin is from the ground water system (Lewis, 1976). This being the case, the streams are good integrators of the composition of the ground water.

As the preceding may be a controversial statement, it must be pointed out that the headwater streams mentioned below were sampled at low flow for that

Table 3. Average Ca, Mg and ^{210}Pb concentrations of ground water and streams sampled

	June 1974						Headwater Streams			
							Driftwood Br.		Buffalo Creek	
	Spring RV-3	Spring RV-7	Spring RV-4	Well RV-6	Spring RV-5	SM-Spring	March 1974	June 1974	March 1974	June 1974
Ca (mg/ℓ)	5.9	5.8	6.8	4.9	3.8	3.1	4.0	4.3	18.4	21.1
Mg (mg/ℓ)	1.8	1.6	1.5	0.8	1.0	0.8	1.2	1.2	5.8	6.3
^{210}Pb (dpm/ℓ)	.007	-	-	-	.974	1.116	0.011	0.010	0.023	0.011

particular time of year and therefore would represent the classical "base flow" (SHERMAN, 1949). However, even if there was an overland runoff component in the streams when sampled, it would be expected to have higher ^{210}Pb concentrations consistent with precipitation values and would increase the concentration of ^{210}Pb in the stream waters above that expected from ground water alone. As a result, the ^{210}Pb concentration in the streams would represent a maximum value for ground water.

Headwater streams of the Susquehanna River system, such as the Driftwood Branch of Sinnemahoning Creek which drains a silicate sedimentary terrane and Buffalo Creek (Union Co., PA) which drains a carbonate terrane, contain water very recently discharged from the ground water system and therefore should be good indicators of the average ^{210}Pb in the shallow ground water. The concentration of ^{210}Pb in these streams is shown in Table 3. The concentration of ^{210}Pb in the Driftwood Branch and Buffalo Creek is 0.01 dpm/l.

HOLTZMAN (1964) reports ^{226}Ra and ^{210}Pb analyses for ground waters in Illinois in deep limestone and sandstone aquifers. If it is assumed that the waters in these deep aquifers have a mean residence time of 100 years or greater, a residence time for ^{210}Pb can be calculated from the ^{226}Ra and ^{210}Pb data. Using the range of concentrations he gives for these deep aquifers, the range in mean residence time is from one year to one day while the average ^{226}Ra/^{210}Pb activity ratio yields a residence time of one month. This result is compatible with the low ^{210}Pb concentrations in the ground water of the Susquehanna River system that also indicate rapid removal of ^{210}Pb from solution.

The data for excess ^{210}Pb in soils compared with precipitation data indicate loss primarily through radioactive decay. The small concentration of dissolved ^{210}Pb in the shallow ground water of the region compared with the expected value from precipitation also confirms this. Therefore, all the data together indicate that soils are virtually 100% efficient at sequestering the atmospheric ^{210}Pb flux supplied to a terrain. This sequestering of ^{210}Pb by the soil materials occurs despite low pH in these soil horizons and may be related to the properties of the organic material with which a correlation exists (Table 4).

An interesting situation is presented by those areas affected by coal mining. There the acid streams are high in dissolved ^{210}Pb relative to other streams. However, the concentration of ^{210}Pb in the mine drainage is about 0.3 dpm/l, which is only 1.5% of the expected concentration in net precipitation. Surprisingly then, most of the ^{210}Pb in rain falling on the mined areas is also removed from solution. In areas of strip mining the mine drainage is formed as rain water percolates through the spoil piles made of rock rubble and probably the former soils. However, the data seem to indicate that, even in the absence of organic soil material, most of the ^{210}Pb is removed from the water by contact with rock materials, even at low pH.

FATE OF ^{210}Pb IN RIVER WATER

In the preceding discussion it was mentioned that the water flowing in the river (with the exception of that falling directly on the river) under natural conditions must pass through the soil–ground water system where efficient scavenging of ^{210}Pb occurs. The water flowing into the stream system is very low in dissolved ^{210}Pb, and modeling its behavior downstream becomes impossible.

Table 4. Organic matter and ^{210}Pb in soil profiles

Soil*	Depth cm	^{210}Pb dpm/gm ash	% organic**
CF-1	0-2.9	340	87.7
CF-2	2.9-5.9	62.8	57.8
CF-3	5.9-6.2	9.50	17.5
CF-4	6.2-11.3	2.00	3.79
SM-1	0-0.6	271	86.5
SM-2	0.6-4.4	55.7	45.2
SM-3	4.4-9.5	3.58	7.5
SM-4	9.5-14.6	1.62	2.82
SM-5	14.6-19.0	1.52	3.94

* CF: Cook Forest State Park soil profile.

SM: A soil profile collected in a deciduous forest near an oak tree that was 104 yr old. The site was ~5 miles southeast of Emporium, PA, on a flat hilltop.

** Weight loss on ignition at ~500°C.

Mine drainage streams and sections of the river affected by mine drainage, however, are relatively high in ^{210}Pb (0.3 dpm/l compared with 0.01 dpm/l for normal streams), and some information on the behavior of ^{210}Pb during stream transport can be obtained from this source. The part of the West Branch of the Susquehanna River from Keating, PA, (SR-5a) to Lock Haven, PA, (SR-6) is strongly affected by mine drainage, although very little additional mine drainage is added to the river within this stretch of river (Fig. 1). The river is at low pH ($\sim$4–4.5) and contains relatively high dissolved manganese and iron. Manganese remains in solution in this section of the river but iron is probably precipitating as an oxyhydroxide throughout the region. Below Lock Haven (SR-6) the acid of the West Branch is neutralized and the pH rises to 6.5–7, resulting in the precipitation of iron and manganese. The iron precipitates very rapidly after neutralization and is generally completely removed before the first downriver station (SR-9). On the other hand, the manganese precipitates more slowly and occurs in the entire West Branch below Lock Haven (SR-6). Immediately downriver from the point of acid neutralization, for a distance of about 15 miles, there is precipitation of iron. Below the point of iron removal precipitation of manganese occurs throughout the length of the river (LEWIS, 1976).

Samples for ^{210}Pb analyses were collected on the acid portion of the river in June 1974 at Keating (SR-5a) and Lock Haven (SR-6). The ^{210}Pb concentration for the West Branch at Keating is 0.17 dpm/l. The expected concentration of ^{210}Pb at Lock Haven by dilution alone can be calculated given a starting concentration at Keating (SR-5a) and the concentration in tributary streams. When this is done, it can be seen that the concentration at Lock Haven (0.12 dpm/l) is due to dilution and that the ^{210}Pb is not removed from the river at a pH of 4. It is interesting to note that the ^{210}Pb is not sequestered by the hydrous iron oxides at a pH of 4, whereas ^{210}Pb is sequestered by organic soil material and rock debris at similar pH values.

The observation that ^{210}Pb is not sequestered by hydrous iron oxides at pH 4 is compatible with the Pb^{2+} adsorption experiments of GADDE and LAITINEN (1974). They show that the specific adsorption of Pb^{2+} by amorphous hydrous iron oxides is accompanied by release of hydrogen ion and decreases dramatically from pH 6 to 4 for most experimental conditions. The amount of adsorption of Pb^{2+} at pH 4 is less than 10%.

Samples were collected for ^{210}Pb analyses below Lock Haven (SR-6) in October 1973, March 1974 and June 1974. In June 1974 samples were collected at all river stations from Lock Haven (SR-6) to the mouth of the West Branch so that detailed information could be obtained on the removal of ^{210}Pb. In October 1973 samples were collected at Lock Haven (SR-6) and Northumberland (SR-13a). In March 1974 samples were collected only at Keating (SR-5a) and Northumberland (SR-13a). A starting concentration for the West Branch at Lock Haven (SR-6) can be calculated, however, as the June data above show that ^{210}Pb is not removed in the section of river between Keating (SR-5a) and Lock Haven (SR-6).

Time can be introduced as a variable by conversion from river distance and flow velocity. Time downriver from a point of reference is determined by calculation from the mean velocity of the river in this region and the distance of the station downriver from the point. Using USGS data (DAVID BARTON, written communication, 1975) plots of log discharge vs log mean velocity have been made for the river gaging sites at Williamsport, PA, and Lewisburg, PA (Fig. 2). From these rating curves the mean river velocity at the gaging stations can be determined for the time of sampling using the daily discharge data collected by the USGS at these stations (U.S. GEOLOGICAL SURVEY, 1975). Discharge at the time of sampling is marked for each curve. Since both the discharge and velocity of a river increase downstream (LEOPOLD and MADDOCK, 1953), an average velocity between the stations is used in the calculation.

The most complete ^{210}Pb data are available for June 1974. The concentration of ^{210}Pb vs time in hours downriver from the point of acid neutralization (taken to be the confluence with Bald Eagle Creek) is shown in Fig. 3. The ^{210}Pb concentration is nearly zero by the time the first station is reached. The apparent increase downriver from site SR-9 is consistent with addition of tributary waters containing significant ^{210}Pb concentrations below this point or may be attributed to a steady-state ^{210}Pb concentration in the river below the region of iron hydroxide coprecipitation. The higher downriver values may also be due to particles passing the 0.4 μm filter, whereas in the area of iron precipitation filtering is more effi-

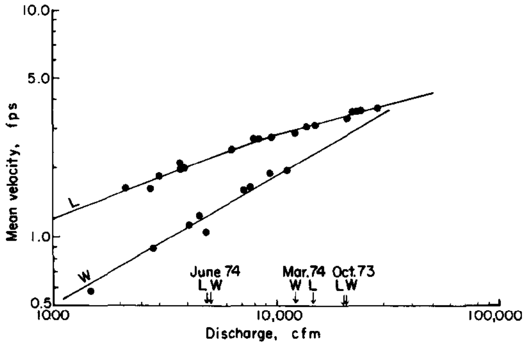

Fig. 2. Plot of log mean velocity vs log discharge for USGS gaging stations on the West Branch of the Susquehanna at Williamsport (W) and Lewisburg (L). The USGS measurements were supplied by David Barton, Harrisburg, PA. The Williamsport curve is based on data from August 1973 to November 1974. The Lewisburg curve is based on data from September 1972 to October 1974. Arrows along the abscissa indicate the discharge at each site (W and L) for the three times of sampling referred to in the text.

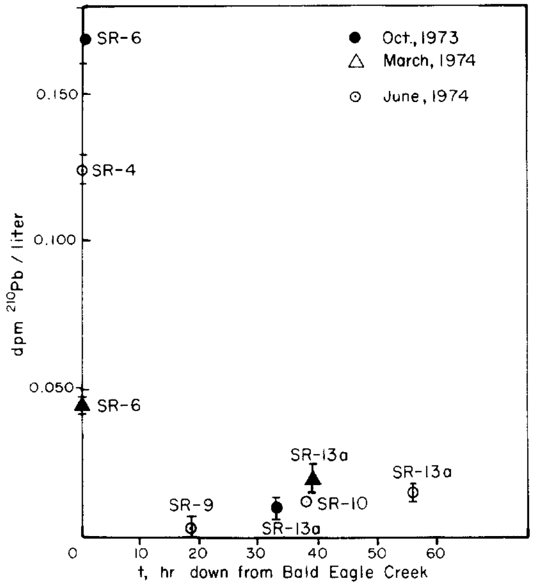

Fig. 3. Dissolved ^{210}Pb ($<0.4\,\mu$m) in the West Branch of the Susquehanna River below the point of acid neutralization.

cient. These removal data indicate a mean residence time of <0.7 d when calculated as a first order rate process.

Similar data for October 1973 and March 1974 (Fig. 3) show that by the time the water reaches Northumberland (SR-13a) the ^{210}Pb in solution at Lock Haven (SR-6) has been reduced to low levels similar to those observed at Northumberland (SR-13a) for June 1974. Also, a sample collected in January 1974 at Northumberland (SR-13a) has a similar dissolved ^{210}Pb concentration, although it must be surmised that dissolved ^{210}Pb was present in the river at Lock Haven (SR-6). These data indicate a residence time for ^{210}Pb in the river water of <1.5 d based on first order removal.

THE FATE OF PARTICULATE ^{210}Pb

The ^{210}Pb which falls on the Susquehanna River basin is lost from solution to the soils. Therefore, no ^{210}Pb in solution is lost from the terrane with the exception of that released in mine drainage. All the ^{210}Pb is retained on particles in the soil, and the only way it can be lost from a terrane is by erosion.

The stream-borne particles with their associated ^{210}Pb are derived mainly from soil. It can be determined how much ^{210}Pb derived from atmospheric precipitation on a terrane leaves the system via streams if the sediment flux and excess ^{210}Pb concentration of the particles are known. Table 5 shows the results of the calculation for the entire Susquehanna River based on the long-term annual sediment yield of Williams and Reed (1972). This flux is equivalent to 0.05% of the soil standing crop of excess ^{210}Pb.

The ^{210}Pb data for soil profiles show a ^{210}Pb/organic matter ratio which is nearly constant with depth in the soil (Table 6). This implies that the ^{210}Pb added to the soil surface is rapidly homogenized within the organic-rich layers. This homogenization is most likely the result of physical mixing by the various animal organisms that inhabit the forest soil. Nearly the same ratio of ^{210}Pb/organic matter (30 dpm/g) is observed in the suspended matter of streams. This indicates that stream sediments directly reflect the metal content of soils. The removal of 0.05% of the standing crop of ^{210}Pb is equivalent to a mean residence time of 2000 yr for metals similar to ^{210}Pb in soil profiles, or a first order removal constant for ^{210}Pb by erosion of $\lambda = 5 \times 10^{-4}\,\text{yr}^{-1}$.

If ^{210}Pb is analogous in behavior to stable Pb and

Table 5. ^{210}Pb particle mass balance calculated for the Susquehanna River at Harrisburg, PA

^{226}Ra dpm/gm	^{210}Pb dpm/gm	^{210}Pb excess dpm/gm	Sed. Flux*	^{210}Pb Flux	Soil Standing Crop	Soil Metal Removal
3.5-4.0	7.5-8.0	4	3.78×10^{-3} gm cm^{-2} yr^{-1}	0.015 dpm cm^{-2} yr^{-1}	30 dpm cm^{-2}	0.05%/yr

* Based on Williams and Reed (1972).

Table 6. ^{210}Pb$_{\text{excess}}$/organic matter ratio in soil profiles

Soil Horizon	^{210}Pb dpm/gm organic	Soil Horizon	^{210}Pb dpm/gm organic
CF-1	48	SM-1	41
CF-2	45	SM-2	65
CF-3	40	SM-3	28
CF-4	24	SM-4	13

Stream sediment 30 ^{210}Pb$_{\text{excess}}$ dpm/g organic.

Table 7. Dissolved and particulate ^{210}Pb concentrations in Susquehanna River samples

Site	Dissolved (< 0.4 μm) dpm/ℓ	Particulate dpm/gm	^{210}Pb dpm/ℓ
October 73			
SR-8	0.003	6.47	1.07
SR-11	0.025	6.54	0.16
SR-13a	0.010	7.43	0.42
SR-17	0.005	7.58	0.06
January 74			
SR-13a	0.014	11.24	0.21
SR-17	0.005	8.76	0.15

other trace metals in the natural system (including those supplied by human perturbations), then the ^{210}Pb results can be applied to problems involving these other metals. The first question that arises is whether ^{210}Pb becomes homogenized with the stable Pb in a system. The dominant source of Pb injection into the environment today is from combustion of leaded gasoline in internal combustion engines. The Pb in such exhaust is vented into the atmosphere as Pb bromo-chlorides. However, studies of Pb in soils in areas of pronounced pollution show that the soil Pb is present as Pb oxides and Pb sulfate (OLSON and SKOGERBOE, 1975). Furthermore, research on aerosol chemistry shows that the trend of reaction is to replace the chloride (and presumably other halogens) in the aerosols with NO_3^- and other anions (MARTENS *et al.*, 1973). Collectively this indicates that the ^{210}Pb should become homogenized with stable Pb in the atmosphere and thus be an effective tracer. The nature of ^{210}Pb and stable Pb in the riverine system cannot be evaluated and remains open to research; but it is likely, however, that ^{210}Pb will be a useful tracer in aquatic systems.

Using their analyses for dissolved trace metals (Ag, Mo, Cr and Co) in various rivers and comparing them with the particulate trace metal data reported for the same samples TUREKIAN and SCOTT (1967), and KHARKAR *et al.* (1968) concluded that there was no relation between dissolved trace metal concentrations and the concentration or amount of the same trace metals in the suspended sediment. The striking feature of their data is that all the elements studied appear to behave similarly: they have low dissolved concentrations which have no relation with the concentrations of the elements in the suspended sediment. Similarly, the ^{210}Pb data for the Susquehanna River and tributaries at points beyond the effects of mine drainage (Table 7) show no relation between dissolved ^{210}Pb and the concentration of ^{210}Pb in the sediment or for total ^{210}Pb in the suspended sediment. In fact, it appears that regardless of the sediment concentration the dissolved ^{210}Pb (<0.4 μm) is at a very low concentration of <0.01 dpm/l.

The study of manganese and iron in the Susquehanna River has shown that if they are introduced into the river system, precipitation will occur and ^{210}Pb will be removed from solution and maintained at a very low concentration. One way that iron and manganese are introduced into natural rivers is from the ground water that feeds the river system. However, in many rivers, as in the case for the Susquehanna, major ground water input occurs in the tributaries while the main trunk flow is merely a total of the tributary flow. Therefore, the water in the main trunk may have already precipitated all of its iron and much of its manganese due to distance (time) from the source. From jar experiments with Susquehanna River bottom sediment there is qualitative evidence of a flux of iron and manganese from the fine-grained river bottom sediments into the river water. Similarly, a recent study of fine-grained bottom sediment of the White Oak River, North Carolina, shows high dissolved iron (~5 ppm) in the interstitial waters along with the formation of iron sulfide in zero salinity pore waters (GOLDHABER and MARTENS, 1975, personal communication). This indicates a source for a flux of dissolved manganese and iron into the river water where they will precipitate and become part of the suspended sediment as fresh hydroxides. The presence of sulfide in these bottom sediments would prevent the concomitant release of ^{210}Pb and other heavy metals (mass action resulting in the precipitation of the metals as sulfides). In addition to the iron and manganese chemistry of a river, there is a supply of eroded soil organic matter which is an excellent scavenger of heavy metals. Therefore, it is concluded that the continual production of iron and manganese hydroxides which are added to the suspended sediment and the introduction of organic matter are responsible for a unidirectional removal process of dissolved heavy metals onto particles, resulting in a low concentration of many heavy metals dissolved in streams and rivers. The ^{210}Pb rate studies show that removal is relatively fast; but if the flux of metals from pollution sources exceeds this removal term, the standing crop of dissolved heavy metals could be quite high.

Acknowledgements—This study is part of the work included in the author's Ph.D. thesis completed at Yale University. Professor K. K. Turekian supervised the work which has benefited from his involvement. Discussions of the work with Drs. L. Benninger and J. Thomson have been beneficial. Dr. Y. Nozaki analyzed ^{210}Pb and ^{226}Ra in the soil samples and assisted in modeling the soil ^{210}Pb flux retention.

Financial support was provided by a National Science Foundation Graduate Fellowship and by Energy Research and Development Agency Grant E (11-1)-3573.

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