Chemical Procedures for the analysis of dissolved Po-210 and Pb-210:

Mark Baskaran, Wayne State University

1. Introduction:

Both Po and Pb are particle-reactive, the samples were filtered within 1-2 hours after collection. The water samples were collected from the Niskin bottles in acid-cleaned cubitainers. The filtered 12 to 22 liter of seawater samples were stored in acid-cleaned polyethylene (LDPE) cubitainers, and acidified with trace-metal grade 6M HCl to a pH of ~2 (60 mL of 6M HCl for each of the sample, ~20 L) within two hours after collection (as soon as possible, details given below). The cubitainer cap was sealed with plastic wrap (e.g., Parafilm) and stored double bagged in black plastic bags. The samples were appropriately labeled with the GEOTRACES specific number ID according to sample station, date and depth. The date is requisite in the radionuclide decay and in-growth equations.

2 Laboratory Analysis

The determination of ^{210}Po and ^{210}Pb in dissolved water samples is routinely conducted on the same sample, first by measuring ^{210}Po (called 'in-situ' ^{210}Po) and then keeping the sample for a period of 6 months to 2 years for the in-growth of ^{210}Po from ^{210}Pb. Detailed procedure is given in the *Sampling and Sample-handling Protocols for GEOTRACES Cruises* (Cookbook) available at http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf. The second ^{210}Po (called 'parent-supported') measurement provides the data on the concentration of ^{210}Pb. There is a number of important decay and in-growth corrections that need to be applied in the calculation of the final activities of in-situ ^{210}Po and ^{210}Pb activities. Reference is made to Baskaran et al. (2013) for evaluation of these corrections and basis for their calculations.

The most widely used instrument for analyzing dissolved ^{210}Po and ^{210}Pb in seawater is isotope dilution using alpha spectroscopy (Sarin et al., 1992; Radakovitch et al., 1998; Hong et al., 1999; Kim et al., 1999; Rutgers van der Loeff and Moore, 1999; Baskaran et al., 2009). For this study, two of the Octete PC 8-input alpha spectrometers (a total of 16 detectors) were used. The background of each of the detector used for the measurements of ^{210}Po was monitored periodically and the backgrounds of the detectors are given in Table 1. The efficiency of each of the alpha detectors was determined using standard Am and Pu source. Note that the alpha detector efficiency is not required in the calculation of the ^{210}Po count rates or activities, as ^{209}Po is an internal tracer and the $^{210}Po/^{209}Po$ ratio and the activity of ^{209}Po are only involved in the calculation of ^{210}Po activity.

Table 1: Alpha detector Efficiency and Background Counts per hour (cph)

Detector #	^{209}Po Bkg cph	^{210}Po Bkg cph	Am-based detector efficency (%)
D-1	0.06 ± 0.01	0.05 ± 0.01	27.4
D-2	0.08 ± 0.01	0.01 ± 0.01	16.7
D-3	0.09 ± 0.02	0.01 ± 0.01	17.7
D-4	0.04 ± 0.01	0.02 ± 0.01	28.7
D-5	0.06 ± 0.01	0.02 ± 0.01	27.0
D-6	0.06 ± 0.02	0.03 ± 0.01	26.7
D-7	0.07 ± 0.02	0.04 ± 0.01	26.6
D-8	0.04 ± 0.01	0.03 ± 0.01	27.6
D-9	0.06 ± 0.01	0.03 ± 0.01	27.2
D-10	0.04 ± 0.01	0.02 ± 0.01	27.4
D-11	0.03 ± 0.01	0.02 ± 0.01	27.1
D-12	0.06 ± 0.01	0.02 ± 0.01	26.6
D-13	0.05 ± 0.01	0.03 ± 0.01	28.0
D-14	0.07 ± 0.01	0.04 ± 0.01	27.9
D-15	0.06 ± 0.01	0.04 ± 0.01	26.9
D-16	0.06 ± 0.01	0.03 ± 0.01	26.9

The total weight of the sample was measured on a balance to a precision ± 1 g. Each batch comprised of ten water samples along with a reagent blank. Each batch of samples were transferred in to pre-acid-cleaned 20-L buckets. To each of the water sample a pre-weighed amount of NIST Standard Reference Material ^{209}Po, corresponding to an activity of ~ 1-2 dpm for 20-L water sample was added. It is assumed that there is no loss of ^{210}Po and ^{210}Pb to walls of the container during the storage period (from collection onboard the ship till beginning of sample processing offshore laboratory). However, some of the water sample stored cubitainers were leached for adsorbed ^{210}Po and ^{210}Pb (details given later). To the water sample, 20 mg of stable

Pb carrier was added as $PbCl_2$ prepared from a fossil lead (to have minimum blank ^{210}Pb and ^{210}Po) and 100 mg of iron carrier (5 mg Fe/L of water) in the form of $FeCl_3$ was also added. The

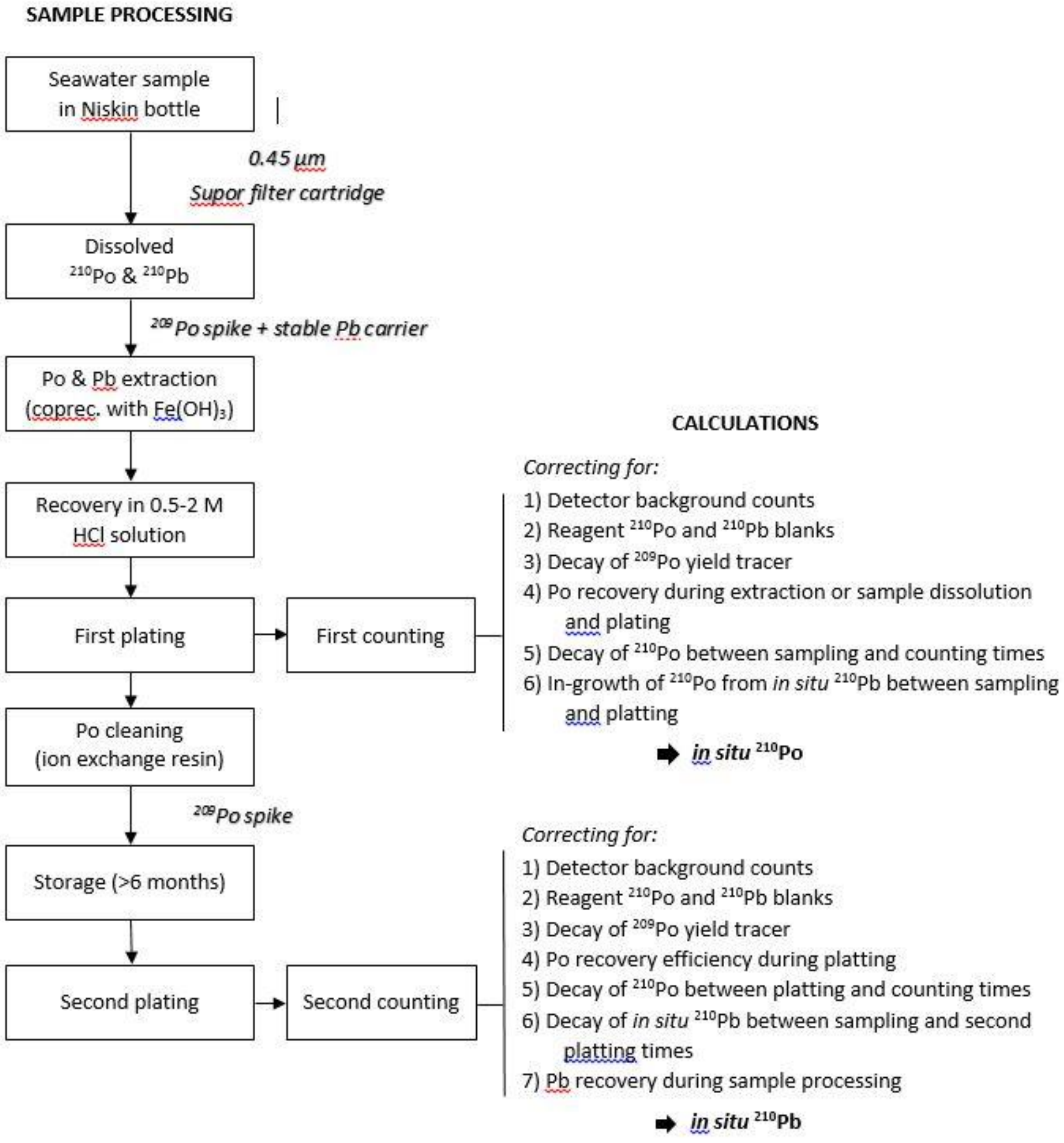

Figure 1: Flow chart of chemical processing for dissolved ^{210}Po and ^{210}Pb.

acidified and spiked sample with stable Pb, ^{209}Po and Fe carriers was allowed to equilibrate for about 24 hours. After equilibration, Pb and Po were simultaneously co-precipitated with

$Fe(OH)_3$ by adding ammonium hydroxide to a pH of first to 4 and add 1 ml of 10% sodium chromate to enhance the Pb yields by co-precipitation of lead chromate. The precipitate and the solution were separated by successive decanting, followed by filtration. The precipitate was dissolved by adding a few milliliters of 6M HCl to the filter paper followed by washing of the filter paper with deionized water to bring the volume for plating to 0.2-0.5 N HCl medium. To this solution, 200 mg of ascorbic acid was added to yield a colorless solution and adjusted the pH ~2. The Po isotopes are separated by spontaneous electroplating onto a polished silver disc or planchet, where the reverse side is covered by a transparent tape (Lee et al., 2014). This residual solution is dried completely and the residue is taken in 5 ml of 9M HCl for the separation of residual Po from the Pb using an anion-exchange column, AG1-X8 (Baskaran et al., 2013). The purified Pb fraction was spiked again with ^{209}Po and stored in a clean plastic bottle for at least 6 - 12 months after which the ^{210}Pb activity was measured by the ingrown activity of its granddaughter ^{210}Po. In a couple of Po plates (out of a total of 135 samples + 13 reagent blanks), the thickness of the source was found to be thick likely from iron compounds, and the Ag planchets were leached for one hour with concentrated (~12 M) HCl. After a major portion of the impurities plated on the Ag disk was removed, and the same cleaned plate was recounted without further loss of Po and improved resolution.

For the determination of ^{210}Pb yield, a precise aliquot of the stored solution (5%) was taken after column separation (and ^{209}Po addition) in an acid cleaned polyethylene bottle for stable Pb determination. The concentrations of stable Pb were determined using ICP-OES. The remaining solution was utilized for the electroplating of ingrown ^{210}Po as described above. The final activity of ^{210}Pb calculation involves the in-growth factor for ^{210}Po, decay of ^{210}Pb from collection to the second ^{210}Po plating, and chemical recovery of Pb.

References:

Baskaran, M., G.-H. Hong and P.H. Santschi (2009). Radionuclide analysis is seawater. In.: “Practical Guidelines for the analysis of seawater” *In:* Practical Guidelines for the Analysis of Seawater, *Ed. Oliver Wurl, CRC Press, 259-304.*

Church, T.M., S. Rigaud, M. Baskaran, A. Kumar, J. Friedrich, P. Masque, V. Puigcorbé, G. Kim, O. Radakovitch, G. Hong, H.-Y. Choi and G. Stewart (2012). Inter-calibration studies of ^{210}Po and ^{210}Pb in dissolved and particulate sea water samples. Limnol. Oceanogr. (Methods), 10, 776-789.

Baskaran, M., T.M. Church, G.-H. Hong, A. Kumar, M. Qiang, H. Choi, S. Rigaud, K. Maiti (2013). Effects of flow rates and composition of the filter, and decay/in-growth correction factors involved with the determination of in-situ particulate ^{210}Po and ^{210}Pb in seawater. Limnol. Oceanogr. (Methods), 11, 126-140.

Hong, G.-H., Park, S-K., Baskaran, M., Kim, S.-H., Chung, C.-S. and Lee, S.-H., 1999. Lead-210 and polonium-210 in the winter well-mixed turbid waters in the mouth of the Yellow Sea. Conti. Shelf Res., 19: 1049-1064.

Kim, G., Hussain, N., Church, T.M. and Yang, H.S., 1999. A practical and accurate method for the determination of ^{234}Th simultaneously with ^{210}Po and ^{210}Pb in seawater. Talanta 49:851-858.

Lee, H.M., G.-H. Hong, M. Baskaran, S.H. Kim, Y. I. Kim, and K.C. Cho (2014). Evaluation of plating conditions on the recovery of ^{210}Po onto the Ag planchet. Applied Radiat. Isot. 90, 170-176

Radakovitch, O., Cherry, R.D., Heyraud, M. and Heussner, S., 1998. Unusual Po-210/Pb-210 ratios in the surface water of the Gulf of Lions. Oceanologica Acta 21, 459-468.

Rutgers van der Loeff, M. and Moore, W.S., 1999. Determination of natural radioactive tracers. In *Methods of seawater analysis*, ed. K. Grasshof, M. Ehrardt, and K. Kremling, Weinheim, Germany: Wiley-VCH, pp. 365-397.

Sarin, M.M., Bhushan, R., Rengarajan, R., and Yadav, D.N., 1992. The simultaneous determination of ^{238}U series nuclides in seawater: results from the Arabian Sea and Bay of Bengal. Indian Jour. Mar. Sci. 21: 121-127.