Assessment criteria for radionuclides in Geotraces IDP2017

(4th draft version, October 21st, 2015, Walter Geibert, Geotraces S&I committee)

Different half-lives, sources and detection methods for the individual radioisotopes mean that no general recommendations can be made- not even the apparently obvious one for a certified reference material (CRM).

The data quality to be expected for the individual nuclides differs depending on half-life, maturity of the analytical technique, the number of laboratories and several other parameters. Expectations are most rigorous for the **only radionuclide key parameters ^{230}Th and ^{231}Pa**. Additionally, all isotopes for which a Geotraces intercalibration exercise has been conducted should be included in the IDP, namely **^{232}Th, ^{10}Be, ^{226}Ra, ^{228}Ra, ^{224}Ra, ^{223}Ra, ^{234}Th, ^{210}Po, ^{210}Pb, and a number of anthropogenic radionuclides as specified below, if the labs can demonstrate the validity of their data by (1) <u>internal</u> quality control and by (2) suitable <u>external</u> comparison with other institutions.** Additional isotopes of interest can and should be incorporated, if suitable measures to ensure data quality, both internally and externally, can be demonstrated. Often, substantial analytical progress has been made since the intercalibration exercises were initiated. We encourage laboratories who analyze less common isotopes to exchange suitable samples with colleagues at other institutions to demonstrate the reproducibility of the analyses. We also welcome new efforts to intercalibrate additional radioisotopes at a larger scale.

Please find specified below which quality criteria would be expected to be met for the individual isotopes. I also include a number of isotopes for which currently an intercalibration exercise does not yet exist, in order to find ways these data can still make their way in to the next IDP, or the final product. Many of the less common radioisotopes provide unique information, and constant analytical progress, not least as a result of GEOTRACES, brings them within analytical reach.

1 GEOTRACES KEY PARAMETERS

1.1 ^{230}TH

^{230}Th has been intercalibrated (Anderson et al. 2012). There is a good number of labs that can produce data of high quality. Particulate samples are a challenge due to lab requirements for perchloric/hydrofluoric use, with very low blanks needed. Recent results of a comparison of a full digestion and a nitric acid-HF leach indicate that comparable results may be obtained without digesting the filter material, as long as the silicates are fully dissolved.

<u>Requirements</u>

Intercalibrated lab (if not part of initial intercalibration, this needs to be done using shared reference materials/standards with a lab that was part of the initial exercise). LDEO offers the distribution of an artificial sea water reference material. Results of the intercalibration need to be documented so they can be part of the IDP assessment.

Crossover stations/ duplicate analyses by a separate lab

Regular analysis of reference material(s) together with samples

Methods

MC-ICP-MS, SF-ICP-MS or TIMS

1.2 ^{231}Pa

^{231}Pa has been intercalibrated (Anderson et al. 2012). There are a small number of labs that can produce data of high quality. Particulate samples are a challenge due to lab requirements for perchloric/hydrofluoric use, with very low blanks needed. HNO3/HF leach seems to provide full digestion of particulate material as for ^{230}Th.

Requirements

Intercalibrated lab (if not part of initial intercalibration, this needs to be done using shared reference materials/standards with a lab that was part of the initial exercise). Results of the intercalibration need to be documented so they can be part of the assessment.

Crossover stations/duplicate analyses by separate lab

Regular analysis of reference material(s) together with samples

Methods

MC-ICP-MS, SF-ICP-MS or TIMS

2 Other long-lived natural isotopes

2.1 ^{232}Th

^{232}Th should be treated with the same care as other contamination-prone elements. In this context, the only exception is that it is usually measured by isotope dilution, as a byproduct of ^{230}Th analysis (key parameter). It has been intercalibrated as part of the ^{230}Th/^{231}Pa study (Anderson et al. 2012). A comparison of ^{232}Th via isotope dilution and ^{232}Th measured as part of multielement analyses still stands out. We encourage the community to identify suitable crossover stations to explore comparability of the analytical approaches.

2.2 ^{10}Be

Has been included in the intercalibration, but very few or no samples have actually been taken to my knowledge. Only two labs reported results for the intercalibration (which were of good quality) (Anderson et al. 2012).

3 RADIUM ISOTOPES

3.1 ^{226}Ra

^{226}Ra has been intercalibrated (Charette et al. 2012). Results indicate that **data validation is essential**.

Minimum requirements for data is:

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment, and
B) regular analysis of ^{226}Ra standards traceable to certified standards or reference materials

Additional credibility by

A) Crossover stations
B) Comparison to historical datasets of data that were validated with certified standards

Methods:

- Gamma-spectrometry (with specifics about the control of gas loss- ^{222}Rn decay products)
- MC-ICP-MS or SF-ICP-MS. TIMS possible.
- Alpha-scintillation after controlled (sealed) ingrowth of ^{222}Rn

3.2 ^{228}Ra

^{228}Ra has been intercalibrated (Charette et al. 2012). Data are generally consistent, but precision is typically not great.

Minimum requirements for data is:

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment.
B) Analysis of ^{228}Ra in samples traceable to CRMs (e.g., established equilibrium with certified ^{232}Th)

Additional credibility by

A) Crossover stations
B) Comparison to historical datasets of data that were validated with certified standards

Methods:

- Gamma-spectrometry
- MC-ICP-MS or SF-ICP-MS
- ^{228}Th-ingrowth and alpha-spectrometry

3.3 ^{224}Ra, ^{223}Ra

The short-lived Ra isotopes were intercalibrated (Charette et al. 2012). Short half-lives make obtaining a CRM for the isotopes difficult; only samples of the parent isotopes ^{227}Ac and ^{232}Th or ^{232}U in equilibrium can be used as an alternative. There are some concerns about the stability of ^{227}Ac (parent of ^{223}Ra) on fiber, but deviations are typically below the analytical error on real samples. The verification of adsorption efficiencies is relevant, as the intercalibration exercise has shown that the assumption of quantitative adsorption does not always hold true.

Minimum requirements for data is:

A) participation in intercalibration, or post-intercalibration analysis of intercalibrated shared standards. These results need to be reported for the assessment.
B) Reproducibility checks with in-house standards

Crossover stations bring no real additional credibility due to short half-lives and variable sources.

Methods:

Radium delayed coincidence counting (RaDeCC)
Gamma counting (less common)

3.4 ^{234}TH

^{234}Th has been intercalibrated (Maiti et al. 2012). Results indicate that there is a good number of labs producing high quality data. Quality suffers with smaller activities (particulate samples) and higher corrections (decay of ^{234}Th in older samples). There is no simple way of shipping CRMs for an analysis. However, it is known that ^{234}Th is in equilibrium with ^{238}U (known from salinity) in depths below about 1000 m in most oceanographic settings (away from nepheloid layers and plumes, and using sufficiently large volumes to avoid potential inhomogeneities). This allows the determination of a reference value on most stations. This part is essential, as it also can serve to verify detector efficiencies. The exchange of sample material between groups for external verification of the data is encouraged, but not always possible.

Minimum requirements for data is:

Intercalibration (or post-intercalibration exchange of filters to calibrate counters)

Reporting replicate results for deep samples (~1000 m) in equilibrium from each cruise

Methods:

On-board beta-counting combined with thorium yield tracer (ICP-MS or alpha counting)

4 POLONIUM/LEAD DISEQUILIBRIUM

4.1 ^{210}PO AND ^{210}PB

These isotopes are measured in a very similar manner on the same samples and are therefore treated together. Eight labs took part in an intercalibration exercise (Church et al. 2012). Results for solid CRMs are excellent. Standard deviations increase quickly for lower sample volumes, and there seems to be a variation in sensitivity of the labs to blank issues. It is worth noting that Po shows a high affinity for PES (Supor®) filters.

Minimum requirements

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment.
B) Rigorous assessment of blank (reported), especially for small volumes and particulate material, and analysis of CRMs

Additional credibility of data by

A) Reporting analyses for locations that can serve as a reference (historical data of high quality in deep waters or similar).
B) Crossover stations

Method

- Alpha-spectrometry

5 INTERCALIBRATED ANTHROPOGENIC NUCLIDES

In general, the analysis of anthropogenic nuclides in seawater requires very large sample volumes (min 10s, often 100s of liters), and very few labs are specialized on this type of analyses. This makes crossover stations as well as the shipping of sea water reference materials nearly impossible. For a number of isotopes, only two labs took part in the exercise, and these two will be carrying the main load of analyses. It is essential that each lab wishing to contribute data to the IDP is in direct exchange with one of the intercalibrated labs to share materials (standards, spikes, solid reference materials as appropriate).

5.1 ^{137}Cs

This has been measured by four labs as part of an intercalibration exercise (Kenna et al. 2012).

Minimum requirements

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment.
B) Reported analysis of CRMs

Additional credibility

Crossover stations (Historical data not suitable)

Methods

- High resolution gamma spectroscopy

5.2 $^{239,240}Pu$ ACTIVITY AND ^{238}Pu

$^{239,240}Pu$ has been measured by six labs as part of an intercalibration exercise (Kenna et al. 2012). An important outcome of the intercalibration was the verification of expected ^{242}Pu spike concentrations, showing deviations of up to 20% (four labs verified).

Minimum requirements

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment.
B) Reported analysis of CRMs

Additional credibility

- Crossover stations (historical data not suitable)
- Spike independently verified

Methods

- Alpha spectrometry

5.3 ^{239}Pu/^{240}Pu atom ratio

^{239}Pu and ^{240}Pu are not distinguishable by alpha spectrometry. The ratio of ^{239}Pu and ^{240} Pu can be determined by extremely sensitive mass spectrometers. ^{238}Pu is currently not accessible via ICP-MS due to its extremely low abundance and very abundant isobaric ^{238}U.

Minimum requirements

A) participation in intercalibration, or post-intercalibration analysis of shared material. These results need to be reported for the assessment.
B) Reported analysis of CRMs

Additional credibility

- Crossover stations (Historical data not suitable)

Methods

- SF-ICP-MS
- MC-ICP-MS
- TIMS
- AMS

5.4 ^{237}Np

This isotope was included in an intercalibration exercise. Two labs reported data. One lab could handle significantly smaller volumes. Results between the labs differed systematically by a factor 1.5-2. An independent verification of data seems desirable.

Minimum requirement would be:

A crossover station (or shared sample) with reasonable agreement, analyzed by two different labs.

Methods

SF-ICP-MS or MC-ICP-MS. Possibly alpha-spectrometry. No suitable spike.

5.5 ^{241}Am

This isotope was included in an intercalibration exercise. Two labs reported data. Results between the labs differed systematically by a factor 2. An independent verification of data is desirable.

Minimum requirement would be:

A crossover station (or shared sample) with reasonable agreement, analyzed by two different labs.

Methods

SF-ICP-MS or MC-ICP-MS. Possibly alpha-spectrometry. No suitable spike.

5.6 ^{90}Sr

This isotope was included in an intercalibration exercise. Two labs reported data, which were in good agreement.

Minimum requirement would be:

A) External comparison with a different lab
B) Internal quality check

Methods not specified in the intercalibration exercise. ICP-MS seems maybe not mature yet, but promising. Established techniques are based on counting.

6 Non-intercalibrated nuclides

6.1 ^{227}Ac

During the evolution of Geotraces (and partly as a result), capabilities to measure ^{227}Ac have grown considerably. Still, robust values require large volumes (typical 100 L) that exceed the possibilities on most cruises. Key problem is the absence of a second nuclide that would allow the determination of efficiencies. This can in part be overcome by indirect measurement via ^{223}Ra.

Submersible pumps equipped with manganese adsorbers can extract Ac from large volumes, but their extraction efficiency needs to be assessed carefully. Alternatively, the data can be considered robust if ^{227}Ac can be assumed to be in equilibrium with the actually measured ^{223}Ra, and ^{223}Ra efficiencies can be determined independently with known concentrations of another Ra isotope. Other than that, only quantitative extraction of sea water delivers reliable ^{227}Ac data.

Minimum requirements

Replicate analyses of standards

Analysis of standards shared with other labs

Convincing assessment of adsorber efficiency for ^{227}Ac

Methods

- Radium delayed coincidence counting
- Alpha spectrometry (currently not used as part of Geotraces to my knowledge)

6.2 ^{238}Pu

While ^{238}Pu was included in an intercalibration exercise (Kenna et al. 2012), only one lab could detect it in sea water at the time of the assessment; reported uncertainties were 30%.

6.3 ^{236}U

A very significant ^{236}U transect has already been produced by the community. While this has not been intercalibrated to my knowledge in a strict sense, the data seem very reliable as ^{236}U is determined as a ratio to the very well established ^{238}U, via AMS. The requirement of an AMS (at least for sufficiently small samples) also reduces the possibilities for independent verification. However, at least some of the available data have been validated by limited crossover station analysis.

I recommend that the ^{236}U data can be included in the IDP, if they are partly verified/confirmed by an independent lab, and if they are supplied according to other requirements.

6.4 ^{134}Cs

Not intercalibrated yet but measured as part of some cruises. Exchange of samples or reference materials with other labs desirable.

6.5 ^{129}I

Not intercalibrated yet but measured as part of some cruises. Exchange of samples or reference materials with other labs desirable.

6.6 ^{7}Be

Not intercalibrated yet but to be analyzed as part of some cruises. Exchange of samples or reference materials with other labs desirable.

7 References

Anderson, R. F. and others 2012. GEOTRACES intercalibration of 230Th, 232Th, 231Pa, and prospects for 10Be. Limnology and Oceanography: Methods **10:** 179-213.

Charette, M. A. and others 2012. GEOTRACES radium isotopes interlaboratory comparison experiment. Limnol. Oceanogr. Meth. **10:** 451-463.

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