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COMMON ANALYTICAL ERRORS IN THE
RADIODATING OF RECENT SEDIMENTS

S.R. Joshi

Lakes Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

. Environment Canada

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ERREURS D'ANALYSE COURANTES DANS LA DATATION DE SÉDIMENTS RÉCENTS PAR DES ÉLÉMENTS RADIOACTIFS

S.R. Joshi

MANAGEMENT PERSPECTIVE:

Naturally-occurring Pb-210 and nuclear weapons testing-derived radionuclides such as Cs-137 are commonly used to derive sedimentation rates in recent sediments. Intricate mathematical models are used to interpret the observed anomalies in sediment core profiles of these radionuclides. Virtually no attention is paid to the possibility that some of these anomalies may, in fact, be due to some error in the measurement technique used. Four such possible errors are pointed out. It is shown that simple analytical considerations can significantly improve the quality of these measurements.

PERSPECTIVE GESTION

On utilise souvent le ^{210}Pb et les radionucléides dérivés des essais d'armes nucléaires comme le ^{137}Cs pour calculer les taux de sédimentation des sédiments récents. Des modèles mathématiques complexes sont utilisés pour l'interprétation des anomalies observées dans les profils de carottage pour la mesure de ces radionucléides. À toutes fins pratiques, on ne prête aucune attention à la possibilité que certains de ces anomalies soient attribuables, en fait, à une erreur ou l'autre dans la technique de mesure appliquée. Quatre de ces erreurs possibles sont indiquées. Il est montré que des considérations analytiques simples peuvent considérablement améliorer la qualité de ces mesures.

ABSTRACT

Four possible sources of analytical error in the measurement of
unsupported ^{210}Pb and/or nuclear fallout radionuclide (such as ^{137}Cs)
profiles in sediment cores are pointed out. Each of these errors, if
present, can significantly alter the true profile of the radionuclide
under consideration. It is shown that simple procedural modifications
can substantially improve the quality of analytical data that are
subsequently used to develop intricate mathematical models to aid the
interpretation of observed radionuclide profiles.

RÉSUMÉ

On indique quatre sources possibles d'erreurs analytiques dans
l'établissement de profils non confirmés de ^{210}Pb ou de
radionucléides de retombées radioactives (p.ex., ^{137}Cs) dans des
carottes de sédiments. Le cas échéant, chacune de ces erreurs
peut modifier considérablement le profil véritable du
radionucléide dosé. Il est montré que de simples changements
apportés aux méthodes peuvent radicalement améliorer la qualité
des données analytiques à l'origine de modèles mathématiques
complexes qui aident à l'interprétation de profils observés de
radionucléides.

Introduction

In the recent past, a number of investigators have used unsupported ^{210}Pb (half-life 22.26 y) and/or fallout radionuclides such as ^{137}Cs (half-life 30.1 y) in deriving recent sedimentation rates for various purposes (see Joshi 1985 and the references therein). In the past ten years or so, much effort has been expended in devising increasingly complex mathematical models to account for the observed anomalies in the expected sedimentary radionuclide, especially ^{210}Pb, profiles, and virtually no attention is paid to the possibility that some of these anomalies may, in fact, be due to some error in the measurement technique used. Since mathematical models undoubtedly help in the interpretation of radionuclide profiles, it would be prudent to ensure that the analytical data which form the backbone of all the subsequent modelling/interpretation efforts are of the highest quality possible. The present communication thus addresses the issue of laboratory measurements and attempts to show that simple manipulations can significantly improve the quality of these measurements.

Sediment Core Sectioning

Two general techniques are usually employed to section the sediment core. In the first, the entire sediment core is frozen prior to precise sectioning. In the second, and more common, the sediment

core is sectioned at room temperature or lower (4°C usually) by pushing it outward using an extruder. Both methods can distort the profile of a radionuclide such as ^{137}Cs due to the shearing effect of the sampler and/or corer. The effect would be more serious when extrusion method is applied. The plots shown for the ^{137}Cs profile (Figure 1) in a Lake Huron sediment core (Durham and Joshi, 1980a) illustrate this point. This core was retrieved using a Benthos gravity triple corer and extruded using a NWRI-designed extrusion unit. The sediment core sections were carefully subdivided into central and outer portions both of which were separately assayed for ^{210}Pb, ^{226}Ra and ^{137}Cs. While the ^{210}Pb and ^{226}Ra measurements were virtually identical for the two portions, considerable downward migration of ^{137}Cs was easily discernible in the outer portion. In the absence of the sectioning procedure used, the ^{137}Cs profile would obviously have depicted much deeper downward migration of this radionuclide than was actually the case. Clearly, the quality of ^{137}Cs measurements can be substantially improved if the outer portions of the core sections are excluded prior to analyses.

Core Section Thickness

In most situations involving the use of a core extruder, one generally relies on visual measurement of the section thickness. In almost all cases, one finds that the individual section thicknesses do not add up to the original length of the sediment core. The situation is usually worse in cases where core was sectioned at smaller

intervals. This is a very simple correction to apply, yet many laboratories underestimate its importance. Discordant results are often obtained in studies where different groups analyze different cores obtained simultaneously (say, using a Benthos gravity triple corer) but only one group corrects the section depths. The importance of this correction may be realized by comparing the ^{137}Cs profile shown in Figure 1 (where corrected depths are used) with that obtained using uncorrected depths. The two plots are shown in Figure 2 from which it can be easily discerned that the uncorrected depth plot underestimates the true depth by nearly 40%. Precise sample thicknesses can be obtained simply by dividing the wet mass of the sediment by its bulk density and area. This correction is based on very simple considerations:

The volume, V, of sediment in a core section is given by

$$V = A.t , \tag{1}$$

where A is the area of the section and t its thickness. The volume is also given by

$$V = \frac{M}{D} , \tag{2}$$

where M is the wet mass of the sediment and D its density (i.e. bulk density).

From (1) and (2), the true thickness (i.e. t) is simply

$$t = \frac{M}{A.D} \tag{3}$$

^{210}Pb Measurements

At least three different approaches are available for deriving the levels of total ^{210}Pb in sediment core sections. Only one of these - the γ-ray spectrometric technique - provides a direct determination of ^{210}Pb, the other two determine ^{210}Pb either via its 5.01-day half-life β-emitting ($E_{max} = 1.17$ MeV) daughter ^{210}Bi or the 138-day α-emitting (5.3 MeV) granddaughter ^{210}Po.

The direct measurement of ^{210}Pb is possible only via its 46.5-keV gamma-emission (4%), since, at the moment, its low-energy β-emission ($E_{max} = 61$ keV) can not be routinely measured at the desired level of sensitivity. To date very few researchers have utilized direct γ-ray spectrometric measurement techniques since its introduction in 1976 although the nondestructive nature of the technique and its capability in providing simultaneous measurements for ^{226}Ra (Joshi in press) and other low-energy γ-emitters makes it by far the preferred of the three common approaches. A major point in applying this technique to sediment samples concerns the self-absorption of low-energy gamma-rays. This can lead to unrealistic values of ^{210}Pb in the sample unless the detector efficiency is also based on the same

sample material. The self-absorption can also be accounted for by measuring the transmission of the y-ray through the sample and the reference material (Cutshall and others 1983; Joshi in press). With the recent commercial availability of reliable planar germanium detectors required for the unambiguous measurement of low-energy y-rays, this technique is likely to gain in popularity and should indeed be preferred in environmental studies as it not only provides a simultaneous scan for a number of other radionuclides but also allows the subsequent assay of the same sample for non-radioactive pollutants. The technique provides adequate sensitivity for most practical situations.

The measurement of ^{210}Pb via ^{210}Bi is an established method. The method, however, is destructive and requires elaborate chemical manipulations to ensure removal of possible interferences (Joshi and Durham 1976). Due to the complexity of the wet chemistry involved, this method has been used by very few researchers although it permits simultaneous measurements on ^{226}Ra as well as ^{137}Cs.

By far the most popular method for assaying ^{210}Pb in sediments is based on the ^{210}Po measurements. The destructive procedure derives its popularity from the fact that polonium can be autoplated on metallic silver or copper discs following very simply hydrochloric acid extraction. This is a near-specific feature of the procedure (Flynn 1968). Ironically, it is this procedure which is most often incorrectly used. The assumption of equilibrium between ^{210}Po and

^{210}Pb, especially in the top few sections of a sediment core, constitutes the first possible error. The unstated, but implicit, assumption of identical behavior of both lead and polonium in the aquatic ecosystem under consideration is also an unrecognized source of error. By far the most common - and easily preventable - error in polonium measurement involves complete ignorance of the fundamental principles of radioanalytical chemistry. Two types of errors in this class are readily discerned. In the first, the measurements are carried out without adding any tracer (^{208}Po) to obtain the overall yield for the entire procedure. In the second type of radioanalytical error, the tracer is added but the counting is done on an α-particle counter rather than on an α-particle spectrometer. Some of these studies by non-chemists may rely on the 'average yield' obtained in several separate measurements without realizing that in the radioanalytical work there is no such thing as the 'average yield' and one must determine yield for each sample assayed. Such analytical oversights naturally undermine the quality of the work where often much effort has been devoted to model these same very data. Having said this about the misuse of the ^{210}Po procedure, given below are some general suggestions for consideration by non-radiochemists doing radioanalytical work:

1. Always store subsamples for sufficiently long periods of time to ensure equilibrium between ^{210}Po and unsupported ^{210}Pb. Theoretically, this requires a storage time of at least 1.9 y since ^{210}Po grows in with a half-life of 138 days. In most

situations, however, an investigator can not afford such long waiting periods and proceeds to complete the analyses without worrying about the equilibrium status of ^{210}Po with respect to ^{210}Pb. The magnitude of this error would obviously be in proportion to the sedimentation rate, i.e. higher the sedimentation rate, higher the extent of this type of error. In cases where the equilibrium status of ^{210}Po is in doubt, the subsample should be stripped off all existing ^{210}Po and the solution set aside for at least four months prior to autoplatiang the ^{210}Po ingrown since the initial removal. The amount of total ^{210}Pb present in the subsample should then be calcualted with reference to this growth of ^{210}Po. This approach necessitates an unambiguous measurement of the ^{226}Ra level using an independent technique since all ^{210}Po associated with the ^{226}Ra-supported ^{210}Pb will also be removed.

2. Always use ^{208}Po as yield monitor and assay autoplated sources on an α-particle spectrometer and not on an α-particle counter since the α-particle energies of ^{208}Po (5.11 MeV) and ^{210}Po (5.305 MeV) are separable only on a spectrometer using a detector such as the commonly-available silicon surface-barrier detector. Furthermore, the relatively low background of a typical surface barrier detector (3-4 counts per day vs. 50-60 counts per day for the α-particle region of a relatively high-priced low-background gas-flow proportional counter) can provide better sensitivity if the detection efficiencies of the two systems are similar.

3. Never use any glassware for radiochemical work involving polonium since several polonium compounds are known to adsorb onto glass surfaces. Quartz is perhaps the best choice though Teflon or similar materials are also suitable for most situations. Avoid heating above 120°C during HCl leaching and above 90°C during plating since $PoCl_4$ is highly volatile.

Estimation of ^{226}Ra-Supported ^{210}Pb

In order to derive the concentrations of unsupported or atmospherically-delivered ^{210}Pb in the sediment core samples, it is necessary to subtract the contribution of ^{210}Pb originating from sedimentary ^{226}Ra from total ^{210}Pb present in samples. The implicit assumptions are that ^{226}Ra-delivered ^{210}Pb behaves similarly to unsupported ^{210}Pb in the deposited sediments and that the precursor of supported ^{210}Pb, ^{222}Rn - the 3.85-day half-life gaseous daughter of ^{226}Ra - shows little or no migration in the sediment core. Both these assumptions are difficult to verify for the particular system under consideration. It is possible that the known solubility of ^{222}Rn in water (pore water) could result in subsequent migration of supported ^{210}Pb. Fortunately, in most cases, the general levels of supported ^{210}Pb are usually very low compared to those of the unsupported ^{210}Pb and, therefore, the introduced error is very low. However, in cases where the two levels are comparable, the error would be significant.

Two approaches are used in deriving estimates of supported ^{210}Pb. In the first, the levels are inferred from simultaneous measurements of the ^{226}Ra content of the sample, the assumption being that supported ^{210}Pb is in equilibrium with detrital ^{226}Ra. In the second, the supported ^{210}Pb level is inferred from few measurements on deeper sections of the sediment where unsupported ^{210}Pb is deemed to have decayed completely, the major assumption being that supported ^{210}Pb is constant throughout the core. That this may not be a valid assumption is obvious from the data (Durham and Joshi 1980b) shown in Table 1 where levels of ^{226}Ra are found to vary considerably within the sediment core. Table 2 gives the values of parameters derived, following Durham and Joshi (1980a, 1980b), using this data and the above two approaches. It is easily discerned that the values obtained using the two approaches can differ by as much as 22%. The discrepancy would be even higher for the Lake Quevillon (Durham and Joshi 1980b) data (not shown) where the levels of supported and unsupported ^{210}Pb are comparable. Obviously in such instances it is more logical to base estimates of supported ^{210}Pb levels on individual measurements of the ^{226}Ra contents of the samples.

In conclusion, four possible sources of analytical error in the assay of unsupported ^{210}Pb and/or nuclear fallout radionuclides such as ^{137}Cs in sediments are discussed. Each of these errors, if present, can substantially alter the radionuclide profile. It is shown that simple experimental procedures can significantly improve the quality of analytical data that are subsequently used to formulate

complex mathematical expressions to evaluate the observed radionuclide profiles. Perhaps, even more importantly, this communication underlines the need for eliminating any other possible errors. One such error could reside in the assumption of constant flux of atmospherically-derived ^{210}Pb as has recently been pointed out by Nevissi (1985). Work is in progress to examine the historical variations in the flux of this unsupported ^{210}Pb.

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Table 1. Total ^{210}Pb and ^{226}Ra in a Lake Matagami sediment core[a].

Section depth in core (cm)	Activity (pCi/g dry)	
	Total ^{210}Pb	^{226}Ra
0.0 – 0.9	5.65 ± 0.32	0.45 ± 0.05
0.9 – 1.6	3.68 ± 0.27	0.33 ± 0.05
1.6 – 2.3	2.83 ± 0.14	0.74 ± 0.07
2.3 – 2.9	2.97 ± 0.19	0.55 ± 0.05
2.9 – 3.5	3.00 ± 0.14	0.59 ± 0.06
3.5 – 4.3	2.17 ± 0.17	0.59 ± 0.05
4.3 – 5.0	1.84 ± 0.21	0.28 ± 0.16
5.0 – 5.8	0.97 ± 0.26	0.62 ± 0.05

[a]Data source Durham and Joshi (1980b).

Table 2. Values of parameters derived from analytical measurements[a]

Approach	Linear sedimentation rate (mm yr^{-1})	Mass sedimentation rate (mg cm^{-2} yr^{-1})	Flux of unsupported ^{210}Pb at the sediment/water interface (pCi cm^{-2} yr^{-1})
Variable ^{226}Ra	0.81	59	0.36
Constant ^{226}Ra (0.74 pCi/g)	0.69	50	0.32
Constant ^{226}Ra (0.28 pCi/g)	1.00	72	0.42

[a]Data source Durham and Joshi (1980b).

FIGURE CAPTIONS

Figure 1. Effect of sub-sample selection on the observed ^{137}Cs profile
in a Lake Huron sediment core.

Figure 2. The 'measured' and 'corrected' depth profile of ^{137}Cs in a
Lake Huron sediment core.

Central portion
Outer portion
* Not detected

^{137}Cs (p Ci / g dry sediment)

Measured depth in core (cm)

Figure showing ^{137}Cs (pCi/g dry sediment) versus Depth in Core (cm), comparing Corrected depth (solid line) and Uncorrected depth (dashed line).