Proposal for Relevant Comparisons of Natural and Related Reference Materials

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In the field of radionuclide metrology (radioactivity measurements), a particular issue has arisen with regards to CMCs of reference materials (soils, organic matrices, natural waters, etc.), most of which have not been subject to either key or supplementary comparisons. While the measurement of their contributing radionuclides (such as ^{137}Cs) have been compared, and such comparisons are used to support the CMC of ^{137}Cs in soil, the comparison of the reference materials themselves offers very specific and often recalcitrant difficulties. In addition to the preponderance of a vast variety of reference materials, many of which are considered by only one laboratory, how such material is to be handled (sampling) and prepared for analysis (i.e., procedures used to extract the nuclides of interest from the matrix quantitatively) present potential problems for any kind of comparison.

The NIST has, over many years, performed comparisons (not to be considered either key or supplementary as they have not followed the guidelines for such) of reference materials as a crucial part of the development of a variety of matrix-based Standard Reference Materials (SRMs). In addition, NIST prepares, distributes, and analyzes reference materials as part of the performance evaluation program referred to as the "NRIP," the NIST Radiochemistry Intercomparison Program. This is a comparison program among several (12 in 2004) laboratories in the United States with expertise in radiochemistry and the measurement of radionuclides in natural matrix materials, including many of the National Labs of the US Department of Energy (laboratories with a history of research and development with radiation and radioactive materials). Details of the NRIP are in the public domain and for example in "NIST Radiochemistry Intercomparison Program: a summary of four-year performance evaluation study", Z. Wu, K. G. Inn, Z. C. Lin, C. A. McMahon, L. R. Karam, ***Applied Radiation Isotopes***, **56**, 379-385 (2002).

At the present time, three reference material-based SRMs are under development at NIST. Rocky Flats II (soil), seaweed (vegetation), and shellfish meat (biological material) have been recognized by the respective user communities as of importance for environmental monitoring and oceanic studies. In addition to US laboratories participating in the analyses of these reference materials, a large variety of international labs are contributing measurement results for the characterization of these SRMs (MRA signatories are indicated in **bold**):

SRM 4353A (Rocky Flats -II)

- **International Atomic Energy Agency (Monaco)**
- National Research Center for Environment and Health, Institute of Radiation Protection (Germany)
- British Nuclear Fuels (United Kingdom)
- **National Institute of Standards and Technology (NIST) (USA)**

Seaweed SRM

- **Australian Nuclear Science and Technology Organization (Australia)**
- Australian National University (Australia)
- The Centre for Environment, Fisheries and Aquaculture Science (United Kingdom)

- **Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (Spain)**
- Institute for Energy Technology (Norway)
- Institute of Nuclear Energy Research (Taiwan)
- Interfaculty Reactor Institute (The Netherlands)
- **Institut de Radioprotection et de Sûreté Nucléaire (France)**
- IsoTrace Laboratory (Canada)
- Institute for Transuranium Elements (Germany)
- Korea Ocean Research and Development Institute (Korea)
- Lund University Department of Radiation Physics (Sweden)
- Agricultural University (Norway)
- **National Physical Laboratory (United Kingdom)**
- National Radiological Protection Board (United Kingdom)
- **Physikalisch-Technische Bundesanstalt (Germany)**
- ***Risø National Laboratory (Denmark) (?)***
- Southampton Oceanography Centre (United Kingdom)
- **Radiation and Nuclear Safety (Finland)**
- Scientific Production Association "Typhoon" (Russia)
- Universitat Autónoma de Barcelona (Spain)
- **National Institute of Standards and Technology (NIST) (USA)**

Shellfish SRM

- **Institute for Reference Material & Measurements (Belgium)**
- Institute of Oceanography (Poland)
- Taiwan Radiation Monitoring Center (Taiwan)
- Bedford Institute of Oceanography (Canada)
- Laboratoire de Mesure de la Radioactivité de l'Environnement (France)
- **National Physical Laboratory (United Kingdom)**
- **Institute of Nuclear Energy Research (Taiwan)**
- Scientific Production Association (Russia)
- University College Dublin (Ireland)
- **National Institute of Metrology (PR China)**
- National Institute of Radiological Sciences (Japan)
- Japan Chemical Analysis Center (Japan)
- **National Institute of Standards and Technology (NIST) (USA)**

Experiences from these types of exercises suggest how to best approach the design and implementation of comparisons of reference materials to support the CMCs. Specific points which must be considered include not only what types of matrices should be used and which radionuclides to include, but, perhaps most importantly, at what levels (ambient, spiked, high, low) should the activity be so as to verify the capability.

Proposal: Rather than carrying out comparisons for each individual reference material, some sort of representation should be developed for specific materials. For example, an comparison of a high calcium content soil should support claims for other high calcium content soils or sediments.

While reference materials indicated in the Appendix C of the CIPM MRA show a wide variety of radionuclides, some attempt should be made to optimize the combination from a radiological and chemical point of view. A relatively small number, on the order of 10 to 12, carefully selected nuclides in a given matrix should be adequate to evaluate the capability for a wider range of potential analytes. Particular attention must be paid to the suite of nuclides to be considered in a reference material since, while a given nuclide might be rated as comparatively easy to quantity ("green" in the generic groupings), the chemistry for its extraction might result in a sample much more difficult to analyze. Examples of matrices are given in Table 1.

Table 1

Matrices	Special considerations	Previous and similar comparisons
Soils/sediments	high/low organic content high/low calcium content	Rocky Flats I Ocean Sediment (high Ca) Lake Sediment (high organics)
Vegetation	Water content	Mate tea Seaweed
Biological materials (food, tissues, etc.)	Water content Sample storage (refrigeration?)	Milk Powder Bone Shell Fish
Aqueous	high/low salt content	Synthetic Urine (high salt) Spiked Water (low salt)
Building materials	Inhomogeneity in composition	None yet

Experience has shown that the general process of allowing the measuring laboratory to choose its preferred sample preparation and analytical methods, with the stipulation that the details of said preparation and analyses are documented, is the preferred approach to assure that the comparison laboratory uses its most experienced and best-documented procedure. In general, the same type of information requested for any radionuclide comparison (reference time, half lives used, radionuclides measured, etc.) apply to comparisons of reference materials. It may also be appropriate to specify certain other points such as defining the sample size and yield monitor to be used, see Table 2.

Table 2

Information to be Included on Data Sheet	Considerations	Responsibility of Lead Laboratory (before distribution to participants)
Counting time	Time needs to be long enough for good statistics (may take longer than conventional comparisons)	Counting time appropriate for the specific material should be determined
Chemical yield	Must be certain to trace the entire extraction process	Leachability and total sample digestion (or non-destructive analysis) to confirm suitability of material for use
Interferences	Especially important when a suite of radionuclides is involved (similar to any mixed-nuclide source)	

Software	For measurement and statistical analysis	State to participants the software used to evaluate the material before distribution
Measurement method(s)	Standard approaches; perhaps confirmatory measurements are particularly useful?	
Efficiencies	Usual issues, complicated by interferences	
Sample size	Sampling, verification of sub-sample homogeneity, checking for “hot” spots, etc.	Validate an homogenous sample, or assess the degree of heterogeneity
Radiochemical methodologies	Source handling (e.g., combustion to remove organics, etc.), chemical preparation, etc.	Recommend procedures for storage of material, sub-sampling, and drying of material; determine particle size (soils/sediments and other solids), etc.
Yield monitor (tracer)	Appropriateness (chemical and radiological) and traceability of monitoring tracer	Recommend chemically-appropriate tracer to be used
Low level measurements (i.e., lower limit)	The minimum value (in the CMC) would be the lowest level obtained in the comparison quoted	

Several items should be considered before a comparison of reference materials is designed. Firstly, it is very unlikely that measurements of these types of material could reasonably provide an activity value – only an activity per mass or per volume. This has as much to do with the nature of large samples with very low activity levels as with the vagaries of extraction processes. **Therefore, the first recommendation would be to remove any CMC which states an activity measurement for a reference material, and to not accept any in the future.**

A second issue to be addressed is the handling of those CMCs which address a unique object or material (such as metal spoons, metal discs or semiconductors) which probably should not be considered as actual “reference” materials. While the measurements of such items presents interesting research possibilities, they are too specialized to be useful to the community at large. Since the sample preparation of such materials would be extremely complex, no comparisons of other reference materials (soils/sediments, flora, water, etc.) would be applicable to support claims for these items. **Therefore, CMCs of specialized materials should not be acceptable in Appendix C.**

After considering these two issues, and eliminating efforts for them, the list of CMCs for matrix reference materials can be narrowed down to those specified in Table 3.

Table 3

Type of material	NMIs claiming CMCs	Radionuclides	Matrices
Foods	CNEA, IRMM	Co-57, Cs-134, Cs-137, K-40, Mn-54, Na-22, Zn-65	Grains, soy meal, milk powder
Water (aqueous)	NIST, LNMRI	Am-241, Ba-133, Co-57, Co-58, Co-60, Cs-134, Cs-137, Mn-54, Na-22, Pu-238, Pu-240, Ra-228, Sr-90, Th-230, U-234, U-238, Zn-65	Spiked water
Biological materials	NIST, BEV, IRMM	Ac-228, Am-241, Co-60, Cs-137, Pb-210, Pu-238, Pu-239+240, Ra-226, Sr-90, Th-228,Th-230, Th-232, Tl-208, U-234, U-238	Synthetic spiked urine, human liver, human lung, ashed bone, ocean shellfish
Soils/sediments	NIST, BEV, IRMM	Ac-228, Al-26, Am-241, Ba-133, Cd-109, Co-57, Co-58, Co-60, Cd-134, Cs-137, Eu-152, Eu-154, Mn-54, Pu-238, Pu-239+240, Sr-85, Sr-90, Th-228, Th-230, Th-232, U-234, U-238, Y-88, Zn-65	High level soil (Rocky Flats), low level soil (Peruvian), river sediment, ocean sediment, spiked soil, fresh water lake sediment, bentonite (clay), quartz (sand), meteorite
Flora (vegetation)	CNEA, NIST	Co-57, Cs-134, Cs-137, Mn-54, Na-22, Zn-65	Mate tea (seaweed, in process)
Building materials			None at the present time
Other	BEV, IRMM	Am-241, Ba-133, Cd-109, Ce-139, Co-57, Co-60, Cs-134, Cs-137, Mn-54, Pb-210, Ra-226, Sb-125, Sr-85, Th-234, U-235, Y-88, Zn-65	ML-1, 2, 4; filter paper

Proposed Exercise:

Reference Material Choice As there seem to be more soil/sediment reference materials than anything else, running the initial comparison to support those CMCs seems prudent. Two possible approaches are apparent –

- Use an existing material (such as NIST Ocean Sediment SRM, bentonite from BEV, or some other for which results are already known), for the comparison
- Develop new material (pilot lab)
  - With natural level of nuclides (to optimize the low level value)
  - With a spiked level of nuclides (easier to measure and to confirm results)

Using a pre-existing reference material would simplify preparation and shorten the comparison time. Experience shows that to prepare a reference material for metrological applications takes on the order of 18 to 24 months to acquire the raw material, process it, and analyze its composition, all before samples can be distributed to participants. If an existing material were used, the comparison could be completed within a year. If an existing material is chosen for the comparison, the suite of radionuclides would be pre-determined to be those already contained therein. If a new material is to be prepared, the radionuclides would have to be chosen (probably best done by the willing participants) before preparation (and whether they would be those inherently in the material, added as a spike, or a mixture of the two).

Sample Handling Once the reference material has been received by the participant, certain general conditions should be followed to assure comparability in measurements (as NIST advises recipients of reference material SRMs). This will be specified in the protocol.

Determining Heterogeneity Received material should be tested, using sample sizes of 10 to 50 gram, to determine the heterogeneity of detectable gamma-ray-emitting radionuclides.

Uncertainties The contributions to the uncertainty will be, as usual, radionuclide specific. In addition, uncertainty contributions can be expected from any and all of the elements indicated in Table 2, as well as from unique aspects of the specific reference material.

Final Recommendations: Soils/sediments represent the largest single type of reference materials currently published in the CMCs**. The first reference material comparison, therefore, should support this category (i.e., a comparison of a soil or sediment).**

A comparison of radionuclide content of reference materials is complicated, at best. If a material were to be developed specifically for such a comparison, the pilot laboratory can expect 2 years or so of effort just to prepare the material for distribution**. Therefore, using a pre-existing and pre-characterized material would be preferable.**

Radionuclides to be evaluated should be decided upon before the beginning of preparations (including production of material) for the comparison. In addition, laboratories should be allowed to declare values for some or all of those radionuclides (i.e., it should not be all or nothing).

Minimal **sample handling instructions** regarding storage, water content ("wet" vs. "dry" weight), and sample size should be provided for the participant, in the protocol. The reporting sheet should be thorough enough to provide all necessary information to assess the methodologies and analysis (including uncertainties) used by the participant laboratory.

Uncertainties must be carefully handled not only by each participant, but for the final determination of the reference value. More details on this point should be developed when a comparison is organized.

Participants should be gathered from any NMI or MRA signatory (designate) that performs radionuclide analysis of reference materials and who is willing to participant. This should include even those institutions which do not have any related CMCs currently published. If inadequate participation is forthcoming from this pool, the idea of using other capable laboratories (not NMIs) might have to be revisited. Listed in Table 4 are those signatories to the MRA who either claim CMCs for reference materials or who participate in the development of reference material SRMs with NIST.

Attached to this document are **three proposals for comparisons of radionuclides in reference materials** as a starting point in comparisons to support the relevant CMCs.

Table 4

Laboratory (signatory to MRA)	**Country**
National Commission on Atomic Energy (CNEA)	Argentina
Australian Nuclear Science and Technology Organization	Australia
Bundesamt für Eich- und Vermessungswesen	Austria
Institute for Reference Material & Measurements	Belgium
Laboratório Nacional de Metologia das Radiações Ionizantes, Instituto de Radioproteção e Dosimetria	Brazil
Risø National Laboratory (?)	*Denmark*
Radiation and Nuclear Safety	Finland
Institut de Radioprotection et de Sûreté Nucléaire	France
Physikalisch-Technische Bundesanstalt	Germany
International Atomic Energy Agency	Monaco
D.I. Mendeleyev Institute for Metrology, Gosstandart of Russia	Russia
National Institute of Metrology	PR China
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas	Spain
Institute of Nuclear Energy Research	Taiwan
National Physical Laboratory	United Kingdom
National Institute of Standards and Technology	United States of America

STATUS REPORT ON CCRI OR RMO COMPARISON

1. CCRI Section: II, measurement of radionuclides

2. CCRI Ref No (to be completed by the BIPM):

3. Type of comparison: CCRI [ ] RMO [ ] Key [ ] Supplementary [x] Pilot study [ ]

4. Subject area: Radionuclides in Reference Materials

5. Participating institutes (*and countries*): International Atomic Energy Agency (*Monaco*); National Institute of Standards and Technology (*USA*); open to others

6. Pilot laboratory: National Institute of Standards and Technology (NIST; USA)

7. Measurand / unit (nominal value(s)):
Activity per unit mass, mBq/g, nominal value from 0.0003 to 0.6 (nuclide dependent)

8. Description: Assorted radionuclides (^{228}Ac; ^{241}Am; ^{212}Bi; ^{214}Bi; ^{137}Cs; ^{210}Pb; ^{212}Pb; ^{214}Pb; ^{238}Pu; ^{239,240}Pu; ^{241}Pu; ^{234}U; ^{235}U; ^{238}U; ^{226}Ra; ^{90}Sr; ^{228}Th; ^{230}Th; ^{232}Th; ^{234}Th; ^{208}Tl) in NIST Rocky Flats II SRM-4353A (ca. 80 g dried soil)

9. Progress: *(Please note date and tick appropriate box to indicate current status)*

Date	Status	Pilot	Supplementary	Key
	Proposed to CCRI	[ ]	[ ]	[ ]
	Accepted and registered	[ ]	[ ]	[ ]
	Protocol submitted to CCRI	[ ]	[ ]	[ ]
	Protocol agreed	[ ]	[ ]	[ ]
	Measurements in progress	[ ]	[ ]	[ ]
	Measurements completed	[ ]	[ ]	[ ]
	Report agreed	[ ]	Draft A [ ]	Draft A [ ]
			Draft B [ ]	Draft B [ ]
			[ ]	[ ]
	Report submitted to CCRI	[ ]	[ ]	[ ]
	Results approved	[ ]	[ ]	[ ]
	Approved for Equivalence			[ ]
	Progression to Key Comparison	[ ]		
	Abandoned	[ ]	[ ]	[ ]

Comments:

Publication reference:

10. Measurement start date:

11. Expected measurement completion date:

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13. Contact Person's signature:

14. Date:
29 March 2005

Completed copy to be forwarded to a) CCRI Executive Secretary, b) Regional coordinator and c) relevant Key Comparison WG Chairman

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5. Participating institutes (*and countries*): Institute for Reference Material & Measurements (*Belgium*); National Physical Laboratory (*United Kingdom*); Institute of Nuclear Energy Research (*Taiwan*); National Institute of Metrology (*PR China*); National Institute of Standards and Technology (*USA*); open to others

6. Pilot laboratory: National Institute of Standards and Technology (NIST; USA)

7. Measurand / unit (nominal value(s)):
Activity per unit mass, mBq/g, nominal value from 0.02 to 2 (nuclide dependent)

8. Description: Assorted radionuclides (^{230}Th; ^{228}Th; ^{234}U; ^{235}U; ^{238}U; ^{238}Pu; $^{239+240}$Pu; ^{241}Am; ^{137}Cs) in NIST Shellfish SRM-4358 (ca. 120 g dried shellfish powder)

9. Progress: *(Please note date and tick appropriate box to indicate current status)*

Date	Status	Pilot	Supplementary	Key
	Proposed to CCRI	[ ]	[ ]	[ ]
	Accepted and registered	[ ]	[ ]	[ ]
	Protocol submitted to CCRI	[ ]	[ ]	[ ]
	Protocol agreed	[ ]	[ ]	[ ]
	Measurements in progress	[ ]	[ ]	[ ]
	Measurements completed	[ ]	[ ]	[ ]
	Report agreed	[ ]	Draft A [ ]	Draft A [ ]
			Draft B [ ]	Draft B [ ]
	Report submitted to CCRI	[ ]	[ ]	[ ]
	Results approved	[ ]	[ ]	[ ]
	Approved for Equivalence			[ ]
	Progression to Key Comparison	[ ]		
	Abandoned	[ ]	[ ]	[ ]

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6. Pilot laboratory: National Institute of Standards and Technology (NIST; USA)

7. Measurand / unit (nominal value(s)):
Activity per unit mass, mBq/g, nominal value from 0.001 to 1000 (nuclide dependent)

8. Description: Assorted radionuclides (^{228}Ac [^{228}Ra]; ^{241}Am; ^{137}Cs; ^{40}K; ^{210}Pb; ^{210}Po; ^{238}Pu; ^{239,240}Pu; ^{239}Pu; ^{240}Pu; ^{234}U; ^{235}U; ^{238}U; ^{226}Ra [Bi-214; Pb-214]; ^{230}Th; ^{232}Th; ^{99}Tc) in NIST Seaweed SRM-4359 (ca. 300 g dried seaweed material)

9. Progress: *(Please note date and tick appropriate box to indicate current status)*

Date	Status	Pilot	Supplementary	Key
	Proposed to CCRI	[ ]	[ ]	[ ]
	Accepted and registered	[ ]	[ ]	[ ]
	Protocol submitted to CCRI	[ ]	[ ]	[ ]
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	Measurements in progress	[ ]	[ ]	[ ]
	Measurements completed	[ ]	[ ]	[ ]
	Report agreed	[ ]	Draft A [ ]	Draft A [ ]
			Draft B [ ]	Draft B [ ]
	Report submitted to CCRI	[ ]	[ ]	[ ]
	Results approved	[ ]	[ ]	[ ]
	Approved for Equivalence			[ ]
	Progression to Key Comparison	[ ]		
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