JRP EPM 21GRD09 MetroPOEM
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News from 21GRD09 MetroPOEM

The first progress meeting (M09) was held at **Norges miljø- og biovitenskapelige universitet** in Ås, Norway at the end of June 2023 and was attended by 25 participants in person and a further 24 on-line participants, including 14 from the stakeholder community.

Participants were welcomed to NMBU on 25th June by Hans Fredrik Hoen, Dean of Fakultet for miljøvitenskap og naturforvaltning.

Project management board meeting

A new partner, Göteborgs Universitet, has joined the project consortium as an external partner. It is possible that the EC JRC may also join as an unfunded partner. Collaborators were also discussed; Fizinių ir technologijos mokslų centras (Lithuania), as well as Triskem International (France) will become project collaborators (see also the notes under WP6 below).

Internal discussions concerning the project Data Management Plan (DMP), the Dissemination, Communication and Exploitation Plan (DCE) and Intellectual Property Rights (IPR) were held, as required by EURAMET management.

Project progress meeting

The project work packages were presented by their respective WP leaders; in general, all the technical work packages are on schedule. The main points were:

- WP1: Strontium-90 will not be included in the list of radionuclides for WP1, and shipping of materials was due to take place in the autumn of 2023.
- WP2: Measurements had started, with the possible inclusion of characterizing the proposed reference material for lithium. The lack of isotopic reference materials for nickel and antimony was noted.

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- WP3: Target uncertainties and concentration levels for the included radionuclides had been completed, although ^{226}Ra will not be included. Reporting forms, compliant with ISO Guide 35 have been prepared.
- WP4: Preparatory work for this work package is largely complete, and both short- and long-term stability are being investigated. Hereon have completed the sampling of water from the North Sea (250 L) and processing of this material has been started.

Stakeholder meeting

The meeting was chaired by Anders Lund Eide of Direktoratet for strålevern og atomsikkerhet. The stakeholder participants were from EURAMET, JRC (both EU), VTT (Finland), BfS (Germany), Thermo Fisher (Germany), Agilent (Germany and UK), FTMC (Lithuania), BABS (Switzerland), CEFAS (UK), NIST (USA) as well as CCRI(II) and the ICRM (both international).

Progress in all the project work packages was reported, and the link to the recent BIPM CCQM/CCRI(II) workshop was noted. The following points concerning reference materials produced within the project were raised by the stakeholders and discussed by the meeting participants:

- Was there to be one matrix with different analyte concentrations or two matrices with the same/different concentrations?
- What nuclides were to be included at what concentrations, proportions, and isotopic compositions?
- How were the materials to be produced and verified and what were the planned aliquot size, material container and number of units?

Next meeting

The next project management board, project progress and stakeholder meetings will be held in Paris 19th-21st March 2024.

Please contact Valérie Lourenço, CEA, France valerie.lourenco@cea.fr for registration and information.

Science Feature - Sampling and preparation of seawater from the North Sea.

This has been carried out by TÜBİTAK (Türkiye) and Hereon (Germany)

Sampling (Hereon)

To provide a suitable seawater matrix for the MetroPOEM consortium as basis for the development of two new certified reference materials in total 250 L Seawater have been sampled to produce the different reference materials as well as to provide additional test matrix for the project partners.

Preparation of the sampling material

The equipment for ultra trace water analysis for trace metals was prepared in accordance with GEOTRACES procedures:
https://www.geotraces.org/wp-content/uploads/2015/01/documents_intercalibration_Cookbook.pdf
as well as internally approved and validated protocols for trace analysis in seawater. All materials were prepared in advance to minimise contamination during sampling.

New 25 L HDPE carboys specified for food applications were used for the sample storage of the large seawater sample. They were prepared by flushing 3 times with DI water, and then filled with 1% HCl (prepared from sub-boiled HCl and MilliQ water). After 1 week the solution was removed and the carboy was rinsed 3 times with MilliQ water. The carboy was refilled with 1% HCl (prepared as before). After 1 more week the solution was removed, and the carboy was rinsed 3 times with MilliQ water and then filled with with 1% HNO_3 (prepared from sub-boiled HNO_3 and MilliQ water). After 2 weeks this solution was removed, and the carboy was rinsed 3 times with MilliQ water and refilled with 1% HNO_3 (prepared as before). After 1 additional week the solution was removed, and the carboy was flushed again three times with MilliQ water. The carboy was dried inside a cleanroom (class 1000) before it was sealed and packed for shipment.

The Pall AcroPak 1500 0,8/0,2 µm filters were cleaned three times by flushing them with 1,2 M HCl and storing them filled with this acid overnight. Afterwards they were flushed several times with MilliQ water until the typical pH of MilliQ water was achieved and were then stored in MilliQ water until ready for use on board ship. Prior to use the filter was flushed with at least 2 L seawater prior to use to remove the MilliQ as well as to condition the filtration membrane.

The tubing used in sampling as well as the clean seawater system was operated the entire day during sampling to continuously flush the system with fresh seawater.

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Sampling location

The sampling was conducted as part of the regular monitoring research cruise AT 020 (started at Bremerhaven, Germany on 2023-05-15, and ended at Bremerhaven on 2023-05-26) with the RV ATAIR (Figure 1) operated by the German BSH covering the entire German EEZ as shown on the map presented in Figure 2.

Fig. 1: ATAIR in Bremerhaven, Germany

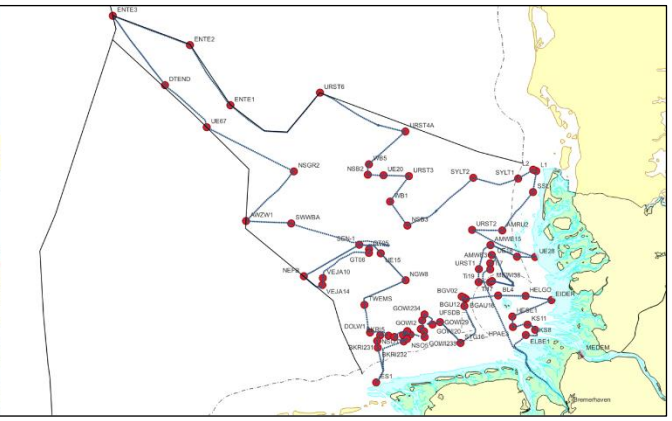

Fig. 2: Route of the sampling cruise AT020

The sampling for the lager volume water samples was conducted at station UE67, which is located at the edge of the German EEZ.

Sampling procedure

The water was sampled using the trace metal clean PVDF made clean seawater inlet system of the German research vessel ATAIR. The water was pumped into the ship at a depth of 5 m below sea level. The water was directly filtered on Board using pre cleaned trace metal free filter cartridges (Pall AcroPak 1500 0,8/0,2 µm), into 25 L acid cleaned carboys to obtain the dissolved metal fraction. Before collecting the final sample, each carboy was rinsed three times with ca. One litre of seawater filtrate was used to precondition the surface of the carboy. In total two filter units were necessary to process the total volume of ~250 L seawater. After filling the carboys, they were closed, and the outside was rinsed with MilliQ water to remove any residual seawater from the surface. All additional handling was performed inside the trace metal analysis container of the BSH to prevent contaminations from the ship atmosphere.

Fig. 3: Direct filtration of the continuously sampled seawater using Pall AcroPak 1500 0,8/0,2 µm filters

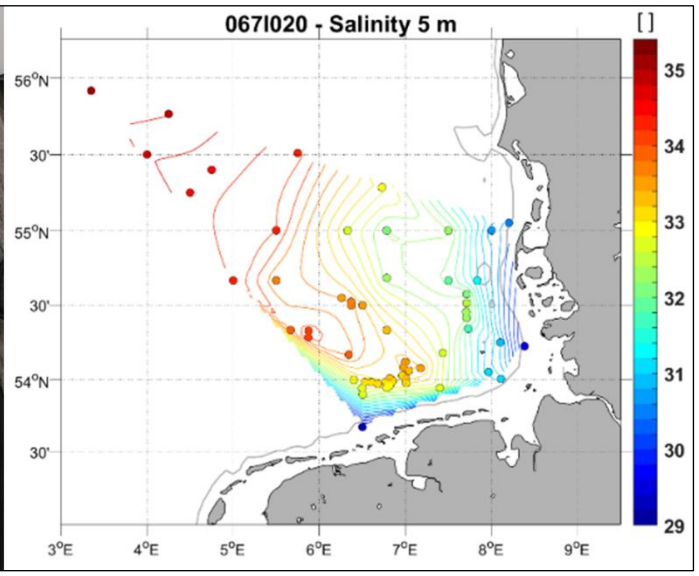

Fig. 4: Salinity measured at a depth of 5 m using a CDT at the different sampling locations

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Material preservation and storage

The filtered raw material was acidified using HNO_3 (sub-boiled twice) to stabilise the material. The carboys were sealed and individually packed in clean PE foil and stored at 4°C until their further transport to Hereon and then to TÜBİTAK.

Meta Data

Meta data on the exact sampling location as well as other parameters such as pH, Salinity, &c are currently compiled by the BSH and will be available.

Preliminary analysis

After the transport to the Hereon lab 50 mL samples from each carboy were taken under cleanroom conditions to allow a preliminary analysis of the total dissolved trace metal content of the individual water samples. The aim is to get first information on the initial concentration as well as between sample variability. The analysis will be conducted using SeaFAST-ICP-MS/MS (Agilent 8900 #100) using a He/H_2 mixed gas mode. Details on the applied setup can be found in:

Ebeling, A., Zimmermann, T., Klein, O., Irrgeher, J. and Pröfrock, D., 2022. *Analysis of Seventeen Certified Water Reference Materials for Trace and Technology-Critical Elements*. Geostandards and Geoanalytical Research, **46(2)**, 351-378. https://doi.org/10.1111/ggr.12422

Preparation (TÜBİTAK)

The complete processing of reference materials including spiking, homogenisation and filling has been carried out in ISO class 6 Clean Chemical Laboratory at TÜBİTAK UME.

Approximately 120 L raw material was transferred into a 120 L HDPE drum, and the material was homogenised for four hours after spiking. Finally, all this spiked water was transferred to a second drum with filtration through 0,8/0,2 µm (Pall Corp, Supor® Membrane, AcroPackTM 1000, PN 12992).

The filling of the bottles was performed manually in ISO class 6 Clean laboratory where 470 labelled bottles, each containing 250 ml of water were prepared. These have been sterilised by γ-irradiation with a total exposure of 25 kGy. The bottles are stored at a reference temperature of 4°C.

Fig. 5: Preparation of samples at TÜBİTAK

MetroPOEM

Metrology for the harmonisation of measurements of environmental pollutants in Europe

Newsletter 02 – Winter 2023

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Short reports from the technical work packages.

WP1: NPL

The aim of this work package is to produce a series of individual and mixed radionuclide standards, focusing on actinides (^{237}Np, ^{234,235,236,238}U, ^{239,240}Pu, ^{241}Am). These will be distributed to participating laboratories and measured using a range of mass spectrometric techniques, including different plasma mass spectrometers, thermal ionisation mass spectrometry and accelerator mass spectrometry. The labs will report a range of information about the measurements made, which will result in a report documenting the advantages and limitations of different mass spectrometer designs for radionuclide measurement. This will be a valuable resource for end users interested in investing in this capability for their own radioanalytical work.

Preparation of samples is at an advanced stage and the next step is to distribute the materials at the start of 2024 to participating laboratories.

WP2: IJS

The aim of this work package is to develop new and improved generic methods for measuring the ratio of stable and long-lived radioactive isotopes by mass spectrometry with uncertainties that allow the natural mass-dependent isotope fractionation to be resolved. The environmentally relevant elements selected as key indicators for the development and optimisation of measurement procedures include Li, B, Cr, Cd, Ni, Sb, Pb and U.

A range of instrumental techniques are used in the measurements, including MC-ICP-MS, sector field ICP-MS, quadrupole ICP-MS, ICP-MS/MS and TIMS. The performance of these techniques and existing calibration approaches will be evaluated and compared in terms of accuracy and precision of measurement results to demonstrate the potential of recent advances in ICP-MS technology.

So far, a list of existing isotopic reference materials for individual elements (iRM) has been compiled. For elements for which no iRM exists, agreement has been reached on the elemental solutions to be used (Table 1). Since no isotopic CRM is available for Sb and Ni, various candidate materials were selected for use in MetroPOEM. Currently, IUPAC tabulated values must be used for the isotope ratio (Meija et al. Isotopic compositions of the elements 2013 (IUPAC Technical Report), Pure and Applied Chemistry 88 (2016) 293-306). New absolute isotope ratios will be made available once appropriate calibration strategies have been selected and calibrated measurements have been performed.

The WP2 partners are currently working on the development of new techniques for the separation of selected elements from the sea matrix and are optimising the instrumental parameters for an accurate and precise determination of the isotope ratios.

Single element solutions with isotope ratio values.

	Reference material	Isotope ratio values with expanded uncertainty, $k = 2$
Li	LSVEC	$n(^6\text{Li})/n(^7\text{Li}) = 0.08215(23)$
B	BAM-AE123	$n(^{11}\text{B})/n(^{10}\text{B}) = 4.042(6)$
Cr	NIST SRM 979	$n(^{53}\text{Cr})/n(^{52}\text{Cr}) = 0.11339(15)$
Cd	BAM-I012	$n(^{114}\text{Cd})/n(^{111}\text{Cd}) = 2.2437(7)$
Ni	NIST SRM 3136	$n(^{60}\text{Ni})/n(^{58}\text{Ni}) = 0.3854(30)$
Sb	BAM inhouse RM NRC candidate RM	$n(^{123}\text{Sb})/n(^{121}\text{Sb}) = 0.7479(11)$
Pb	NIST SRM 981	$n(^{204}\text{Pb})/n(^{206}\text{Pb}) = 0.059042(37)$ $n(^{207}\text{Pb})/n(^{206}\text{Pb}) = 0.91464(33)$ $n(^{208}\text{Pb})/n(^{206}\text{Pb}) = 2.1681(8)$
	NIST SRM 983	$n(^{204}\text{Pb})/n(^{206}\text{Pb}) = 371(20)\times10^{-6}$ $n(^{207}\text{Pb})/n(^{206}\text{Pb}) = 0.071201(40)$ $n(^{208}\text{Pb})/n(^{206}\text{Pb}) = 0.013619(24)$
U	IRMM 184	$n(^{234}\text{U})/n(^{238}\text{U}) = 53.196(16)\times10^{-6}$ $n(^{235}\text{U})/n(^{238}\text{U}) = 0.0072631(11)$ $n(^{236}\text{U})/n(^{238}\text{U}) = 124.10(96)\times10^{-9}$
	NBL CRM 145	$n(^{234}\text{U})/n(^{238}\text{U}) = 2.841(82)\times10^{-6}$ $n(^{235}\text{U})/n(^{238}\text{U}) = 0.0072543(40)$

WP3: CEA

The aim of this work package is to produce two reference materials (RMs), one liquid and one solid, containing actinide nuclides (^{237}Np, ^{234,235,236,238}U, ^{239,240}Pu, ^{241}Am) addressing end users and stakeholders needs. These RMs will be used in two inter-laboratory comparisons employing techniques used in WP1 to meet objective 1 and will demonstrate the variations in parameters including detection limits, sample preparation requirements, sample introduction methods, total procedural time, and uncertainty budgets.

Seawater was chosen as the liquid reference material matrix and about 400 L of seawater was sampled in the North Sea in May. It was filtered, acidified, and sterilised to be bottle for its initial radionuclide characterisation; seawater contains uranium at a concentration of ~3 µg L^{-1}.

The solid reference material will be a silicate that will be synthesised by sol-gel reaction to ensure maximum traceability. For several months, various formulations have been tested to limit the material's water absorption. Trials involving the manufacture of several kg of inactive material have made it possible to optimise the grinding stages to obtain a particle size distribution below 250 µm. Several protocols for dissolving the material are currently being evaluated (using hydrofluoric acid or alkaline fusion).

The next step is to spike the material with ^{241}Am to estimate its homogeneity by γ-spectrometry directly or after dissolution.

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WP4: TÜBİTAK

A total of 250 litres of seawater was collected from the edge of the German EEZ (North Sea) to serve as the basis for the development of two different reference materials in the project. The baseline amount of target elements in WP4 was measured by HEREON and the material was delivered to TÜBİTAK and CMI laboratories. In meanwhile, production and certification plan were prepared by the help of each partner taking role in WP4.

A new homogenisation system was designed for the candidate certified reference materials for stable analytes and the whole system was subjected to acid cleaning procedures. Systematically, baseline measurements of target analytes were performed in the randomly selected low particulate HDPE bottles from each package. The background levels of the bottles were found to be very low (at low ppt levels) and reproducible results between bottles were observed. However, an additional cleaning procedure is applied to the bottles to minimise the risk of inhomogeneity between bottles.

Processing of the material including spiking, homogenisation, filling, and γ-irradiation for stabilisation was completed in August 2023.

Management and dissemination.

WP5: NMBU

To date, there have been 12 presentations (4 posters) at a variety of national and international events and the work of the project has been disseminated via press releases, the project website (hosted by NPL) and the project pages on LinkedIn and Research Gate. Additionally, project partners have contributed to one ISO Technical Committee and two national standards committees.

As the work of the project gathers momentum, the first peer reviewed papers arising from the project are expected in the next 12 months.

WP6: PTB

The regular M9 reporting documents were sent to EURAMET in August 2023 and were approved in September 2023. To date, the following three collaborators have signed letters of agreement:

- TrisKem International, France,
- FTMC Center for Physical Science and Technology, Lithuania, and
- Spiez Laboratory, Switzerland.

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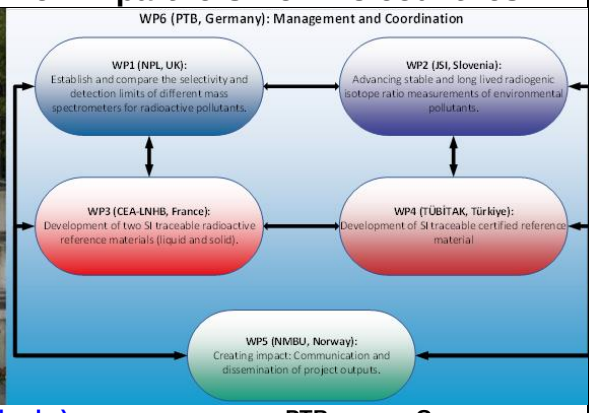
MetroPOEM, coordinated by the Physikalisch-Technische Bundesanstalt of Germany, is delivered by a consortium of 22 partners from 13 countries.



Physikalisch-Technische Bundesanstalt (Coordinator, WP6 leader)	**PTB**	**Germany**
Bundesanstalt für Materialforschung und -prüfung	BAM	Germany
Commissariat à l'énergie atomique et aux énergies alternatives **(WP3 leader)**	CEA	France
Cesky Metrologicky Institut	CMI	Czechia
Institut Jožef Stefan **(WP2 leader)**	JSI	Slovenia
Laboratoire national de métrologie et d'essais	LNE	France
Sateilyturvakeskus	STUK	Finland
Türkiye Bilimsel ve Teknolojik Araştırma Kurumu **(WP4 leader)**	TÜBİTAK	Türkiye
Aarhus Universitet	AU	Denmark
Danmarks Tekniske Universitet	DTU	Denmark
Helmholtz-Zentrum Hereon GmbH	Hereon	Germany
Helmholtz-Zentrum Dresden - Rossendorf e. V.	HZDR	Germany
Institutt for energiteknikk	IFE	Norway
Institutul National de Cercetare-Dezvoltare pentru Fizica si Inginerie Nucleara 'Horia Hulubei'	IFIN-HH	Romania
Gottfried Wilhelm Leibniz Universität Hannover	LUH	Germany
Montanuniversität Leoben	MUL	Austria
Norges miljø- og biovitenskapelige universitet **(WP5 leader)**	NMBU	Norway
Helsingin Yliopisto	UH	Finland
Institut za nuklearne nauke Vinča Institut od nacionalnog značaja za Republiku Srbiju, Univerzitet u Beogradu	VINS	Serbia
Göteborgs universitet	UGOT	Sweden
Eidgenössische Technische Hochschule Zürich	ETHZ	Switzerland
LGC Limited	LGC	United Kingdom
NPL Management Limited **(WP1 leader)**	NPL	United Kingdom

Project information

The overall deliverables and dissemination routes shown in the diagram below

Additionally, the project has an internet presence at:

Project website: https://www.npl.co.uk/euramet/metropoem

Linkedin: https://www.linkedin.com/in/metropoem-project-308762251/

Research gate: https://www.researchgate.net/profile/Metro-Poem

MetroPOEM can be contacted through the project website, or at this email address:

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