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BOTTOM SEDIMENT ALONG OIL SPILL TRAJECTORY IN
PRINCE WILLIAM SOUND AND ALONG KENAI PENINSULA, ALASKA

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Chapter D. Plutonium and ^{210}Pb activities in two cores from
Prince William Sound

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PLUTONIUM AND ^{210}PB ACTIVITIES IN TWO CORES FROM PRINCE WILLIAM SOUND

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INTRODUCTION

From the suite of sediment samples collected from Prince William Sound by the USGS (Carlson and Reimnitz, 1990, this report) following the Exxon Valdez oil spill, two cores were selected for analysis of ^{210}Pb and Pu. These radioactive isotopes have a strong affinity for suspended particles and sediments in coastal sea water, a behavior similar to many contaminants. This similarity is the basis for assuming that these isotopes are analogs for sediment-reactive contaminants. Where the concentration and inventory of these isotopes in sediments are relatively high, the potential for accumulation of contaminants is also high. When these areas in Prince William Sound are identified, samples can be more efficiently selected for more costly analyses of organic compounds specific to petroleum. If no petroleum indicators are found in areas of high ^{210}Pb and Pu inventories, then this could be interpreted as evidence that petroleum is not accumulating in areas known to selectively collect sediment-reactive contaminants.

^{210}Pb is a naturally occurring isotope in the ^{238}U decay series with a half life of 22.3 years. It can be used to extract time information about sedimentary processes over the last century. The isotopes of Pu (^{238}Pu, ^{239}Pu and ^{240}Pu, half-lives 80, 24,360 and 6600 years, respectively) were introduced into the atmosphere via weapons testing, with the greatest introduction around 1963.

^{238}Pu was also introduced to the stratosphere in 1964 with the destruction of a nuclear-powered satellite generator, SNAP-9A, which burned during reentry and introduced its fuel to the stratosphere. The presence, absence, and shape of a Pu activity profile with depth in sediment cores can be used to interpret sediment accumulation and mixing rates.

The objective of this study was to determine isotopic levels in cores collected from two areas presumed to be depositional on the basis of seismic reflection profiles and sediment texture. The scope of this study was limited to analysis of 11 subsamples from the two cores.

METHODS

^{210}Pb was determined on 40- to 50-g samples of dried and gently disaggregated sediment. The material was sealed in a screw-top plastic 8-oz jar and counted, typically for one day, using a 2,000-mm^2 germanium detector designed for low-energy gamma ray spectroscopy. The EPA standard Pitchblende Ore was counted in the same geometry as the samples to calibrate counter efficiency and to determine disintegrations per minute per gram of dry sediment (dpm/g). A correction for self-adsorption of the low energy ^{210}Pb gamma rays was made using the method of Cutshall et al. (1983). Excess ^{210}Pb was calculated by subtracting the activity of ^{214}Pb (352 Kev), a measure of supported ^{210}Pb, from the total ^{210}Pb (46.3 Kev) activity. All values of excess ^{210}Pb were decay corrected to the date of core collection.

Quality control for our procedure was established by analyzing a continental shelf sediment sample previously analyzed by two other radiochemical laboratories. Our determination of ^{210}Pb and ^{214}Pb was within one standard deviation (6 and 9 percent, respectively) of the mean of the other laboratories.

^{239,240}Pu, and ^{238}Pu determinations were performed for the USGS by TMA/Norcal, Richmond, Cal. The procedures were essentially those established by the Environmental Measurements Laboratory, U.S. Dept. of Energy (EML, 1982). Approximately 50 g of dried and disaggregated sediments were subjected to sequential leaching steps using HNO_3-HCl and HNO_3-HCl-HF. Pu isotopes were selectively removed from the leachate and purified using anion exchange resin techniques. Pu activity was determined by alpha spectrometry. Counting times for the alpha spectra ranged from 1,000 minutes for samples having relatively high Pu activity to 4,300 minutes for samples having low activity.

Quality control for the procedure was established by analysis of reagent blanks that were carried through all analytical procedures and by analysis of Columbia River Standard Sediment (CRSS), which is prepared and certified by the National Bureau of Standards. Results of the analysis of CRSS were within +4 percent of accepted values.

Inventories of the isotopes (activity/cm^2) were calculated from the depth profile of measured activity and the estimated average dry density (g dry/cc wet) using the water content and a grain density of 2.65.

Sediment textural analyses were conducted by the standard pipette method (Folk, 1974) on samples that had not been dried. Water content was determined by drying sample splits at 70°C until constant weight was achieved. Water content values are minimum values due to the possible loss of moisture through plastic bags during the few weeks between sampling and processing.

RESULTS AND DISCUSSION

At station 2A (Figure 2 in Carlson and Reimnitz, 1990, this volume), the texture of surface sediment is classified as sand-silt-clay and is fairly uniform with depth in the core (Table 1), suggesting no major changes in depositional conditions over the time represented by the length of this core.

The activity of ^{210}Pb (Table 2, Figure 1A) decreases from the surface, slowly to 11 cm and then more rapidly between 11 and 41 cm where the decrease with depth is nearly log-linear (for dashed line in Fig. 1A, r = .99). The apparent change in slope at 11 cm is probably due to bioturbation (sediment mixing by organisms) of the upper zone which is common in fine-grained coastal sediments overlain by oxygenated water (Santschi an others, 1984). Bioturbation may also explain the nearly uniform activity of Pu from the surface to 11 cm depth (Figure 1B). Additional evidence for mixing in the surface sediments at this location is the presence of ^{7}Be (53.3 day half-life) to a depth of 8 cm (Grebmeier,1990, this volume).

The absence of measurable Pu at 31 and 41 cm suggests that mixing does not extend throughout this particular core. The depth limit of bioturbation could be verified by a radiographic analysis of the cores to observe laminations and by a study of the benthic infauna.

Under the assumption of no mixing below 11 cm, the slope of the ^{210}Pb depth-profile (Figs. 1A and 2A) yields a sediment accumulation rate of 0.32 cm/yr (Nittrouer and others, 1984). This sedimentation rate should be considered to be an upper limit until other data are found which confirm the absence of mixing (undisturbed laminations for example). This rate is in close agreement with the average value of 0.37 cm/yr estimated for the central area of Prince William Sound (Klein, 1983). Klein's was based on ^{210}Pb profiles in the sediment depth interval between 0-15 cm and assumed no mixing. Klein's sedimentation rate is therefore probably an upper limit because the absence of mixing was not thoroughly documented.

At station 4A, there is a change in the sediment texture with depth (Table 1). The top two samples are a silty clay with less than 5 percent sand, and with increasing depth, the sand fraction increases to 55 percent. The ^{210}Pb activity (Figure 2A) is higher than at station 2A at most depths, although the shape of the depth profile is similar. The log-linear slope between 11 and 31 cm (dashed line in Fig. 2A) would predict a maximum accumulation rate of 0.30 cm/yr assuming no mixing throughout this interval.

The Pu data, however, suggests that deep mixing may have affected core 4A. If so, the ^{210}Pb-derived sedimentation rate may be too high. This possibility is based on the measurable Pu in samples 41 cm and 51 cm deep in the core. Post-depositional migration of Pu is assumed not to be significant (Sholkovitz and Mann 1984). Sediment mixing may explain the levels of Pu measured at these depths, assuming that they are not the result of contamination during processing, or an artifact of coring. The mixing process would have to be slow and/or selective with respect to grain size, however, because the texture is not homogeneous.

Evidence for mixing throughout at least 10 cm is seen in the ratio of ^{238}Pu/^{239,240}Pu activity which, in the top three samples of core 4A, is between 0.044 and 0.048 (Table 3). In soil samples collected before 1964, this ratio was 0.024 (Hardy and others, 1973). As a result of the 1964 destruction of the ^{238}Pu-powered satellite generator (SNAP-9A), this ratio as much as doubled in soil samples from Alaska (Hardy and others, 1973). If

we interpret the maximum ^{238}Pu value at 11 cm to be the result of the 1963 maximum in atmospheric weapons testing, then the sample at 21 cm also must have been mixed to have similar isotopic ratios.

The relative magnitude of inventories (dpm/cm^2 or pico Curies per square cm: pCi/cm^2) of these isotopes can be an indication of the relative intensity of sedimentary processes, such as scavenging and/or accumulation. The isotopes can be thought of as a tracer already in the system and used to infer the transport and fate of other sediment reactive-contaminants. The limitation of this analogy is that the sources of these isotopes can be different than the sources of the contaminants. For example, we expect that the sources of the excess ^{210}Pb and Pu to sediments of Prince William Sound are: transport of land deposited isotopes with particulates in river water, direct atmospheric deposition, and transport into the Sound with inflowing bottom waters from the continental shelf. All these sources are thought to be significant in Puget Sound (Carpenter and others, 1984). We are not aware of data showing the relative importance of these routes for isotopes entering Prince William Sound.

The atmospheric flux of ^{210}Pb in this region is probably between 0.73 dpm/cm2 as measured on the coast of Washington (Carpenter and others, 1981) and 2 dpm/cm2 as measured at Hakodate, Japan (Nozaki and Tsunogai, 1973). If we assume an intermediate direct atmospheric flux of 1 dpm/cm2, it could support an inventory of 32 dpm/cm2 in underlying sediments assuming direct transfer to the sediments. If this were the only source, higher inventories would suggest preferential accumulation (by a variety of processes), and lower inventories would suggest non-deposition or erosion. The actual inventories of 91 and 66 dpm/cm^2 at stations 2A and 4A suggest that focussing of fine grained sediments and/or increased scavenging of 210Pb takes place at these areas of suspected deposition. Knowledge of the other sources of 210Pb to Prince William Sound is necessary to confirm this interpretation.

^{239,240}Pu inventories in soil samples from Alaska are between 0.4 and 0.92 millicuries per square km (mCi/km^2, Hardy and others, 1973). At stations 2A and 4A the inventories are 2.1 and 4.4 mCi/km^2, respectively. Reasons similar to those for high ^{210}Pb inventories are thought to explain the enrichment of Pu at the locations sampled. It is unclear however, why station 2A has the higher ^{210}Pb inventory and station 4A has the higher Pu inventory.

PRELIMINARY CONCLUSIONS AND RECOMMENDATIONS

The inventories and depth profiles of ^{210}Pb and Pu in sediments from Prince William Sound indicate that the locations cored have the potential for accumulating contaminants that are associated with particulates in coastal waters. The rates of sediment accumulation are not well defined because the complicating influence of bioturbation has not been evaluated. Assuming that active mixing is restricted to the upper 10 cm, the sedimentation rates may be about 0.3 cm/year at the two locations sampled, but these are taken as upper limits until more data are available.

Recommendations for future sampling and analysis are to increase the scope of the study to include samples from closer depth intervals. This will permit a more precise definition of the depth and magnitude of activity maximums which will aid the interpretation and justify the application of mixing models useful in resolving the effects of mixing and accumulation. Samples should also be analyzed from allocations representing a range of different sedimentary environments. Samples from 1 cm depth intervals through the upper 5 cm should be analyzed for ^{234}Th (half-life 24 days) analysis. Analyses of this isotope would provide an estimate of very recent mixing. In addition, measurements should be made to estimate the flux of these isotopes to Prince William Sound from the atmosphere, from rivers, and from the open ocean (with inflowing bottom water). This would help to explain the distribution of sediments and isotope inventories and help to predict the transport and fate of other sediment-reactive contaminants.

REFERENCES

Carlson, P.R.,and E Reimnitz. 1990, Characterization of sample sites along the oil spill trajectory in Prince William Sound and the Gulf of Alaska, (this volume).

Carpenter, R., M.L. Peterson, J.T. Bennett, and B.L.K. Somoyajulu. 1984. Mixing and cycling of uranium, thorium, and ^{210}Pb in Puget Sound Sediments. Geochemica et Cosmochemica Acta 48:1949-1963.

Carpenter, R., J.T. Bennett, and M.L. Peterson. 1981. ^{210}Pb activities in and fluxes to sediments of the Washington continental slope and shelf. Geochemica et Cosmochemica Acta 45:1155-1172.

Cutshall, N.H., I.L. Larson, and C.R. Olson. 1983. Direct analysis of ^{210}Pb in sediment samples: self-absorption corrections. Nucl. Inst. Methods 26:309-312.

EML Procedures Manual. 1982. Radiochemical Determination of Plutonium in Large Size Soil Samples. E-Pu-06-01. Environmental Measurements Laboratory, U.S. DOE.

Folk, R.L., 1974, Petrology of sedimentary rocks. Austin, Texas, Hemphill Publishing Company, 182 p.

Grebmeier, 1990, A radionuclide tracer and sediment oxygen uptake rates used to identify potential contamination zones on Alaskan shelf in response to the Exxon Valdez oil spill (this volume).

Hardy, E.P., P.W. Krey and H.L. Volchok. 1973. Global inventory and distribution of fallout plutonium. Nature 241:444-5.

Klein, L.H., 1983. Provenances, depositional rates and heavy metal chemistry of sediments, Prince William Sound, South-central Alaska. M.S. Thesis, University of Alaska, Fairbanks, Alaska, 96 p.

Nittrouer, C.A., D.J. DeMaster, B.A. McKee, N.H. Cutshall and A.L. Larsen. 1884. The effect of sediment mixing on Pb-210 accumulation rates for the Washington Continental Shelf. Marine Geology, 54:201-221.

Nozaki Y. and S. Tsunogai. 1973. Lead-210 in the north Pacific and the transport of terrestrial material through the atmosphere. Earth and Planetary Science Letters 20:88-92.

Santschi, P.H., Scott Nixon, Michael Pilson, and Carlton Hunt. 1984. Accumulation of sediments, trace metals (Pb,Cu) and total hydrocarbons in Narragansett Bay, Rhode Island. Estuarine, Coastal and Shelf Science 19:427-449.

Sholkovitz, E.R., and D.R. Mann. 1984. The pore water chemistry of ^{239,240}Pu and ^{137}Cs in the sediments of Buzzards Bay, Massachusetts. Geochem. Cosmochem. Acta 48:1107-1114.

Table 1.   Sediment Characteristics: Prince William Sound

Sample/ Depth (cm)	Water Content (%)	Sand (%)	Silt (%)	Clay (%)
Core 2A				
0-2	38.4	44	28	28
10-12	33.2	34	36	30
20-22	33.3	31	39	30
30-32	34.0	28	41	31
40-42	33.1	29	39	32
Core 4A				
0-2	65.7	5	28	67
10-12	65.8	4	33	63
20-22	52.7	31	24	45
30-32	41.2	45	19	36
40-42	38.1	42	21	37
50-52	36.2	55	17	28

Table 2. Radiochemical Data: Prince William Sound

Sample/ Depth (cm)	Excess ^{210}Pb ($\pm 1\sigma\%$) dpm/g		^{214}Pb ($\pm 1\sigma\%$) dpm/g		^{234,240}Pu ($\pm 1\sigma\%$) pCi/g	
Core 2A						
0-2	5.58	(4.3)	2.24	(2.9)	1.63 E-2	(10)
10-12	3.57	(4.8)	1.58	(3.0)	1.98 E-2	(13)
20-22	1.42	(9.6)	1.53	(2.6)	4.57 E-4	(33)
30-32	.44	(31.0)	1.48	(3.4)	*	
40-42	.21	(61.0)	1.58	(3.1)	*	
Core 4A						
0-2	8.29	(3.3)	1.48	(4.0)	2.82 E-2	(6)
10-12	6.26	(3.4)	1.50	(3.1)	4.88 E-2	(5)
20-22	2.47	(6.5)	1.21	(3.9)	2.28 E-2	(5)
30-32	.61	(18.0)	1.30	(2.8)	*	
40-42	*		1.30	(3.7)	2.25 E-4	(25)
50-52	*		1.23	(4.4)	4.62 E-4	(26)

*Below minimum detectable activity

Table 3. Additional Radiochemical Data: Prince William Sound

Sample/ Depth(cm)	$^{238}Pu(\pm1\sigma\%)$ pCi/g	$^{238}Pu/^{239,240}Pu$
Core 2A		
0-2	9.86 E-4 (38)	0.06
10-12	*	
20-22	*	
30-32	*	
40-42	*	
Core 4A		
0-2	1.36 E-3 (22)	0.048
10-12	2.19 E-3 (15)	0.045
20-22	9.92 E-4 (18)	0.044
30-32	*	
40-42	*	
50-52	*	

*Below minimum detectable activity
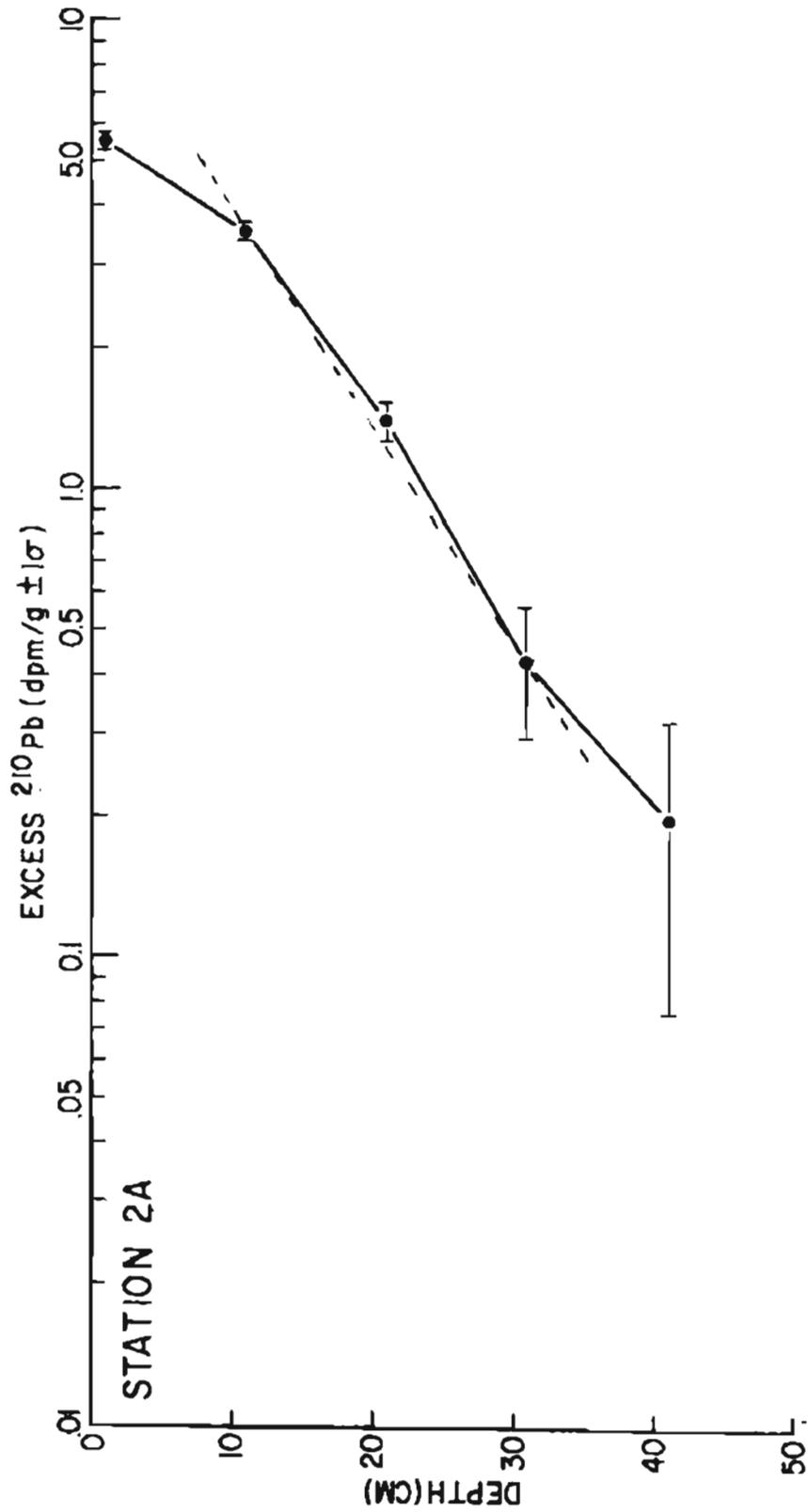
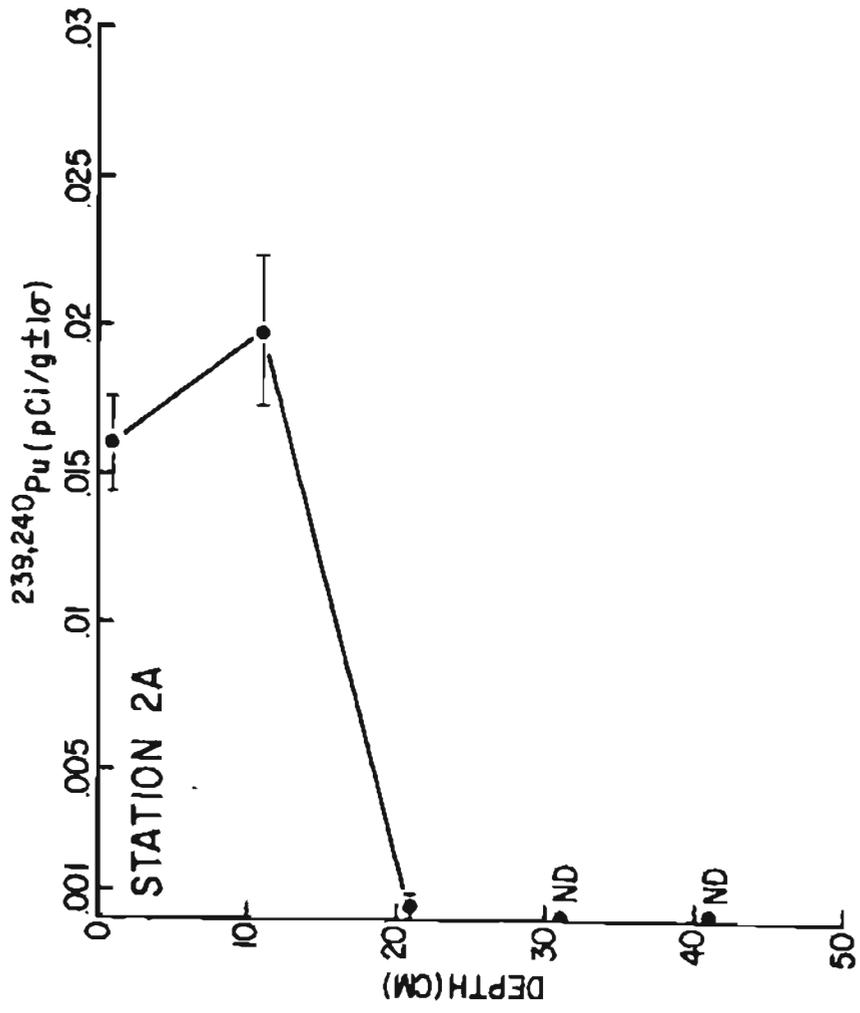Figure 1A. Distribution of excess ^{210}Pb with sediment depth.

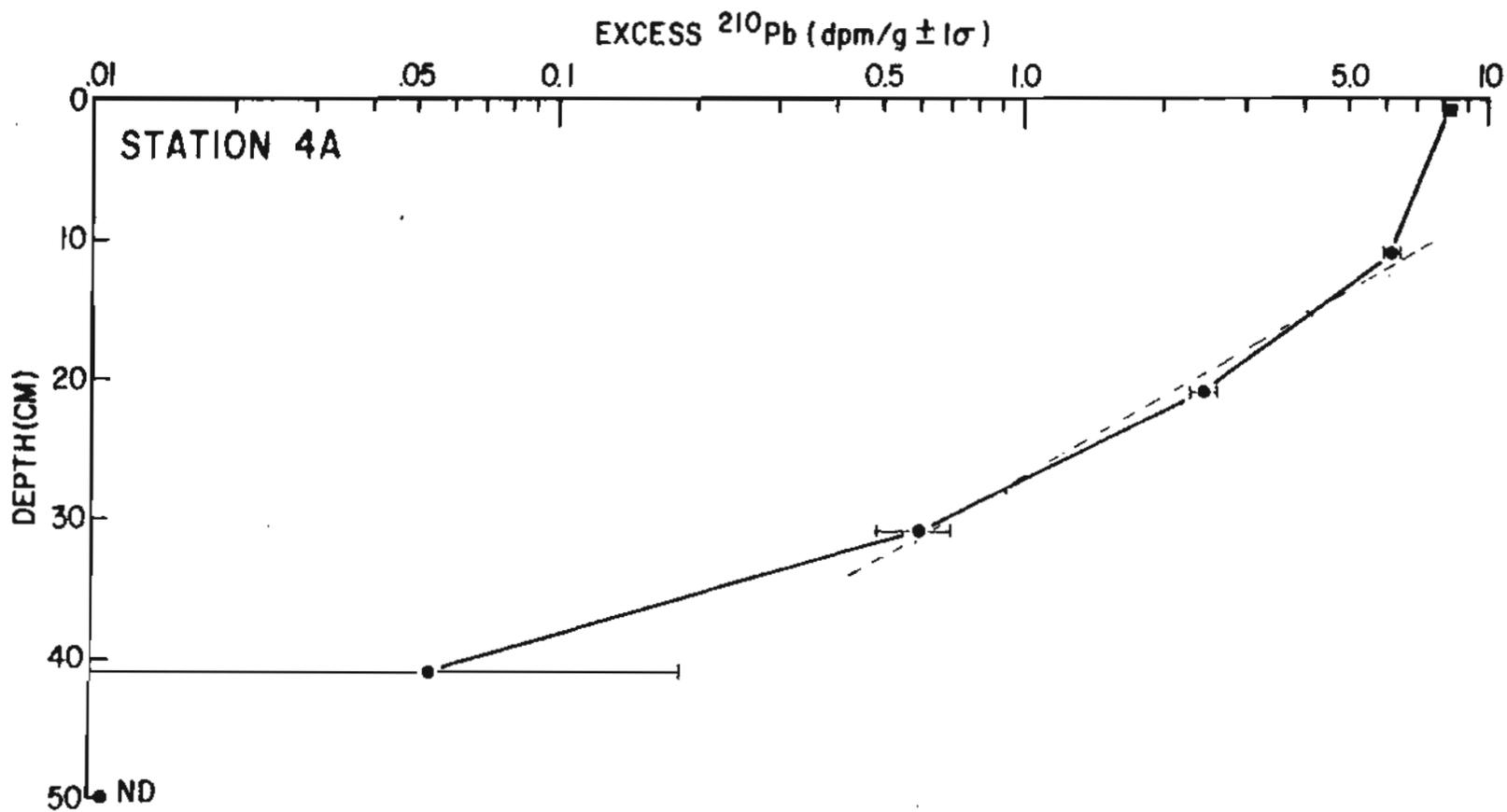Figure 1B. Distribution of ^{239,240}Pu with sediment depth. ND = non detectable.

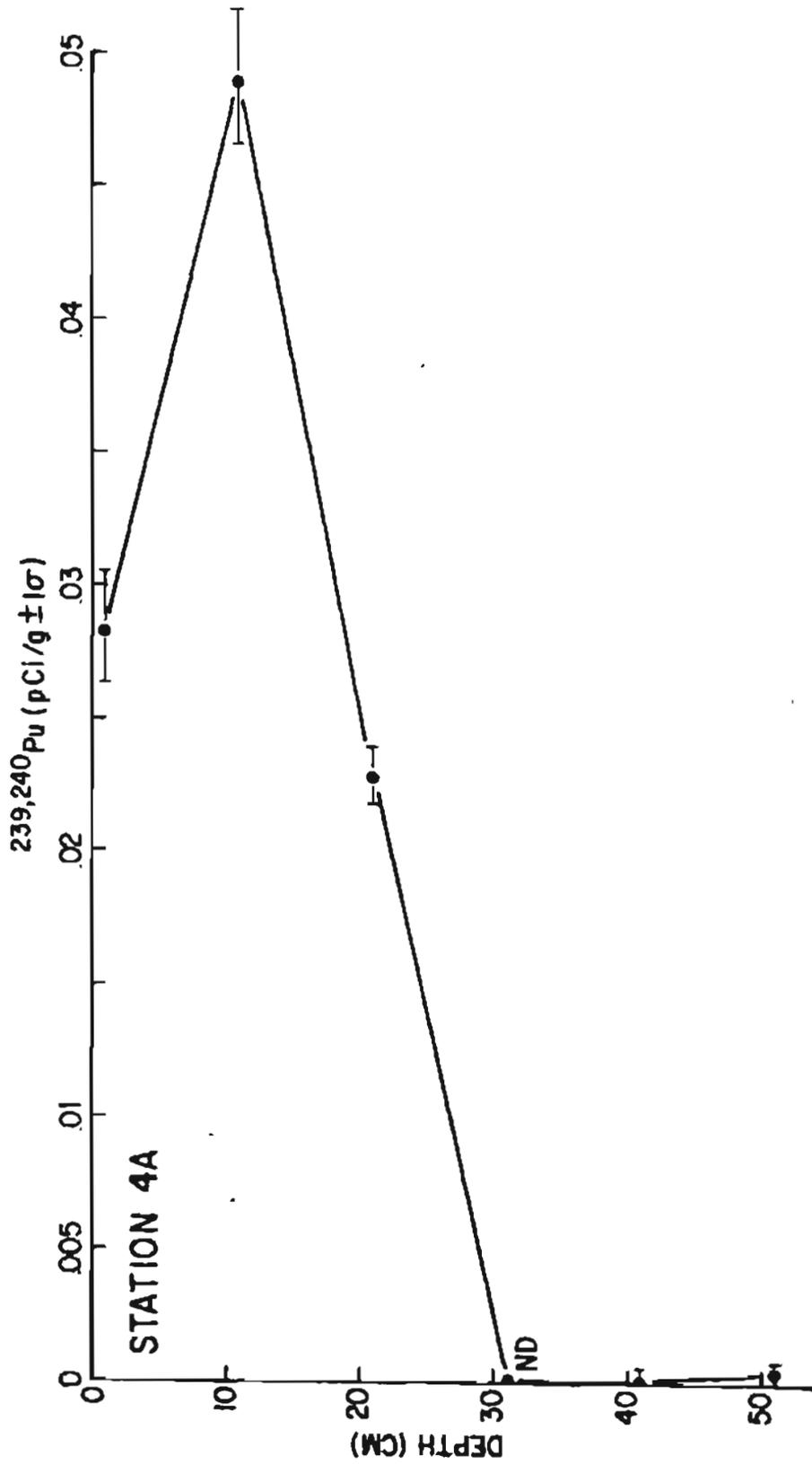Figure 2A. Distribution of excess ^{210}Pb with sediment depth.

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Figure 2B. Distribution of ^{239,240}Pu with sediment depth. ND = non detectable; activity