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1. TUBITAK, Turkey 2. BAM, Germany 3. GUM, Poland 4. JSI, Slovenia 5. IMBiH, Bosnia & Herzegovina 6. DMDM, Serbia 7. SYKE, Finland	1. NTUA, Greece 2. UW, Poland	

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1 Overview

This project aimed to develop capacity to produce certified reference materials (CRMs) for environmental analysis by transferring know-how between the partners and combining their skills to focus on environmental CRM production. The production process included good manufacturing practices for processing materials, method development, the validation and application of homogeneity, stability and characterisation tests, the calculation of individual uncertainties (between-unit inhomogeneity, long term stability, characterisation) and combination of uncertainties to determine overall uncertainty of the matrix reference materials. An interlaboratory comparison registered as a EURAMET project was set as the ultimate project outcome, confirming the partners' capabilities in applying newly acquired skills. As a result of the project, new CRMs are available and the partners have developed strategies for long term research capabilities for environmental CRMs.

2 Need

The need for quality assessment of anthropogenic impact on environmental pollution is increasing due to discharge from various industries, the use of chemicals in agriculture, and the consumption of fossil fuels. Diminishing resources such as drinking water, soil used for the cultivation of agricultural products, and plant and animal habitats are under severe pollution pressure and are at constant risk. The EU has stipulated the maximum allowable concentration of priority pollutants in different classes of surface water under the Water Framework Directive in Directive 2008/105/EC Annex I "Environmental quality standards for priority substances and certain other pollutants", and for the purpose of assessing the quality of river and marine sediment, Canadian and Dutch guidelines are used. Prescribed limits for pollutants are adopted and adapted by regulations at the local level. In addition to ISO 17034, prescribing the general requirements for the competence of reference material producers, standardised methods such as ISO and EN standards for sampling, homogenisation and testing of the pollutants in water, sediment and soil samples are available.

In order to establish a quality system in the testing of environmental samples conducted by dedicated laboratories, it is necessary to provide appropriate quality control materials i.e. matrix CRMs. The term "appropriate" relates to the unique sample matrices representing typical samples in the geomorphological and anthropological sense. In addition to that, bearing in mind the complexity, variability and instability of environmental samples, it is very difficult to obtain appropriate reference materials with no local providers. Dedicated laboratories require strong support from the metrology system for proving competence in performing quantitative tests. Laboratories operating under the watershed, environment and health sectors are recognised as the main stakeholders of this project. Matrix reference materials produced within the project will serve stakeholders locally through the corresponding National Metrology Institutes (NMIs) and Designated Institutes (DIs).

3 Objectives

The overall objective of this project was to develop research capability for the production of environmental reference materials. The specific objectives were:

1. **Production of CRM Candidates –** through design and production of two inorganic (heavy metal) and one organic pollutant candidate CRMs at NMIs having production facilities for developing traceability to SI units of the measurements performed by environmental analysis laboratories.
2. **Homogeneity and Stability Tests of CRM Candidates –** by designing and carrying out tests to measure the analyte composition of a calculated number of randomly selected units covering the whole production batch for each candidate CRM and determining the effect of storage and transport temperature and time on the uncertainties.
3. **Characterisation of the CRM Candidates –** via certification campaigns among NMIs, DIs and university research laboratories with comparable measurement capabilities by employing reference analyte measurement techniques such as IDMS (isotope dilution mass spectrometry) for high accuracy and low uncertainty (target uncertainties will depend on the analytes selected and will be in the range of 10 % to 20 %).
4. **Certification of the CRMs –** by drafting and reviewing certification reports with all the information collected throughout the investigation of the materials.

5. **Long term research capability for environmental CRMs –** via development of individual and/or consortium strategies for each partner with discussions within the consortium in collaboration with the communities of each country to determine the priorities and draw up a road map for quality schemes and develop plans to offer services and products from the established capacities.
6. **Contribution to impact –** via contribution to regional and international standards and committees and dissemination of outputs of the project to the end users (e.g. providing the developed CRMs for use by environmental analysis laboratories).

4 Results

The results of this project are summarised and presented against each of the project’s objectives. At the start of the project in order to identify the certified reference material needs in partnering countries a questionnaire was prepared and sent to the environmental analysis and monitoring laboratories. The answers received from this questionnaire and information collected from the stakeholders in partnering countries have been evaluated and provided important input such as the matrix, list and range of analytes at the planning stage.

4.1 Production of CRM Candidates

Details of the raw material collection and processing of the three CRM candidates are given in the following sections. The aim of this objective was to prepare adequately homogenous and stable materials for for the purpose of quality control applications at the end user laboratories.

4.1.1 Production of PFOS and PFOA in Ground Water Candidate CRM

Ground water was collected from a well operating in İstanbul, Turkey which supplies water for the swimming pools and irrigation of gardens. Prior to collection, 10-litre carboys were cleaned with deionised water and dried at ambient temperature. Ground water samples were transferred directly from the well to the cleaned carboys. The collected samples were then transported to TUBITAK for further processing.

Figure 1. Ground water raw material collection point: satellite view with photo of collection

Representative subsamples were measured for analyte content. Results showed that the candidate raw material had almost none of the target analytes, therefore it was decided to spike this material to reach target levels for the analytes. Filtration, spiking of analytes (PFOS, PFOA) and homogenisation was followed by filling, capping and gamma sterilisation of a total of 1180 units (approximately 98 mL each).

Figure 2: Bottling and capping of the candidate ground water CRM

All stages of processing are summarised and given as a flow diagram in Figure 3.

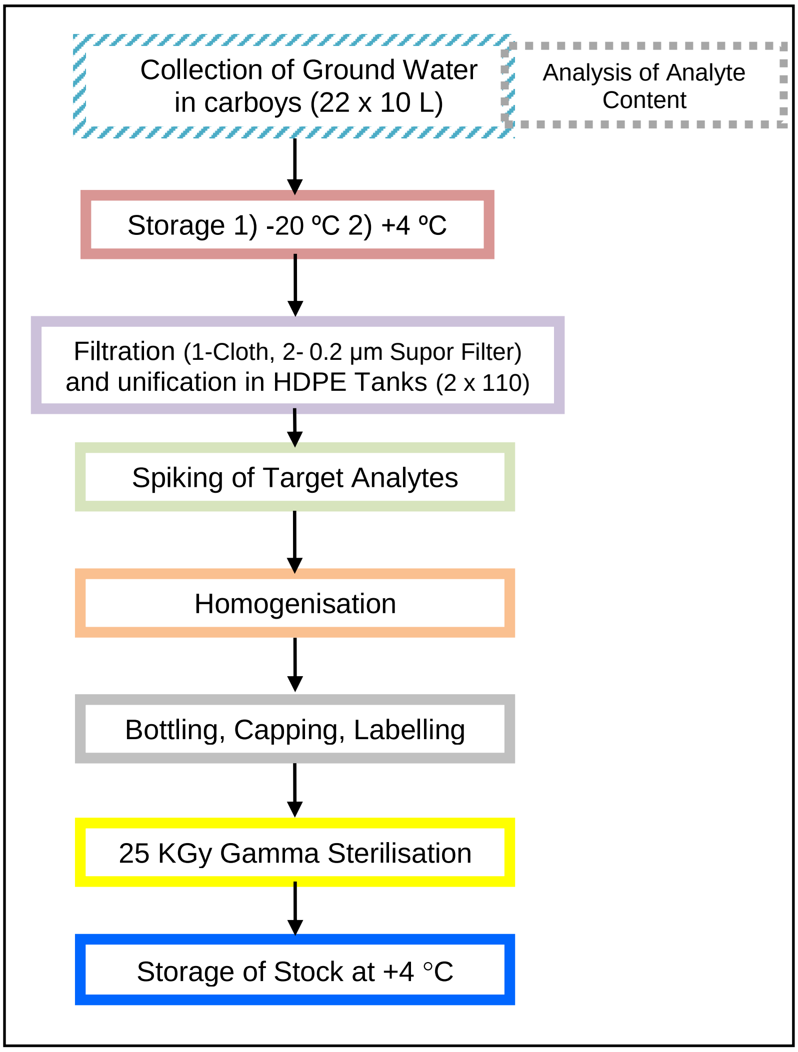


Figure 3: Flow diagram for the processing of candidate ground water CRM

4.1.2 Production of Elements in River Water CRM

The river water used as raw material was collected from a creek feeding an artificial lake (Darlık Dam) which is one of İstanbul's water supplies in Turkey. Prior to collection, 10-litre carboys were cleaned with deionised water and dried at ambient temperature. Collected samples were transported to TUBITAK for further processing.

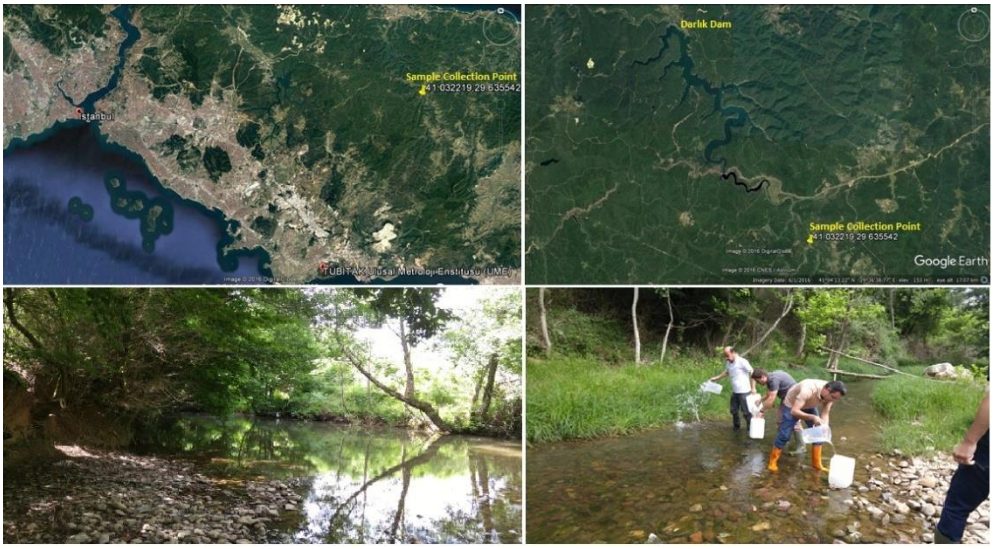


Figure 4. River water raw material collection point satellite view with photo of collection

Upon arrival at TUBITAK, samples were acidified and preliminary measurements on subsamples were performed. Results of these measurements are summarised in Table 1.

Table 1. Natural and target concentration levels of elements in river water

Parameter	Preliminary Measurement Result µg/kg, n=20	Target Level µg/kg	Target Uncertainty Range (%)
As	1.0 ± 0.1	15	10-20
Cd	< 0.1	0.5	
Hg	< 0.05	0.1	
Ni	1.4 ± 0.2	15	
Pb	0.3 ± 0.1	5	
Se	< 0.1	5	

± represents standard deviation

Results showed that the candidate raw material had lower element content than the target levels, therefore it was decided to spike this material to reach the target level for all elements. Prior to the filling, low particulate bottles were filled with deionised water and dried in an ISO Class 6 clean laboratory. Filtration, spiking of analytes and homogenisation was followed by filling, capping and gamma sterilisation of a total of 1250 units (approximately 100 mL each).

Figure 5. Cleaning and drying of bottles in ISO Class 6 Clean Laboratory

All stages of processing are summarised and given as a flow diagram in Figure 6.

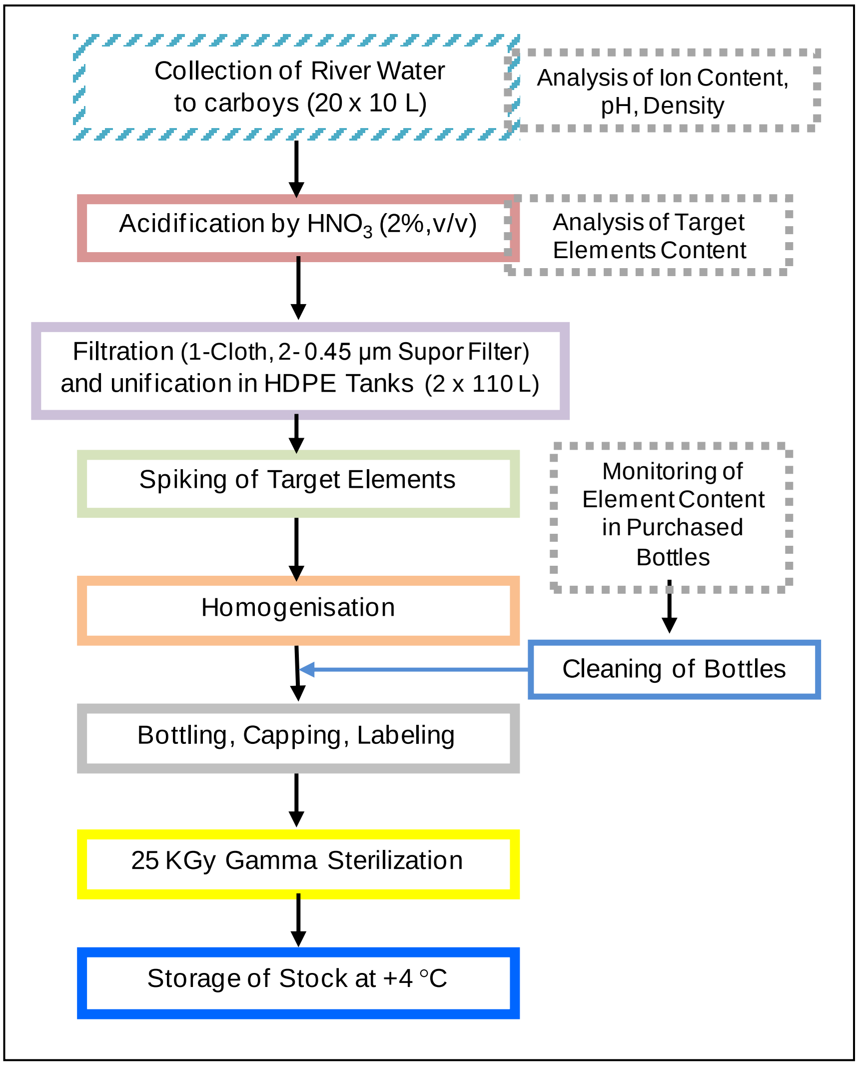


Figure 6: Flow diagram for the processing of candidate river water CRM

4.1.3 Production of Elements in Soil CRM

The soil raw material was collected from an area close to the coal burning Çayırhan Power Plant in Ankara, Turkey, to ensure levels of elements similar to the determined target levels. A 60 kg soil sample was transported to TUBITAK for further processing. The collected soil was placed in aluminium trays and dried at 35 °C for a week. Large visible impurities (roots, stones, etc.) were removed manually.

Figure 7. Soil raw material collection point satellite view with photo of collection

Preliminary measurement results on subsamples of approximately 2 kg of dried soil are summarised in Table 2.

Table 2. Preliminary analysis results of soil subsamples

Element	Mass Fraction (mg/kg)	Target Range (mg/kg)	Maximum Target Uncertainty (%)
As	44 ± 5	40-80	20
Cd	0.11 ± 0.02	0.5-1.5	7
Co	6.3 ± 0.5	20-60	20
Cr	61 ± 7	50-110	20
Cu	10 ± 1	40-80	20
Hg	0.078 ± 0.022	0.2-1.5	20
Ni	29 ± 2	40-80	20
Pb	6.4 ± 0.1	40-80	11
Sb	0.43 ± 0.02	1.0-3.0	20
V	85 ± 5	30-100	20
Zn	36 ± 4	100-200	20

± represents standard deviation

Results showed that the candidate raw material contained less than the targeted amount of most elements (Cd, Co, Cu, Hg, Ni, Pb, Sb, Zn). It was decided to blend this soil with a contaminated soil to reach target elemental content in the final product. Arsenic, chromium, iron, manganese and vanadium levels were present at target levels in the candidate soil.

Dried soil material was sieved and successively milled to yield fine soil smaller than 100 micrometre particle size. After homogenisation of the soil with 3-D mixing and riffle mixing, the material was stored at room temperature.

Figure 8. Milling, sieving and filling of soil CRM candidate

In order to obtain a soil product close to the target levels of elements in the final product, it was decided to produce a contaminated soil to blend with the homogenised soil. The contaminated soil was prepared from the original homogenised soil. A mix solution for spiking was prepared from Cd, Hg, Sb, Co, Cu, Ni, Pb and Zn and mixed with homogenised soil. A slurry of soil and mix solution was prepared, placed into an aluminium tray and oven dried. Ball milling and sieving followed by 3-D homogenisation yielded the desired contaminated soil. Stepwise blending continued until a 30.1 kg mixture of spiked soil and original soil was achieved. Final homogenisation on a 3-D mixer was followed by splitting the homogenised final product into 25 g portions in plastic containers. 1179 units were filled and capped then underwent gamma sterilisation. All stages of processing are summarised and given as a flow diagram in Figure 9.

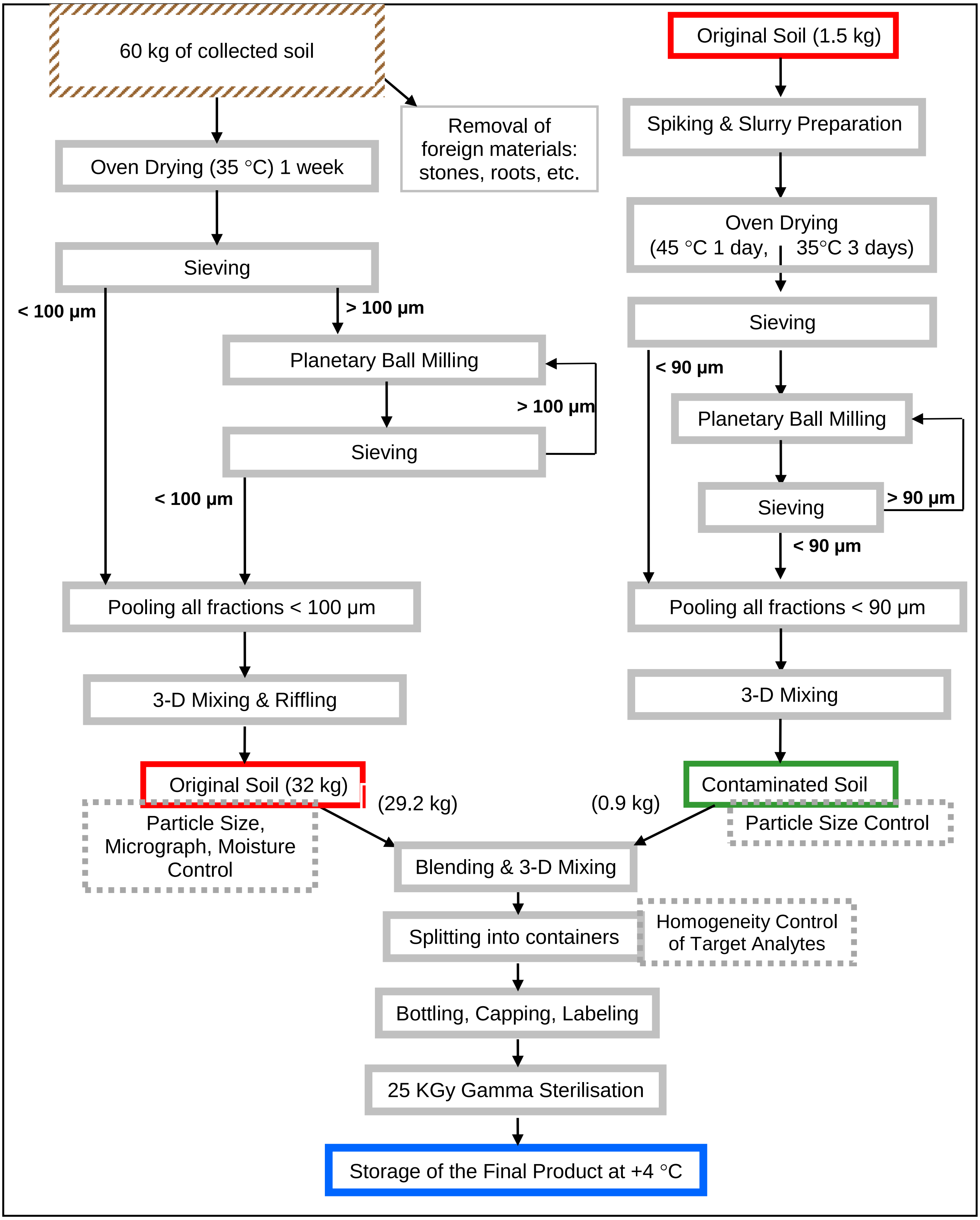


Figure 9: Flow diagram for the processing of candidate soil CRM

4.1.4 Conclusion

The objective to produce CRM candidates was achieved. Three CRM candidates – a ground water for organic analytes, a river water and a soil for inorganic analytes – have been produced in three stages. In the first stage, the needs of the environmental analysis and monitoring laboratories were collected and detailed planning for sampling and production was carried out. In the second stage, candidate raw samples were collected and their suitability checked. In the third stage, raw materials were processed according to the prepared plans.

Figure 10: Three CRM candidates in their final containers

4.2 Homogeneity and Stability Tests of CRM Candidates

The aim of this objective was to obtain information about the homogeneity and stability of the candidate CRMs which are key requirements for any reference material.

4.2.1 Homogeneity and Stability of Organic Analytes in Candidate Ground Water CRM

Homogeneity Tests

Homogeneity studies are performed to show that the assigned values are valid for all produced units within the stated uncertainty. 24 units of the candidate ground water CRM were selected by using random stratified sampling. For the evaluation of homogeneity, since samples are for single use, bulk material left from production of the candidate reference material was used to quantify within-unit heterogeneity which is calculated from the measurement results variance of 24 subsamples prepared from the bulk material. Between-units homogeneity is calculated from the variance in measurement results of 24 units selected by stratified sampling scheme covering the whole batch. The measurements were performed under repeatable conditions, using validated methods and according to a random sequence to clarify the possible trends in analytical sequence and filling order. The evaluation of homogeneity and calculation of uncertainty between and within units was performed by using equations (1) and (2).

The s_{bb} is calculated using the equation given below;

$$s_{\mathrm{bb}}^2 = \frac{MS_{between}-MS_{within}}{n},\ n = 1 \qquad (1)$$

Alternatively u_{bb}^* is calculated using equation below;

$$u_{\mathrm{bb}}^* = \sqrt{\frac{MS\text{ within}}{n}}\,\mathrm{x}\,\sqrt[4]{\frac{2}{df MS\text{ within}}}\quad n=1, \qquad (2)$$

where,

s_{bb} : Between-bottles standard deviation
$u*_{bb}$: Standard uncertainty of heterogeneity that can be hidden by method repeatability
$MS_{between}$: Mean of square of variance between units
MS_{within} : Mean of square of variance within the unit
n : Number of measurements within unit
df : Degree of freedom

The between-bottles homogeneity, s_{bb} and u_{bb} values are given in Table 3. As a conservative approach, the larger value of $s_{\mathrm{bb,rel}}$ and $u_{\mathrm{bb,rel}}^*$ was accepted as the estimate for the relative between units uncertainty, $u_{\mathrm{bb,rel}}$.

Table 3. Results of the Homogeneity Study for Candidate Organic CRM

	L-PFOA	L-PFOS
$s_{\mathrm{bb,rel}}(\%)$	4.19	cannot be calculated since MS $_{\mathrm{between}}$ <MS $_{\mathrm{within}}$
$u^{*}_{\mathrm{bb,rel}}(\%)$	1.94	4.54
$u_{\mathrm{bb,rel}}(\%)$	**4.19**	**4.54**

Stability Tests

Stability studies were performed with isochronous design. For the Short Term Stability (STS) test, two different temperatures (+18 ˚C and +60 ˚C) and 4 time points (0, 1, 2 and 4 weeks) were tested. 28 units were selected by using a stratified sampling scheme covering whole batch. 24 samples were subjected to the test temperatures for the specified time intervals. For the Long Term Stability (LTS) test, 16 units for each laboratory (TUBITAK and SYKE) were tested at +18 ˚C at 0, 3, 6 and 12 months time points.

Units were moved to +4 ˚C (reference temperature) after completion of the test time. All units were analysed at the same time. Samples were prepared based on the single use for each unit and were analysed by two laboratories under the repeatability conditions to determine the mass concentration of L-PFOA and L-PFOS.

The data for each temperature were first examined by single Grubbs test for both 95 % and 99 % confidence intervals to find out outliers. Number of detected outliers are given in the Table 4 for STS and Table 5 for LTS. Values calculated for each time point were plotted against the time. The relationship between variables were analysed in order to determine if any significant change exists with the testing time (regression analysis). For STS assessment, it was found that the slopes were significant for both L-PFOS and L-PFOA reported by SYKE (except for 60 °C in 99 % confidence interval).

As a consequence for the cases for which the slopes were significant, degradation is taken into account in the calculation of u_{sts} and u_{lts}. Uncertainty calculations were done using equation (3). Maximum time for transfer is chosen as 2 weeks for STS and shelf life is chosen as 12 months for LTS.

$$u_{sts}\ or\ u_{lts} = \frac{RSD}{\sqrt{\sum(t_i-\bar{t})^2}}\ x\ t \qquad (3)$$

where,

RSD: Relative standard deviation of the slope on stability regression plot
t_i : time point for each replicate
$\bar{t}$: mean of all time points
t : maximum transfer time suggested for STS or shelf life suggested for LTS

The results are summarised in Table 4 and Table 5.

Table 4. Short Term Stability Test Results

Parameter (Lab)	18 °C $u_{\mathrm{sts,rel}}$ for 2 weeks (%)	60 °C $u_{\mathrm{sts,rel}}$ for 2 weeks (%)	**Number of outliers in 95 % confidence interval[1]**		**Number of outliers in 99 % confidence interval[1]**		**Is there a significant trend in 95 % confidence interval?**		**Is there a significant trend in 99 % confidence interval?**	
			18 °C	**60 °C**	**18°C**	**60 °C**	**18 °C**	**60 °C**	**18°C**	**60 °C**
L-PFOS (TUBITAK)	8.2[2]	5.0[2]	1	1	1	1	No	No	No	No
L-PFOS (SYKE)	**2.4**[3]	1.2	-	-	-	-	Yes	Yes	Yes	No
L-PFOA (TUBITAK)	1.8	1.2	1	-	-	-	No	No	No	No
L-PFOA (SYKE)	2.2[3]	**3.2**[3]	-	-	-	-	Yes	Yes	Yes	Yes

[1] Single Grubbs Test
[2] Technical problem for this measurement was reported by the analyst
[3] u_{sts} was calculated considering the degradation

Table 5. Long Term Stability Test Results

Parameter (Lab)	18 °C $u_{lts,rel}$ for 12 months (%)	Number of outliers in 95 % confidence interval[1]	Number of outliers in 99 % confidence interval[1]	Is there a significant trend in 95 % confidence interval?	Is there a significant trend in 99 % confidence interval?
		18 °C	18°C	18 °C	18°C
L-PFOS (TUBITAK)	1.5	1	1	No	No
L-PFOS (SYKE)	**2.7**	-	-	No	No
L-PFOA (TUBITAK)	1.1*	-	-	Yes	No
L-PFOA (SYKE)	**2.3**	-	-	No	No

*Slope is found to be significant at 95 % confidence interval, u_{lts} is calculated by taking into account the degradation (u_{lts}= slope of reg. line/√3)

4.2.2 Homogeneity and Stability of Inorganic CRMs

Homogeneity Tests

A homogeneity study between the units was performed with 12 units which were selected by using random stratified sampling for each of the two participant laboratories. Homogeneity tests were carried out by measuring 3 sub-samples under repeatable conditions. The samples to be analysed were introduced to the instruments in random order to find out any trend arising from analytical and/or filling sequences.

The measurement results showed inconsistency with the spiked amount for Hg. As a consequence Hg was not investigated further and tests were performed on the remaining five elements. The data obtained by both laboratories were evaluated statistically by regression analysis for the presence of any trend in analytical and filling sequence at 99 % confidence level.

The ANOVA (analysis of variance) allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the following equations:

$$s_{wb} = \sqrt{MS_{within}} \tag{4}$$

MS_{within} : Mean squares within-unit

s_{wb} is equivalent to the standard deviation of the method, provided that subsamples are representative for the whole unit.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \tag{5}$$

$MS_{between}$: Mean squares between-unit
n : Number of replicates per unit

When $MS_{between}$ is smaller than MS_{within}, s_{bb} cannot be calculated. Instead, u^*_{bb}, the heterogeneity that can be hidden by the method repeatability, is calculated, according to the following equation:

$$u_{bb}^{*} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \tag{6}$$

$\nu_{MSwithin}$: Degrees of freedom of MS_{within}

The occurrence of $MS_{between} < MS_{within}$ can be seen, if material heterogeneity is smaller than that can be detected by the analytical methodology used.

Results of the Homogeneity Tests for Candidate River Water CRM

Only analytical sequence trends were found for As (JSI), Cd (TUBITAK) and Ni (TUBITAK) and data was not reprocessed to correct for these trends.

Grubbs test (one sided) was applied to all data for the presence of outlier at 99 % confidence level and no outlier was detected.

For the parameters for which ANOVA was applied, the larger value of s_{bb} or u^*_{bb} is taken as uncertainty contribution for homogeneity, u_{bb} (Table 6). As a conservative approach, the uncertainty contribution for homogeneity, $u_{bb,rel}$ is accepted as the highest value of the two institute's results (except for Se which is only measured by TUBITAK).

Table 6. Results of the Homogeneity Study for Candidate River Water CRM

Parameter (Lab)	$s_{wb,rel}$ %	$s_{bb,rel}$ %	$u^*_{bb,rel}$ %	$u_{bb,rel}$ %
As (TUBITAK)	1.15	$MS_{between}<MS_{within}$	0.36	**0.36**
As (JSI)	0.90	$MS_{between}<MS_{within}$	0.28	0.28
Cd (TUBITAK)	1.73	$MS_{between}<MS_{within}$	0.54	**0.54**
Cd (JSI)	1.72	$MS_{between}<MS_{within}$	0.53	0.53
Ni (TUBITAK)	2.92	$MS_{between}<MS_{within}$	0.90	**0.90**
Ni (JSI)	1.13	$MS_{between}<MS_{within}$	0.35	0.35
Pb (TUBITAK)	0.97	0.15	0.30	0.30
Pb (JSI)	2.17	$MS_{between}<MS_{within}$	0.67	**0.67**
Se (TUBITAK)	2.53	$MS_{between}<MS_{within}$	0.79	**0.79**

Results of the Homogeneity Tests for Candidate Soil CRM

Only analytical sequence trends were found for As, Co, Cu, Hg, Ni, Pb, Zn (for data by TUBITAK) and V (for both institutes) and data were not reprocessed to correct for these trends. A filling sequence was detected for Fe, but the relative uncertainty arising from this heterogeneity was found to be low: 0.32%.

Grubbs test (one sided) was applied to all data for the presence of outlier at 99 % confidence level and one outlier each for Co, Fe and Mn were detected. Since no technical reason can be found to reject these data, all outliers were included in the homogeneity calculations. As a conservative approach, the uncertainty contribution for homogeneity, $u_{bb,rel}$ is accepted as the highest value of the two institute's results (except for Fe and Pb which were only measured by TUBITAK) (Table 7).

Table 7. Results of the Homogeneity Study for Candidate Soil CRM

Parameter (Lab)	$s_{wb,rel}$ %	$s_{bb,rel}$ %	$u^*_{bb,rel}$ %	$u_{bb,rel}$ %
As (TUBITAK)	2.85	MSbetween<MSwithin	0.88	**0.88**
As (JSI)	2.09	0.45	0.65	0.65
Cd (TUBITAK)	1.76	1.12	0.55	**1.12**
Cd (JSI)	1.68	0.71	0.52	0.71
Co (TUBITAK)	2.50	MSbetween<MSwithin	0.78	**0.78**
Co (JSI)	1.28	0.57	0.40	0.57

Table 7. Results of the Homogeneity Study for Candidate Soil CRM (continue)

Parameter (Lab)	$s_{\text{wb,rel}}$ %	$s_{\text{bb,rel}}$ %	$u^*_{\text{bb,rel}}$ %	$u_{\text{bb,rel}}$ %
Cr (TUBITAK)	2.43	2.69	0.75	**2.69**
Cr (JSI)	2.77	0,78	0.86	0.86
Cu (TUBITAK)	2.45	MSbetween<MSwithin	0.76	**0.76**
Cu (JSI)	4.41	2.54	0.82	2.54*
Fe (TUBITAK)	0.90	0.32	0.28	**0.32**
Hg (TUBITAK)	2.85	MSbetween<MSwithin	0.88	0.88
Hg (JSI)	2.96	1.17	0.92	**1.17**
Mn (TUBITAK)	0.68	0.34	0.21	0.34
Mn (JSI)	1.42	MSbetween<MSwithin	0.44	**0.44**
Ni (TUBITAK)	1.85	MSbetween<MSwithin	0.57	0.57
Ni (JSI)	1.73	1.08	0.54	**1.08**
Pb (TUBITAK)	1.39	MSbetween<MSwithin	0.43	**0.43**
Sb (TUBITAK)	1.99	MSbetween<MSwithin	0.62	0.62
Sb (JSI)	3.15	1.22	0.98	**1.22**
V (TUBITAK)	2.12	MSbetween<MSwithin	0.66	0.66
V (JSI)	3.35	MSbetween<MSwithin	1.04	**1.04**
Zn (TUBITAK)	2.31	MSbetween<MSwithin	0.72	**0.72**
Zn (JSI)	1.17	0.38	0.36	0.38

* A technical problem was detected for these measurements

It was decided not to use the Cu result of JSI due to a technical problem detected in the measurements.

Stability Tests

The stability studies were carried out using an isochronous design. In this approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"), effectively "freezing" the degradation status of the materials. At the end of the isochronous storage, the samples are analysed simultaneously under repeatable conditions. Analysis of the material (after various exposure times and temperatures) under repeatable conditions greatly improves the sensitivity of the stability tests.

For the Short Term Stability (STS) test, two different temperatures (18 ˚C and 60 ˚C) and 4 time points (0, 1, 2, and 4 weeks) were tested. 14 samples were randomly selected for each of the participating laboratories and 12 samples were subjected to the test temperatures for the specified time intervals.

Test samples were moved to +4 ˚C (reference temperature) after completion of the test time. All samples were analysed at the same time.

The data for each temperature were first examined by single Grubbs test for both 95 % and 99 % confidence intervals to find outliers.

Values calculated for each time point were plotted against the time for the assessment of short term stability. The relationships between variables were analysed in order to determine if any significant change exists with the testing time (regression analysis).

Short Term Stability Results:

The results obtained from isochronous measurements were first grouped according to the time period and then evaluated for each time point. These evaluations were carried out for both temperatures, separately.

The results were screened for outliers by applying the single Grubbs' test at confidence levels of 95 % and 99 %. The measured concentration values were plotted against time and the regression lines were calculated to check for significant trends indicating possible changes in the concentrations of the analytes by time. The calculated slope values were tested for significance using a t-test, with $t_{\alpha,df}$ being the critical t-value (two-tailed) for a significance level α = 0.05 (95 % confidence level).

Uncertainty calculations are done using equation (7). Maximum time for transfer is chosen as 4 weeks.

$$u_{sts,rel} = \frac{RSD}{\sqrt{\Sigma(t_i - \bar{t})^2}} \times t \qquad (7)$$

where,

RSD : relative standard deviation of the points on the regression line
t_i : time point for each replicate
$\bar{t}$: mean of all time points
t : maximum time suggested for transfer (4 weeks)

Results of the Short Term Stability Tests for Candidate River Water CRM

Outliers for As, Ni, Pb and Se were identified in the statistical evaluation (Grubbs' test) of the data; nevertheless, as there was no technical reason to exclude them from evaluation, they remained in the data set. The data points were plotted against storage time at the test temperature and the regression line was calculated. In all cases the slope of the regression line was not found to be significantly different from zero. The data evaluation results for the short-term stability at +18 °C and +60 °C are summarised in Table 8.

Table 8. Results of short term stability tests of river water CRM

Parameter (Lab)	18 °C $u_{sts,rel}$ **(%)**	60 °C $u_{sts,rel}$ **(%)**	**Number of outliers in 95 % confidence interval***		**Number of outliers in 99 % confidence interval***		**Is there a significant trend in 95 % confidence interval?**		**Is there a significant trend in 99 % confidence interval?**	
			18 °C	**60 °C**	**18 °C**	**60 °C**	**18 °C**	**60 °C**	**18 °C**	**60 °C**
As (TUBITAK)	0.91	**0.97**	1	-	-	-	No	No	No	No
As (JSI)	0.51	0.61	-	1	-	-	No	No	No	No
Cd (TUBITAK)	**0.79**	0.78	-	1	-	-	No	No	No	No
Cd (JSI)	0.58	0.75	-	-	-	-	No	No	No	No
Ni (TUBITAK)	0.94	**0.98**	1	1	1	1	No	No	No	No
Ni (JSI)	0,54	0.79	1	-	1	-	No	No	No	No
Pb (TUBITAK)	0.59	**0.60**	1	-	-	-	No	No	No	No
Pb (JSI)	0.32	0.57	1	-	-	-	No	No	No	No
Se (TUBITAK)	3.19	**3.55**	1	1	1	1	No	No	No	No

*SGT: Single Grubbs' Test

As a conservative approach, the uncertainty contribution for short term stability, $u_{\mathrm{sts,rel}}$ is accepted as the highest value obtained for the two test temperatures by two institute’s (shown in bold, Table 8) except Se which was analysed only by TUBITAK.

Results of the Short Term Stability Tests for Candidate Soil CRM

Outliers (shown in Table 8) were identified in the statistical evaluation (Grubbs’ test) of the data; nevertheless, as there was no technical reason to exclude them from evaluation, they remained in the data set. The data points were plotted against storage time at the test temperature and the regression line was calculated. In all cases the slope of the regression line was not found to be significantly different from zero. The data evaluation results for the short-term stability at +18 °C and +60 °C are summarised in Table 9.

Table 9. Results of short term stability tests of soil CRM

Parameter (Lab)	18 °C $u_{\mathrm{sts,rel}}$ (%)	60 °C $u_{\mathrm{sts,rel}}$ (%)	**Number of outliers in 95 % confidence interval***		**Number of outliers in 99 % confidence interval***		**Is there a significant trend in 95 % confidence interval?**		**Is there a significant trend in 99 % confidence interval?**	
			18 °C	**60 °C**	**18°C**	**60 °C**	**18 °C**	**60 °C**	**18°C**	**60 °C**
As (TUBITAK)	1.12	1.48	-	-	-	-	No	No	No	No
As (JSI)	**1.56**	1.16	-	-	-	-	No	No	No	No
Cd (TUBITAK)	2.04	**2.36**	-	1	-	-	No	Yes	No	No
Cd (JSI)	0.80	0.72	1	1	1	1	No	No	No	No
Co (TUBITAK)	0.92	0.88	-	1	-	1	No	No	No	No
Co (JSI)	**1.00**	0.92	-	-	-	-	No	No	No	No
Cr (TUBITAK)	2.68	**2.80**	-	-	-	-	No	No	No	No
Cr (JSI)	2.56	2.28	-	-	-	-	No	No	No	No
Cu (TUBITAK)	0.80	1.08	-	1	-	1	No	No	No	No
Cu (JSI)	**2.36**	1.88	-	-	-	-	Yes	No	No	No
Fe (TUBITAK)	0.44	**0.56**	-	-	-	-	No	No	No	No
Hg (TUBITAK)	**5.12**	4.80	-	-	-	-	No	No	No	No
Hg (JSI)	2.20	2.20	-	-	-	-	No	No	No	No
Mn (TUBITAK)	0.24	0.40	-	-	-	-	No	No	No	No
Mn (JSI)	0.60	**0.64**	-	-	-	-	No	No	No	No
Ni (TUBITAK)	**1.68**	1.28	-	1	-	-	No	No	No	No
Ni (JSI)	1.00	0.84	-	-	-	-	No	No	No	No
Pb (TUBITAK)	0.88	**1.16**	1	-	-	-	No	No	No	No
Sb (TUBITAK)	1.48	1.32	-	-	-	-	No	No	No	No
Sb (JSI)	2.56	**2.68**	-	-	-	-	No	No	No	No
V (TUBITAK)	0.96	1.08	-	1	-	1	No	No	No	No
V (JSI)	1.68	**1.68**	-	-	-	-	No	No	No	No
Zn (TUBITAK)	1.00	1.04	1	-	-	-	No	No	No	No
Zn (JSI)	**1.44**	1.12	-	-	-	-	No	No	No	No

*SGT: Single Grubbs’ Test

Long Term Stability Results:

The shelf life of the CRM has been determined through long term stability measurements. For the measurements, four units for each of the months of 0, 3, 6 and 12 have been stored at +18 °C and transferred to the reference temperature (+4 °C) after each period of time to be measured isochronously afterwards. Four units, designated as reference units, of the month 0 were stored at +4 °C.

The data for each time point has been calculated by 3 replicate measurements for each of two units. No outlying data was detected by Grubbs' test. The graphs were plotted against time and the regression lines were calculated. The relative long term stability uncertainty, $u_{lts,rel}$ for each parameter is then calculated using equation (8) for the required shelf life as:

$$u_{lts,rel} = \frac{RSD}{\sqrt{\Sigma\left(t_i - \bar{t}\right)^2}} \times t \qquad (8)$$

where,

RSD : the relative standard deviation of the points on the regression line
t_i : being the time point for each replicate
$\bar{t}$: being the average of all time points
t : being the proposed shelf life at 18 °C (12 months)

The uncertainty contribution u_{lts} was calculated for 12 months (t) at 18 °C.

Results of the Long Term Stability Tests for Candidate River Water CRM

As a conservative approach, the relative uncertainty contribution for long term stability, u_{lts},rel is accepted as the highest value obtained by two institutes (shown in bold, Table 10). The results are given in Table 10.

Table 10. Results of the long-term stability tests for candidate river water CRM for12 months

Analyte	Is the slope significantly different from zero at 18 °C?*	$u_{lts,rel}$ [%] for shelf-life of 12 months at 18 °C
As (TUBITAK)	No	**1.48**
As (JSI)	No	0.98
Cd (TUBITAK)	No	0.73
Cd (JSI)	No	**0.95**
Ni (TUBITAK)	No	**0.90**
Ni (JSI)	No	0.88
Pb (TUBITAK)	No	0.52
Pb (JSI)	No	**1.39**
Se (TUBITAK)	No	1.35
Se (JSI)	No	**2.22**

*Data are evaluated at confidence level of 95 %

Results of the Long Term Stability Tests for Candidate Soil CRM

The uncertainty contribution u_{lts} was calculated for 12 months (t) at 18 °C. As a conservative approach, the relative uncertainty contribution for long term stability, ults,rel is accepted as the highest value obtained by two institute's (shown in bold, Table 11).

Table 11. Results of the long-term stability tests for candidate soil CRM for 12 months

Parameter (Lab)	**Is the slope significantly different from zero at 18 °C?***	**$u_{lts,rel}$ [%] for shelf-life of 12 months at 18 °C**
As (TUBITAK)	No	0.71
As (JSI)	No	**0.98**
Cd (TUBITAK)	No	**1.24**
Cd (JSI)	No	0.80
Co (TUBITAK)	No	0.54
Co (JSI)	No	**1.36**
Cr (TUBITAK)	No	**5.83**
Cr (JSI)	No	1.26
Cu (TUBITAK)	No	0,64
Cu (JSI)	No	**0.85**
Fe (TUBITAK)	No	**1.02**
Hg (TUBITAK)	No	**1.84**
Hg (JSI)	No	1.29
Mn (TUBITAK)	No	0.64
Mn (JSI)	No	**0.98**
Ni (TUBITAK)	No	**1.35**
Ni (JSI)	No	1.10
Pb (TUBITAK)	No	**0.67**
Sb (TUBITAK)	No	**3.28**
Sb (JSI)	No	1.36
V (TUBITAK)	No	**1.31**
V (JSI)	No	1.24
Zn (TUBITAK)	No	**0.61**
Zn (JSI)	No	0.57

*Data are evaluated at confidence level of 95 %

4.2.3 Conclusion

The objective to carry out homogeneity and stability tests of the CRM candidates was achieved. Results of the homogeneity tests of the candidate organic analytes in ground water CRM showed that the between-unit variation for PFOS and PFOA are found to be low. The maximum allowed target uncertainty for homogeneity was 5 % and it was achieved.

Results of the homogeneity tests of the inorganic analytes in river water and soil candidate CRMs showed that the between-unit variation for all elements is found to be low. The maximum allowed target uncertainty for homogeneity was 2 % and it was achieved (except Cr in soil). Mercury was removed from the certification investigation of the candidate river water CRM due to inconsistency in the spiked and recovered amounts which is most probably due to instability of this element.

Based on the short term stability tests all candidate CRMs are found to be stable at 18 °C and 60 °C. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 60 °C for up to 2 weeks for organic analytes in ground water and 4 weeks for inorganic analytes in river water and soil, i.e. at ambient temperature without applying any cooling elements.

Based on the long term stability results obtained, 18 °C is found to be suitable to keep all candidate CRMs for up to 12 months.

Data obtained in the homogeneity and stability tests are used to calculate the uncertainty components due to between-bottle homogeneity and short and long term stabilities.

4.3 Characterisation of the CRM Candidates

The aim of this objective was to characterise the candidate CRMs based on inter-comparison studies between the partners. Partners who already had validated methods suitable for the candidate CRMs used their methods directly. Others developed and validated methods for the characterisation studies. BAM provided theoretical and practical training on reference method development and validation for organic and inorganic analytes in relevant matrices to the less experienced partners. Characterisation strategies were developed including EURAMET / CCQM key comparisons for candidate river water and ground water CRMs.

4.3.1 Characterisation of PFOS and PFOA in Ground Water Candidate CRM

The characterisation of the candidate organic analytes in ground water CRM could not be completed within the timeframe of the project due to the crowded CCQM schedule of the organic analysis working group. An international Key and Pilot study (CCQM-K156 and P198 Mass concentration of L-PFOA and L-PFOS in ground water) has been accepted by the organic analysis working group of the BIPM CCQM and is scheduled to be completed by May 2019.

4.3.2 Characterisation of Elements in River Water CRM

According to the ISO 17034 standard, the characterisation and value assignment of reference materials can be performed in different ways. In this project, the characterisation of the material was carried out via an interlaboratory comparison exercise. A EURAMET supplementary comparison study (EURAMET.QM-S11/EURAMET 1424) was organised. Candidate reference material samples were measured by 22 laboratories from 17 countries, including the project partners. Each laboratory received two bottles of sample which were selected from the whole set of samples to represent the whole produced batch. The samples were selected randomly from the set of samples by the random stratified sampling technique. Each laboratory was asked to report at least 6 independent measurement results for two sample units, together with their associated measurement uncertainty values and the approach used for the estimation of measurement uncertainty. In the reports, the details of the reference materials used in the calibration were also requested from the laboratories in order to assure the traceability of the reported results.

If a laboratory provided results using more than one method, all results were taken into account during the assignment of the certified value. A list of project partner with their corresponding methodologies used for the measurements are summarised in Table 12.

Table 12: Characterisation techniques used by project partners

Parameter	BAM	DMDM	GUM	JSI	NTUA	SYKE	TUBITAK	UW
As	-	ICP-MS	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Cd	ID ICP-MS	ICP-MS	ICP-OES	ICP-MS	1-ICP-MS 2-ASV	ICP-MS	ID ICP-MS	ICP-MS
Ni	ID ICP-MS	ICP-MS	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Pb	ID ICP-MS	ICP-MS	ICP-OES	ICP-MS	1-ICP-MS 2-ASV	ID ICP-MS	ID ICP-MS	ICP-MS
Se	-	-	-	ICP-MS	ICP-MS	-	ID ICP-MS	ICP-MS

ASV : Anodic Stripping Voltammetry
ICP-MS : Inductively Coupled Plasma Mass Spectrometry
ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry
ID-ICP-MS : Isotope Dilution ICP-MS

Characterisation standard uncertainty (u_{char}) is calculated using equation (9) by taking into account the uncertainties and the standard deviation of the means reported by the participating laboratories except Se. Characterisation standard uncertainty for selenium is accepted as the uncertainty reported by TUBITAK for the ID-ICP-MS method. Graphs for characterisation results are given in Figures 11-16, where error bars represent expanded uncertainties reported by the laboratories.

$$u_{\mathrm{char}} = \sqrt{\bar{u}^{2}_{\mathrm{labs}} + \left(\frac{SD}{\sqrt{n}}\right)^{2}} \qquad (9)$$

where,

u_{char} : Standard uncertainty arising from characterisation
$\bar{u}_{labs}$: Arithmetic mean of standard uncertainties reported by the participating laboratories
SD : Standard deviation of accepted means of participating laboratories
n : Number of laboratories with accepted results

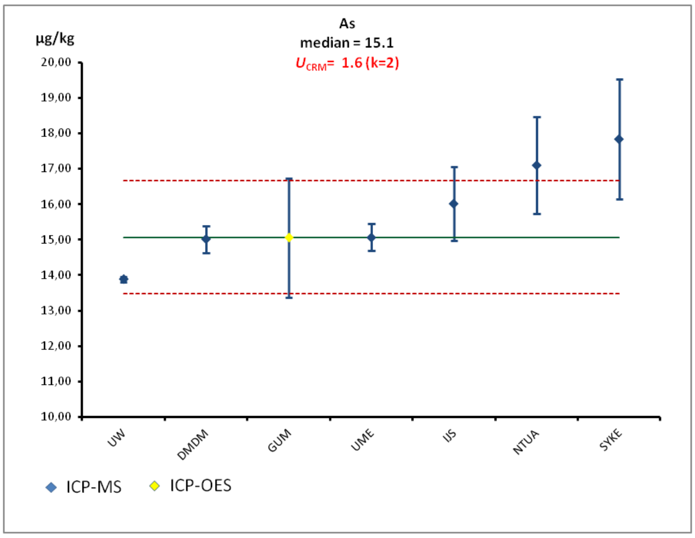


Figure 11. Characterisation study results for As

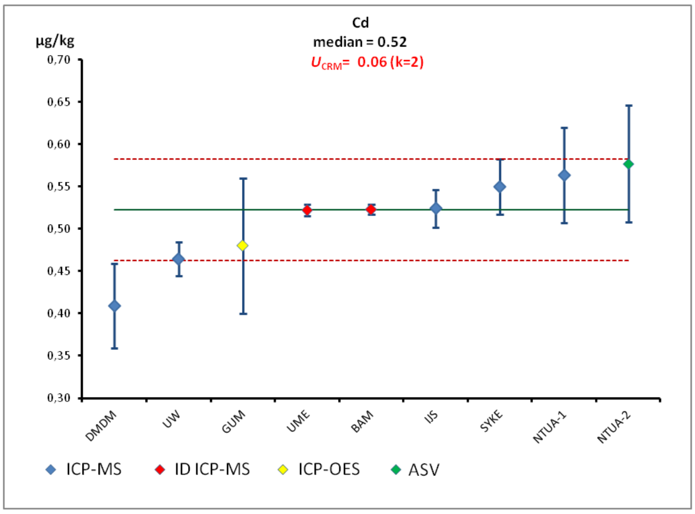


Figure 12. Characterisation study results for Cd

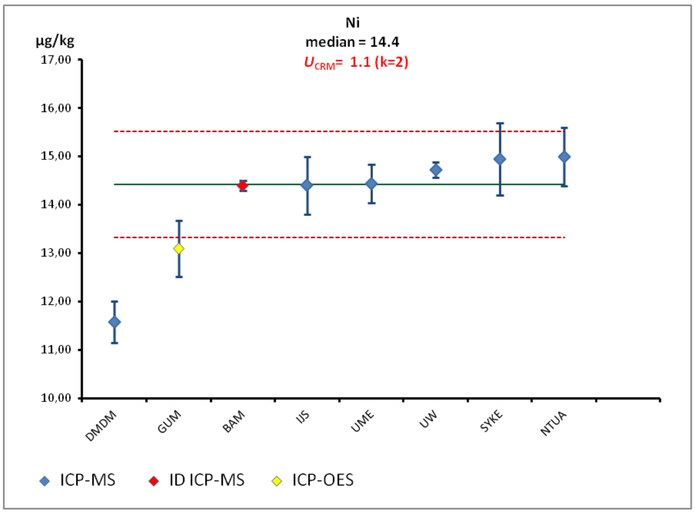


Figure 13. Characterisation study results for Ni

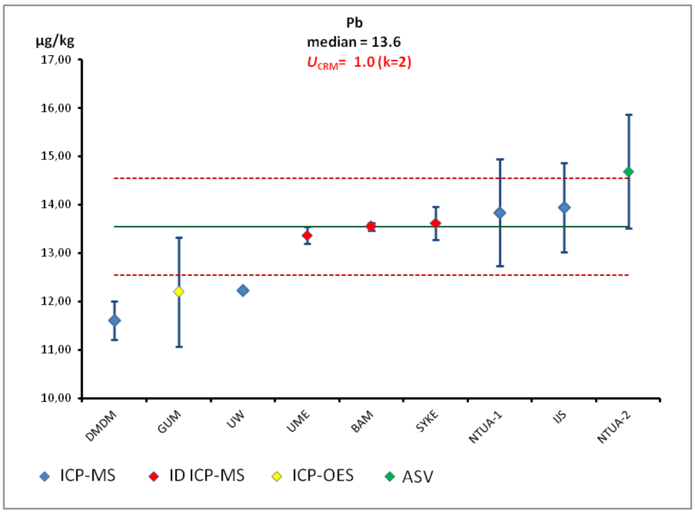


Figure 14. Characterisation study results for Pb

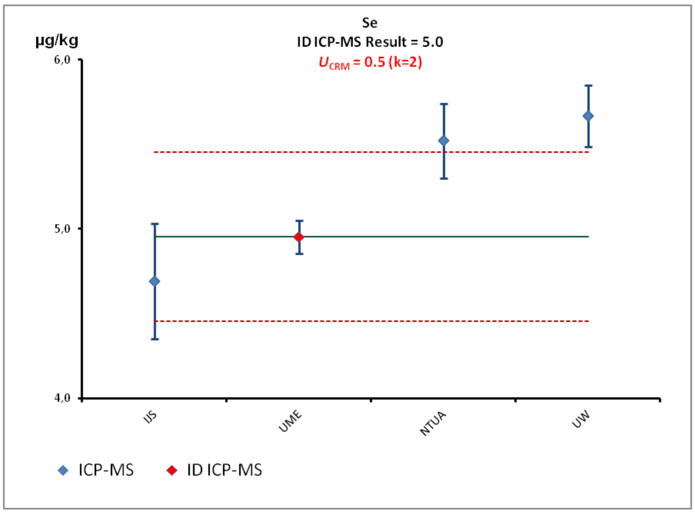


Figure 15. Characterisation study results for Se

4.3.3 Characterisation of Elements in Soil CRM

The characterisation of the material was carried out by an interlaboratory comparison exercise. The participating laboratories used validated methods (including potentially primary methods such as ID ICP-MS and k0-INAA).

Each laboratory received two bottles of sample which were selected such from the whole set of samples that they represent the whole produced batch. The samples were selected randomly from the set of samples by the random stratified sampling technique. Each laboratory was asked to report at least 6 independent measurement results for two sample units, together with their associated measurement uncertainty values and the approach used for the estimation of measurement uncertainty. In the reports, the details of the reference materials used in the calibration were also requested from the laboratories in order to assure the traceability of the reported results.

If a laboratory provided results using more than one method, all results were taken into account during the assignment of the certified value. A list of partners with their corresponding methodologies used for the measurements are summarised in Table 13.

Table 13: Characterisation techniques used by the partners

Parameter	BAM	DMDM	IMBiH	JSI	NTUA	TUBITAK	UW
As	-	ICP-MS	-	1) ICP-MS 2) k_0-INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Cd	ID ICP-MS	ICP-MS	-	ICP-MS	1) ICP-MS 2) ASV	ID ICP-MS	ICP-MS
Co	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Cr	ID ICP-MS	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	1) ICP-MS 2) ICP-OES	ID ICP-MS	ICP-MS
Cu	ID TIMS	ICP-MS	MP-AES	ICP-MS	1) ICP-MS 2) ICP-OES 3) ASV	ICP-MS	ICP-MS
Fe	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	-	1) ID ICP-MS 2) ICP-MS	AAS
Hg	ID ICP-MS	ICP-MS	-	1)CV-AAS; 2) k_0-INAA	ICP-MS	ID ICP-MS	ICP-MS
Mn	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	-	ICP-MS	ICP-MS
Ni	ID ICP-MS	ICP-MS	MP-AES	ICP-MS	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Pb	ID TIMS	ICP-MS	MP-AES	-	1) ICP-MS 2) ICP-OES 3) ASV	ID ICP-MS	ICP-MS
Sb	-	ICP-MS	-	1) ICP-MS 2) k_0-INAA	1) ICP-MS	ICP-MS	ICP-MS
V	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Zn	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0-INAA	1) ICP-MS 2) ICP-OES 3) ASV	ID ICP-MS	ICP-MS

AAS : Atomic Absorption Spectrometry
ASV : Anodic Stripping Voltammetry
CV-AAS : Cold Vapour Atomic Absorption Spectrometry
ICP-MS : Inductively Coupled Plasma Mass Spectrometry
ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry
ID ICP-MS : Isotope Dilution ICP-MS
ID TIMS : Isotope Dilution Thermal Ionisation Mass Spectrometry
k_0-INAA : k0-Instrumental Neutron Activation Analysis
MP-AES : Microwave Plasma Atomic Emission Spectrometry

Characterisation standard uncertainty (u_{char}) is calculated using equation (9) by taking into account the uncertainties and the standard deviation of the means reported by the participating laboratories except As and Sb. Characterisation standard uncertainties for As and Sb are accepted as the uncertainty reported by JSI for the k_0-INAA method. Graphs for characterisation showing both total element and aqua regia extractable element content data are given in Figures 16-28, where error bars represent expanded uncertainties reported by the laboratories.

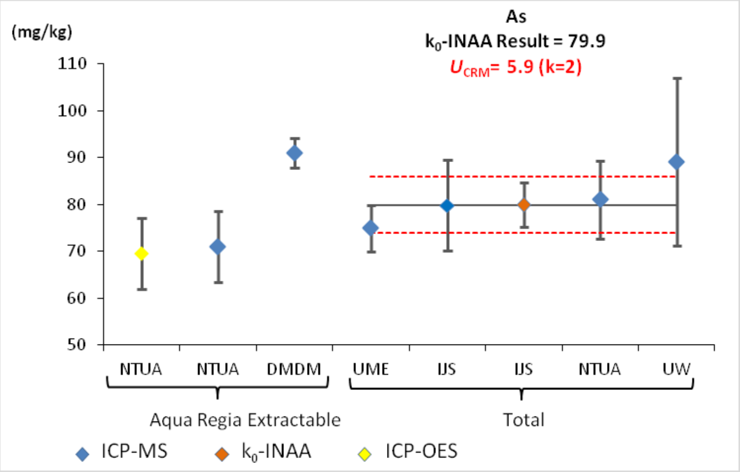


Figure 16. Characterisation study results for As

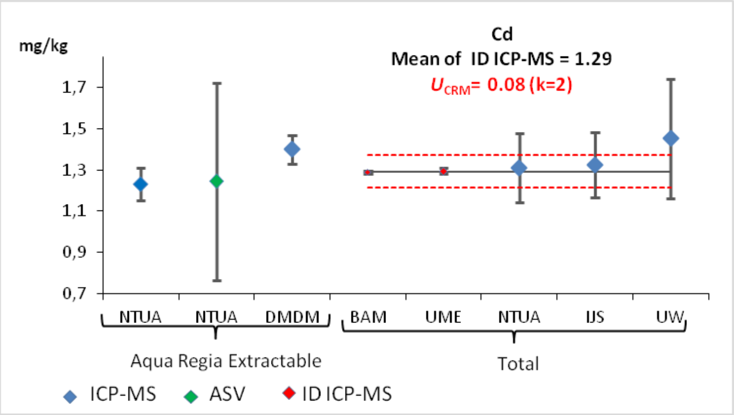


Figure 17. Characterisation study results for Cd

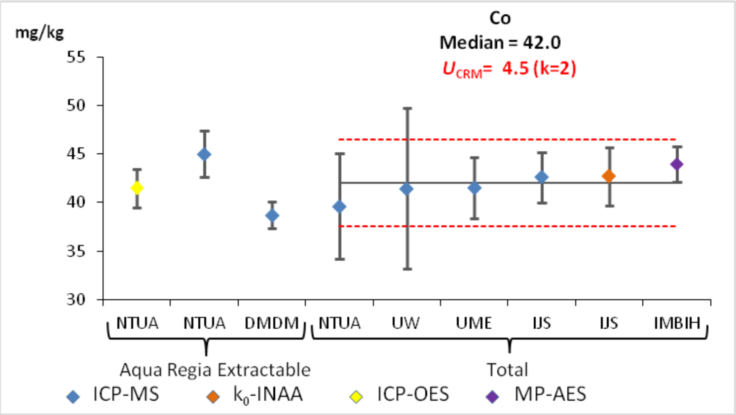


Figure 18. Characterisation study results for Co

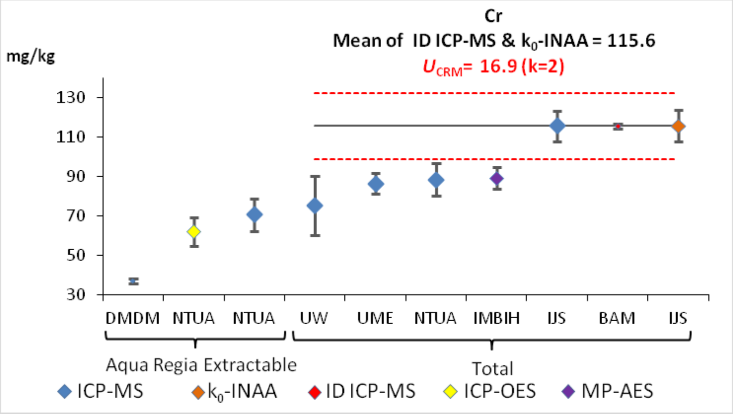


Figure 19. Characterisation study results for Cr

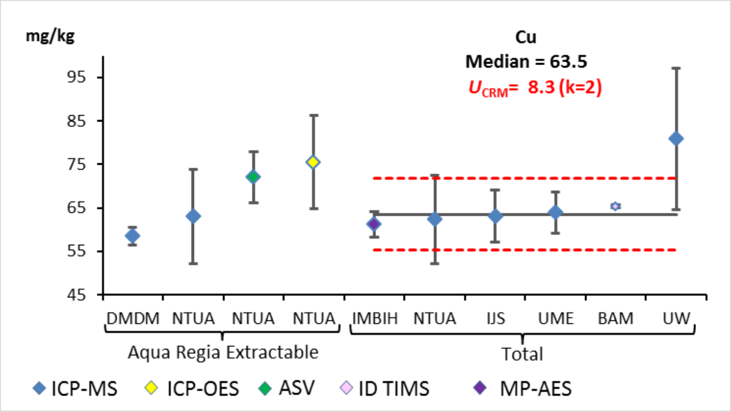


Figure 20. Characterisation study results for Cu

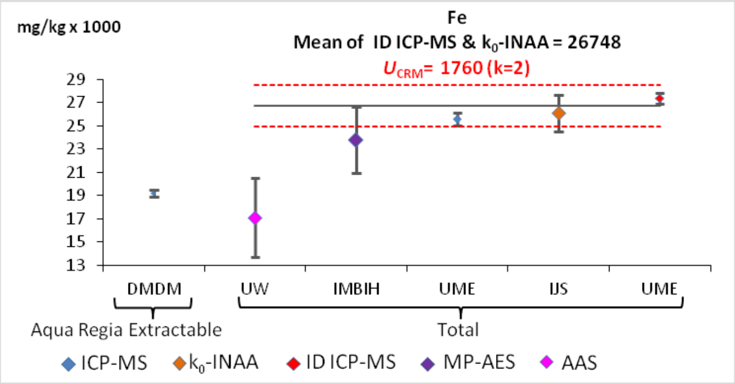


Figure 21. Characterisation study results for Fe

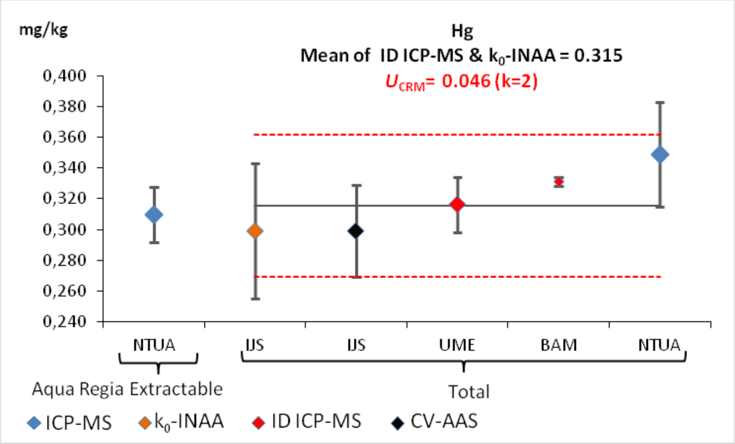


Figure 22. Characterisation study results for Hg

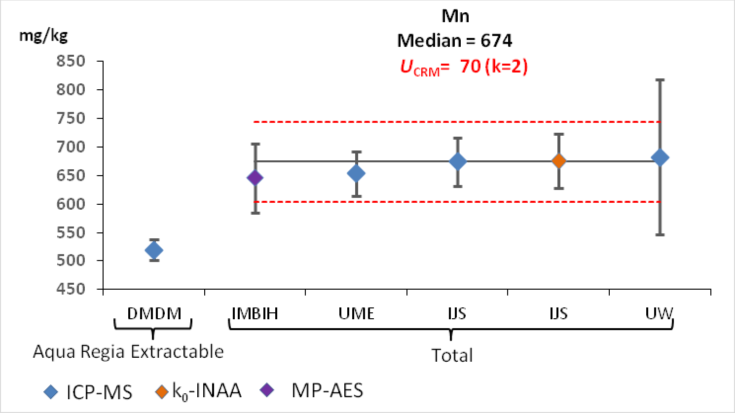


Figure 23. Characterisation study results for Mn

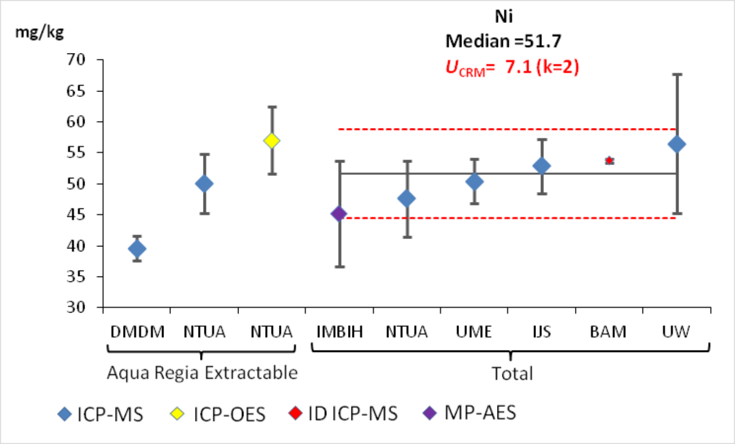


Figure 24. Characterisation study results for Ni

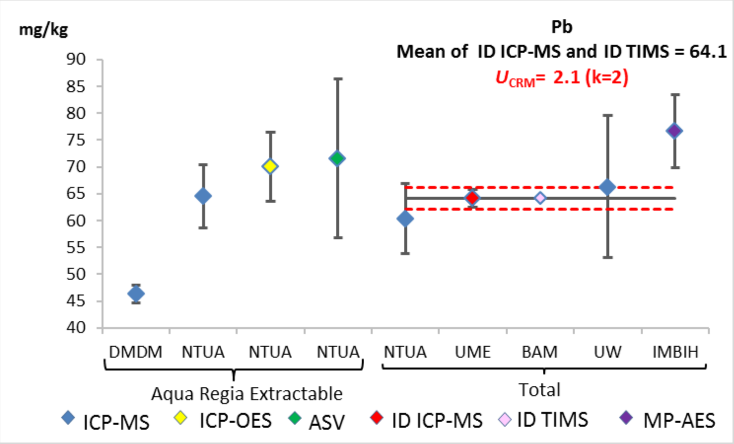


Figure 25. Characterisation study results for Pb

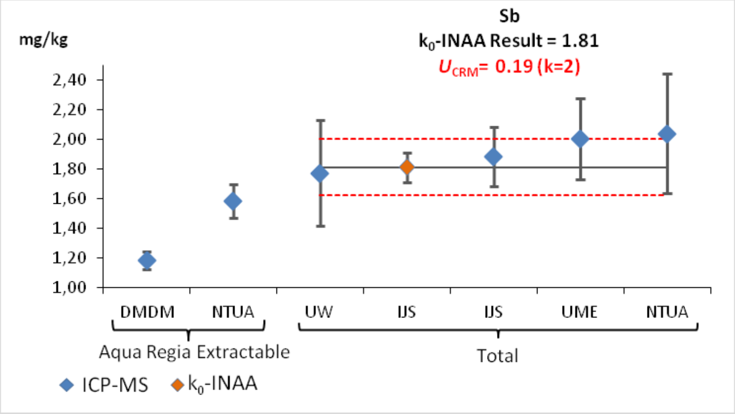


Figure 26. Characterisation study results for Sb

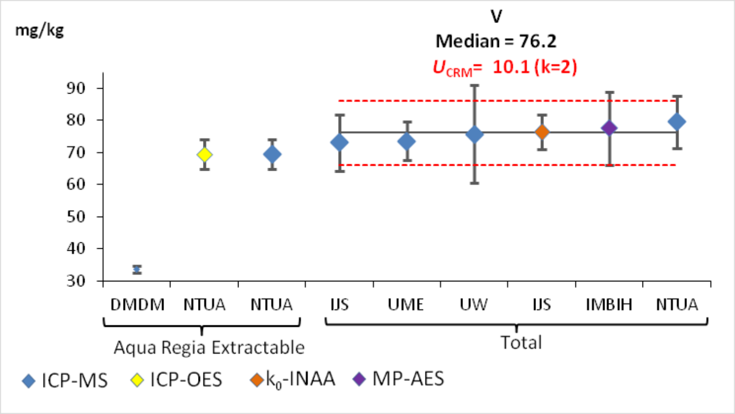


Figure 27. Characterisation study results for V

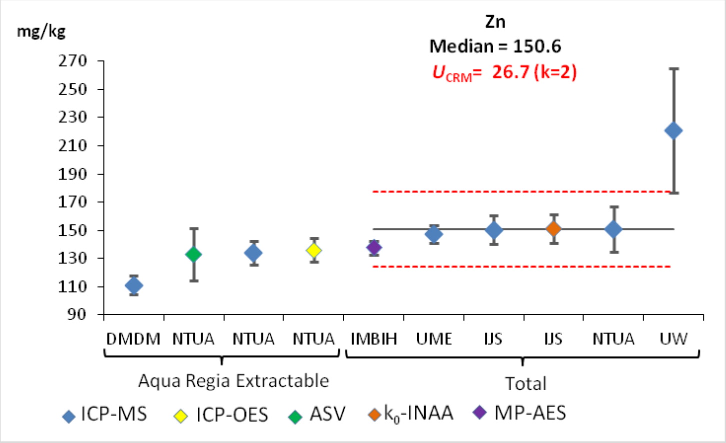


Figure 28. Characterisation study results for Zn

4.3.4 Conclusion

The objective to characterise the CRM candidates was partially achieved.

Characterisation studies for the candidate river water and soil CRMs were successfully completed with the utilisation of validated measurement methods including reference methods such as ID ICP-MS and k_0-INAA.

Characterisation of the candidate organic analytes in ground water CRM will be completed after the international comparison study organised under organic analysis working group of BIPM-CCQM. This study is planned to be completed in May 2019.

4.4 Certification of the CRMs

The aim of this objective was to review all collected data within the project and finalise the certification campaign by drafting certificates and certification reports.

The uncertainty of the certified values contains contributions of the characterisation u_{char}, the homogeneity u_{bb}, the long-term stability u_{lts}, and the short term stability u_{sts}. The different contributions to the CRM uncertainty are combined using equation (10):

$$U_{CRM}=k\ .\ \sqrt{u^2_{char}+u^2_{bb}+u^2_{lts}+u^2_{sts}} \qquad (10)$$

The expanded uncertainty of the certified value UCRM is calculated with a coverage factor of k = 2, representing a confidence level of approximately 95 %.

4.4.1 Certification of PFOS and PFOA in Ground Water Candidate CRM

Certification of the material will be completed after completion of the characterisation study which is planned to be completed in May 2019 via an international BIPM-CCQM comparison study.

4.4.2 Certification of Elements in River Water CRM

The certified values (as obtained from the characterisation study) and overall CRM uncertainties combined by equation 10 are given in Table 14. All the certified values reported are calculated as the median of the laboratory means of all the accepted data sets (except Se). Since there are only four available datasets for Se, assigned value is calculated as the arithmetic mean of the data set obtained by ID-ICP-MS which is a reference method carried out by a single laboratory (TUBITAK). Absence of bias for the assigned value was further confirmed by comparing the values with the median of a larger dataset obtained from the supplementary comparison study EURAMET.QM-S11.

Table 14. Certified values and their uncertainties for river water material

Element	Certified Value Mass fraction (µg/kg)	U_{CRM} (µg/kg) (k = 2)	$U_{\mathrm{CRM,rel}}$ (%) (k = 2)	$u_{\mathrm{char,rel}}$ (%)	n_{char}	$u_{\mathrm{bb,rel}}$ (%)	$u_{\mathrm{lts,rel}}$ (%)	$u_{\mathrm{sts,rel}}$ (%)
As	**15.1**	**1.6**	**10.6**	4.65	7	0.36	1.48	0.97
Cd	**0.52**	**0.06**	**11.5**	4.98	9	0.54	0.95	0.79
Ni	**14.4**	**1.1**	**7.6**	3.27	8	0.9	0.9	0.98
Pb	**13.6**	**1.0**	**7.4**	3.30	9	0.67	1.39	0.60
Se	**5.0**	**0.5**	**10.0**	1.00	1	0.79	2.22	3.55

4.4.3 Certification of Elements in Soil CRM

The certified values (as obtained from the characterisation study) and overall CRM uncertainties combined by equation 10 are given in Table 15.

Certified values are calculated as the median of the laboratory means of the accepted data sets for Co, Cu, Mn, Ni, V and Zn.

For Cd, Cr, Fe, Hg and Pb certified values are assigned as the arithmetic mean of the applied reference methods (ID ICP-MS, k_0-INAA).

For As and Sb certified values are calculated as the mean of the results of a single reference method (k_0-INAA).

Table 15. Certified values and their uncertainties for soil material

Element	Certified Value Mass fraction (mg/kg)	U_{CRM} (mg/kg) (k = 2)	$U_{\mathrm{CRM,rel}}$ (%) (k = 2)	$u_{\mathrm{char,rel}}$ (%)	n_{char}	$u_{\mathrm{bb,rel}}$ (%)	$u_{\mathrm{lts,rel}}$ (%)	$u_{\mathrm{sts,rel}}$ (%)
As	**79.9**	**5.9**	**7.4**	3.00	1	0.88	0.98	1.56
Cd	**1.29**	**0.08**	**6.2**	0.52	2	1.12	1.24	2.36
Co	**42.0**	**4.5**	**10.7**	5.02	6	0.78	1.36	1.00
Cr	**115.6**	**16.9**	**14.6**	2.03	2	2.69	5.83	2.80
Cu	**63.5**	**8.3**	**13.1**	5.96	6	0.76	0.85	2.36
Fe	**26748**	**1760**	**6.6**	3.06	2	0.32	1.02	0.56
Hg	**0.315**	**0.046**	**14.6**	4.53	3	1.17	1.84	5.12
Mn	**674**	**70**	**10.4**	5.01	5	0.44	0.98	0.64
Ni	**51.7**	**7.1**	**13.7**	6.43	6	1.08	1.35	1.68
Pb	**64.1**	**2.1**	**3.3**	0.71	2	0.43	0.67	1.16
Sb	**1.81**	**0.19**	**10.5**	2.76	1	1.22	3.28	2.68
V	**76.2**	**10.1**	**13.3**	6.14	6	1.04	1.31	1.68
Zn	**150.6**	**26.7**	**17.7**	8.69	6	0.72	0.61	1.44

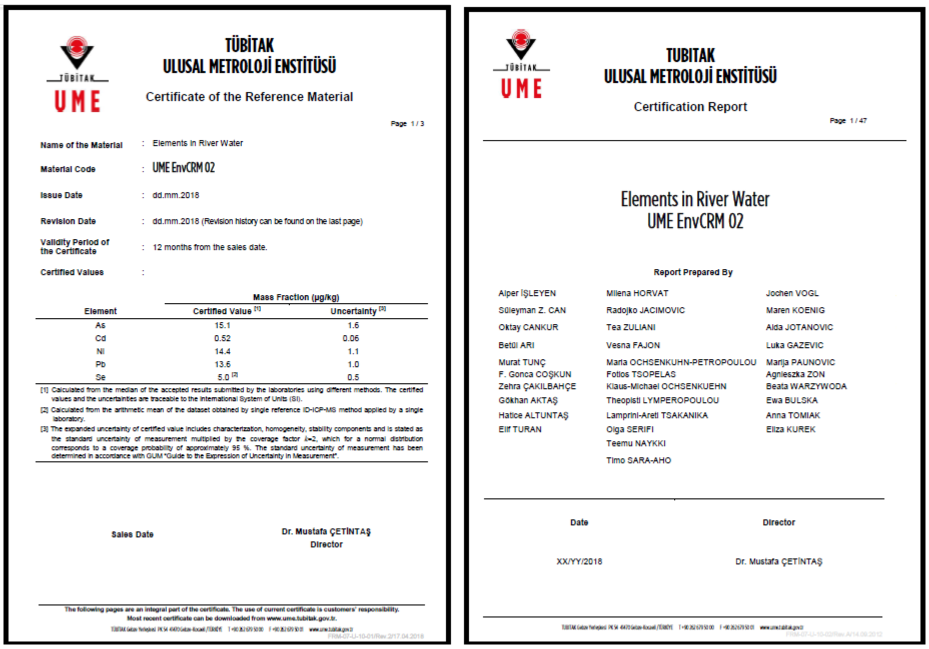
4.4.4 Conclusion

The objective to certify the CRMs was partially achieved.

For the river water material, the certified values and uncertainties were found to be in good agreement with the target values (Table 1) except for Pb. An unforeseen lead contamination might have caused a value 8.6 µg/kg higher than the targeted value. Since there were no signs of inhomogeneity between the produced units and the assigned value with its uncertainty is still useful for the laboratories, it was decided to certify Pb. Hg could not be certified because of the inconsistent results observed at the homogeneity testing stage.

For the soil material, certified values and uncertainties were found to be in good agreement (with the exception of a slightly higher value for Cr) with the target values (Table 2).

The drafting and reviewing of certification reports and certificates for the river water (Figure 29) and soil materials (Figure 30) has been completed. Certification of the organic candidate material will be completed following the end of the comparison in May 2019.



TÜBİTAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certificate of the Reference Material

Page 1 / 3

Name of the Material : Elements in River Water

Material Code : UME EnvCRM 02

Issue Date : dd.mm.2018

Revision Date : dd.mm.2018 (Revision history can be found on the last page)

Validity Period of the Certificate : 12 months from the sales date.

Certified Values :

Element	Mass Fraction (µg/kg)	
	Certified Value [1]	Uncertainty [3]
As	15.1	1.6
Cd	0.52	0.06
Ni	14.4	1.1
Pb	13.6	1.0
Se	5.0 [2]	0.5

[1] Calculated from the median of the accepted results submitted by the laboratories using different methods. The certified values and the uncertainties are traceable to the International System of Units (SI).

[2] Calculated from the arithmetic mean of the dataset obtained by single reference ID-ICP-MS method applied by a single laboratory.

[3] The expanded uncertainty of certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor k=2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

Sales Date

Dr. Mustafa ÇETİNTAŞ
Director

The following pages are an integral part of the certificate. The use of current certificate is customers' responsibility.
Most recent certificate can be downloaded from www.ume.tubitak.gov.tr.

FRM-07-U-10-01/Rev.2/17.04.2018

TUBITAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certification Report

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Elements in River Water
UME EnvCRM 02

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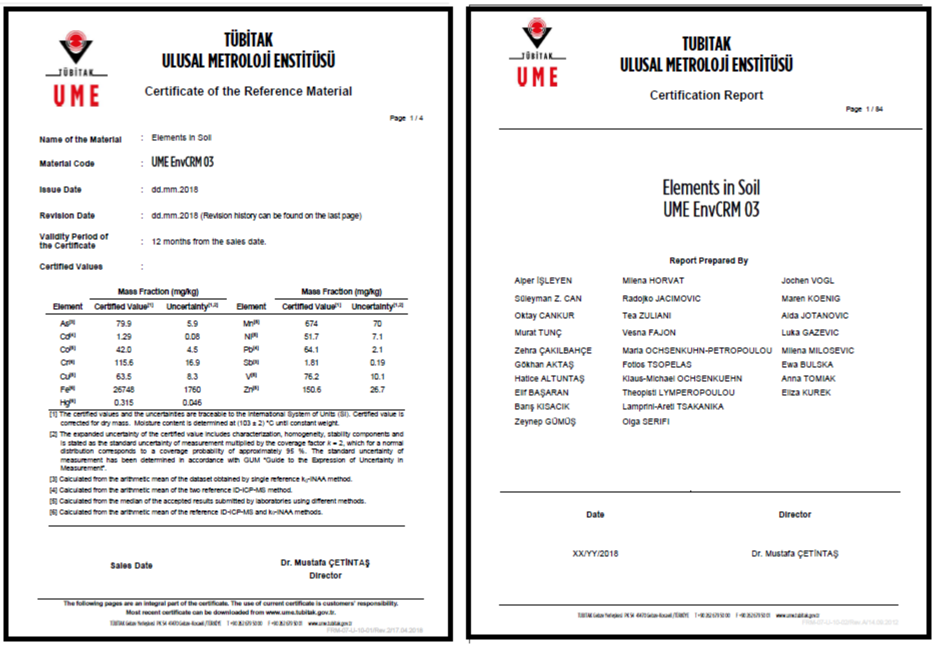
Date	**Director**
XX/YY/2018	Dr. Mustafa ÇETİNTAŞ

FRM-07-U-10-02/Rev.A/14.09.2012

Figure 29. First pages of the prepared certificate and certification report for the river water CRM.



TÜBİTAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certificate of the Reference Material

Page 1 / 4

Name of the Material : Elements in Soil
Material Code : UME EnvCRM 03
Issue Date : dd.mm.2018
Revision Date : dd.mm.2018 (Revision history can be found on the last page)
Validity Period of the Certificate : 12 months from the sales date.
Certified Values :

	Mass Fraction (mg/kg)			Mass Fraction (mg/kg)	
Element	Certified Value[1]	Uncertainty[1,2]	Element	Certified Value[1]	Uncertainty[1,2]
As[3]	79.9	5.9	Mn[5]	674	70
Cd[4]	1.29	0.08	Ni[5]	51.7	7.1
Co[5]	42.0	4.5	Pb[4]	64.1	2.1
Cr[6]	115.6	16.9	Sb[3]	1.81	0.19
Cu[5]	63.5	8.3	V[5]	76.2	10.1
Fe[6]	26748	1760	Zn[5]	150.6	26.7
Hg[5]	0.315	0.046			

[1] The certified values and the uncertainties are traceable to the International System of Units (SI). Certified value is corrected for dry mass. Moisture content is determined at (103 ± 2) °C until constant weight.

[2] The expanded uncertainty of the certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

[3] Calculated from the arithmetic mean of the dataset obtained by single reference k_0-INAA method.

[4] Calculated from the arithmetic mean of the two reference ID-ICP-MS method.

[5] Calculated from the median of the accepted results submitted by laboratories using different methods.

[6] Calculated from the arithmetic mean of the reference ID-ICP-MS and k_0-INAA methods.

Sales Date

Dr. Mustafa ÇETİNTAŞ
Director

The following pages are an integral part of the certificate. The use of current certificate is customers' responsibility.
Most recent certificate can be downloaded from www.ume.tubitak.gov.tr.

FRM-07-U-10-01/Rev.2/17.04.2018

TUBITAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certification Report

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Elements in Soil
UME EnvCRM 03

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Zeynep GÜMÜŞ	Olga SERIFI	

Date	**Director**
XX/YY/2018	Dr. Mustafa ÇETİNTAŞ

FRM-07-U-10-02/Rev.A/14.09.2012

Figure 30. First pages of the prepared certificate and certification report for the soil CRM.

4.5 Long term research capability for environmental CRMs

The aim of this objective was to develop strategies for further CRM research and development in the project partners' countries.

4.5.1 Strategy Development

A short questionnaire was circulated amongst the partners to quantify the sustainability of the research and cooperation funded within the project. The result is that 50 % of the partners confirmed a willingness to cooperate in specific CRM projects (see below). The other partners are not interested in these specific CRM projects. However, their willingness for cooperation is likely, once a suitable CRM project has been identified.

Short- to medium-term basis:

a) Seawater reference material
   Production, homogeneity study, stability study by TUBITAK
   Characterisation of Hg and heavy metals by TUBITAK
   Characterisation of Sr isotope ratios by BAM

b) Fish reference material
   Production by TUBITAK
   Homogeneity study & stability study by IMBiH, SYKE, TUBITAK
   Characterisation of MeHg by JSI, TUBITAK
   Characterisation of Hg and heavy metals by JSI, IMBiH, NTUA, SYKE, TUBITAK,
   Characterisation of Sr isotope ratios by BAM, JSI
   Characterisation of N isotope ratios by JSI
   Characterisation of organic compounds by SYKE

Further partners may be added once the projects are started.

Long-term basis:

c) Red mud reference material
   Provision of the material by NTUA
   Preparation of the material by TUBITAK
   Homogeneity study and stability study potentially by JSI
   Characterisation of Sc and rare earth elements by JSI, NTUA, TUBITAK
   Characterisation of trace and minor elements by JSI, NTUA, TUBITAK

d) Cement and/or gypsum reference material
Provision of the material by JSI
Preparation of the material by TUBITAK
Homogeneity study and stability study by JSI, IMBiH
Characterisation of Hg by JSI, NTUA, TUBITAK
Characterisation of trace and major elements by JSI, IMBiH, NTUA, TUBITAK

Further partners and measurands might be added once the planning phase of the projects are started.

Table 16. Tabular Overview of Strategies for Further CRM Research and Development

Institute	Plans for own CRM	Plans for RM for PT	Cooperation with		Focus on analytical fields
			project partners	other partners	
BAM	YES	YES	YES	YES	- Elastomeric materials - Environment - Food - Gas mixtures - Iron and steel products - Isotopic RMs - Layer and surface RMs - Non ferrous metals & alloys - Optical properties - Particle size distribution - Polymeric RMs - Porous RMs - Primary pure substances - Special materials
DMDM	YES	YES	YES	YES	- Forensic analyses - Environmental monitoring - Food safety - Clinical measurements
GUM	YES	NO	YES	YES	- Environmental monitoring - Food safety
JSI	NO	YES	YES	YES	- Biogeochemical cycling - Food safety & traceability - Radiochemistry/radioecology - Environment and health - Waste treatment - Clean technologies - Modelling, risk assessment and analysis
IMBIH	YES	YES	YES	YES	- Precious metals testing - Environmental monitoring - Gas metrology - Essential oils and fuels
NTUA	NO	NO	YES	YES	- Environment - Material science - Food
SYKE	NO	YES	YES	YES	- Environment
TUBITAK	YES	YES	YES	YES	- Environmental monitoring - Food safety - Clinical measurements
UW	n/a	n/a	n/a	n/a	n/a

4.5.2 Conclusion

The objective to develop strategies for long term research capability for environmental CRMs was achieved.

Eight project partners out of nine plan to participate in and contribute to reference materials projects run either by current project partners or by any other organisation. Interest is mainly limited to projects meeting the partners' fields of work. With eight entries, environmental measurements are the dominant priority area; food analysis is the second most important area followed by clinical measurements. Seven institutes already organise proficiency testing schemes and have plans to extend this with future reference materials developed for these programmes. The strategy for proficiency testing is closely related to the priority areas in most cases. Most partners have provided proficiency testing for several years and, in most cases, are accredited for this purpose. BAM runs the EPTIS database, which provides information on proficiency testing schemes on a worldwide basis.

Five out of the nine partners have clear plans for developing reference materials. BAM has a well-documented record as reference material producer, starting as early as 1912 and TUBITAK started work on reference materials in 2000. The other three partners, DMDM, GUM and IMBiH, started working on reference materials shortly before or during the planning phase of this project. BAM and TUBITAK were granted accreditation according to ISO Guide 34 / ISO 17034 during the project period and DMDM and IMBiH are working according to ISO 17034 with plans for acquiring accreditation in this field.

In summary approximately 90 % of the project partners are planning to contribute to external reference material projects and more than 50 % will run their own reference material projects, now or in the near future.

5 Impact

Summary of dissemination activities

The work carried out in the project has reached a wider scientific audience at scientific conferences such as International Symposium on Biological and Environmental Reference Materials (BERM 14-USA & BERM 15-Germany), 9th and 10th Instrumental Methods of Analysis-Modern Trends and Applications (IMA 2015 and IMA 2017-Greece), ECOBALT Conference (2016-Estonia).

In total 23 oral and poster presentations have been given at international and national conferences and workshops by the partners during the project lifetime.

Two workshops were held in Kocaeli, Turkey in June 2015 and in May 2018, where the needs of environmental analysis laboratories in the partnering countries were shared and discussed among the attendees in the first workshop. In both workshops, research activities of the project partners in the field of environmental analysis were presented. Attendees also benefited from informative presentations on the use of reference materials, reference material search databases, software for uncertainty calculations, primary measurement techniques such as IDMS and INAA and evaluation of standard methods for soil analysis.

Impact on the metrological and scientific communities

The main impact of this project has been to build the capacity and capability in the partner institutes for producing and certifying environmental reference materials. This in turn will have an impact on environmental monitoring in those countries and on the scientific community, who will use the newly developed reference materials. Furthermore, the NMIs/DIs have developed strategies for producing new CRM either on their own or in cooperation with partner institutes. This will lead to regional CRM programmes serving scientific and official laboratories. Further collaboration for the production of sea water and fish candidate reference materials has already been initiated among the project partners.

The NMIs/DIs participating in this project will apply for new Calibration and Measurement Capabilities (CMCs) statements recorded in the BIPM Key Comparison Database (KCDB). The CMCs focus on the determination of inorganic and organic analytes in environmental matrices and on the reference materials certified within this project. An international comparison study will be proposed at BIPM CCQM on rare earth elements with the use of the soil CRM produced within the EnvCRM project.

Additionally the partners have contributed to the EURAMET Technical Committee for Metrology in Chemistry (EURAMET TC-MC) and kept them informed at its annual meetings about the progress achieved in the project.

A possible collaboration with EU COST Action TD1407 (www.costnotice.net) has been initiated for an unforeseen use of the candidate reference materials. This COST Action aims for better characterisation of ‘technology-critical elements’ (e.g. platinum group elements, rare earth elements, Ga, Ge, In, Te, Nb, Ta, Tl) in the environment. One of the objectives is the improvement of analytical methods for the determination of the aforementioned metals in environmental samples.

One of the important problems associated with this is defined as the lack of suitable environmental certified reference materials for these metals; as a consequence the COST action will test the candidate reference materials produced in this project for suitability for an interlaboratory comparison of platinum group elements. Inorganic candidate reference material samples were supplied to laboratories in Spain and France to be tested for suitability.

Impact on industrial and other user communities

The project outputs will have substantial impact on NMIs dealing with the production and certification of matrix reference materials, on the water quality monitoring networks, in particular the National Reference Laboratories (NRLs) involved in QA/QC activities, and with industry dealing with water quality.

Impact is being created by making available:

- Robust and comparable analytical data, based on homogeneity and stability of selected organic and inorganic analytes,
- Improved knowledge and good practice of production and certification of matrix reference materials,
- Better understanding of influencing matrix components and impurities,
- Newly gained and improved traceability in production and certification of matrix reference materials.

The project goal was to achieve data quality objectives set by EU regulation and implement them in participant countries. By doing this, measurements of water pollution will achieve better comparability with European regulations and will have improved traceability in each participant country.

Impact on relevant standards

There are several EC & EU directives and position papers which deal with contaminants in the environment, in food, and in water, and related directives and regulations ensuring environmental and health protection, such as those listed below:

- Water Framework Directive (2000/60/EC, amended by Decision 2455/2001/EC and Directives 2008/32/EC, 2008/105/EC and 2009/31/EC);
- Registration, Evaluation, Authorisation and Restriction of Chemicals, Regulation (EC) No 1907/2006;
- Waste Electrical and Electronic Equipment Directive 2012/19/EU;
- Restriction of the use of certain hazardous substances, directive 2011/65/EU.

All these directives and papers have an underpinning need for more reliable measurement data of environmental contaminants to support their implementation, which in turn requires a larger number of reliable CRMs. Particularly with regard to upcoming new legal limits for contaminants, there is a pressing need for more CRMs. Current reference material institutes are at their limits and therefore it is necessary to introduce or increase the capability and capacity of new upcoming institutes to produce CRMs, which is the primary objective of this project. Institutes producing CRMs automatically contribute to and influence standardisation working groups and technical committees. In light of the findings of the soil characterisation study in this project, information has been shared with ISO technical committees for improvement of relevant standards (ISO 14869-2:2002 and ISO 14869-3:2017) on analysis of soil.

Longer-term economic, social and environmental impacts

The project will result in long term public benefit by providing tools for the reliable analysis of environmental pollutants.

The EU water quality directive 2000/60/EC with corresponding directives (Environmental Quality Standards Directive 2008/105/EC etc.) aims at adequate control of water resources. By conducting specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, long-term deterioration of freshwater quality and quantity can be avoided, therefore achieving sustainable management and protection of freshwater resources.

The impact of the project will be to reduce the risk of exceeding the maximum allowable data quality objectives set by EU directive. This will be achieved by preparing each country for the production and/or certification of matrix CRMs needed for adequate QA/QC activities, and improvement of the services offered by calibration laboratories to end-users by achieving full traceability for CRMs developed in this project. Ultimately, the outcome of this project will contribute to a more reliable and robust water monitoring network incorporating a harmonised approach able to fulfil EU regulation.