EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

IMEP-21
Trace Elements, PCBs, PAHs in Sewage Sludge
Certification Report

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IMEP®

Report EUR 22243 EN

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

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EUR 22243 EN
Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

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Summary

The International Measurement Evaluation Programme (IMEP®) is an Interlaboratory Comparison (ILC) scheme in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). It is founded, owned and co-ordinated by the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate-General Joint Research Centre.
The aim of this interlaboratory comparison programme is to picture objectively the degree of equivalence and the quality of chemical measurements. Contrary to most other external quality assessment schemes, participating laboratories in IMEP® can compare their measurement results and uncertainty statements with external certified reference values, obtained completely independent from the participants' result. These reference values are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. Participants in IMEP® use their routine analytical procedures to measure the IMEP-certified test sample (CTS). Therefore they can assess the quality of their results on an international forum by comparing their values to the IMEP-reference values. IMEP supports quality assurance work at routine level and stresses, particularly, the educational aspect. In this way, IMEP complements the regular and sector-specific proficiency testing (PT) and external quality assessment (EQA) schemes.

The European Union promotes the use of sewage sludge as fertilizer in agriculture. The Council Directive 86/278/EEC of 12 June 1986 sets rules for the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. In this directive limit concentration ranges of metals in sewage sludge are laid down. In national legislation the concentration ranges for metals can be set below these limits. Furthermore limits for Polychlorinated Biphenyls (PCBs), and Polycyclic Aromatic Hydrocarbons (PAHs) congeners in sewage sludge are set in some of the national legislations. The directive 86/278/EEC is discussed to be revised and lower levels for metals and most probably also upper levels for PCBs and PAHs concentrations will be included. Participants in IMEP-21 were offered to measure the total amount content of 7 metals, 6 PCB congeners and 11 PAH congeners: Cd, Cr, Cu, Pb, Hg, Ni, Zn, PCB_28, PCB_52, PCB_101, PCB_118, PCB_153, PCB_180, sum_PCBs, anthracene, benz(a)anthracene, benz(a)pyrene, benz(b+k)fluoranthene, benzo(ghi)perylene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene, sum_PAHs.

IMEP-21 was organised in collaboration with The European Committee for Standardisation (CEN) upon approval of DG EuropAid, the Association of the European Geological Surveys (EuroGeoSurveys) Geoscientific Laboratory Network and the European Co operation for Accreditation (EA). In IMEP-21 3228 measurement results on 26 analytes were reported by 204 participants from 45 countries. Amongst those were participants nominated by CEN, EuroGeoSurvey and by national accreditation bodies (NABs) but also laboratories from Western Balkan countries (IRMM's CARDS support), new member states and other countries participated in MEP-21.

Reference measurements in IMEP are performed by institutes with internationally demonstrated and/or mutually recognised measurement capabilities. The institutes involved in establishing the IMEP-21 certified reference values were IRMM, BAM, SCK-CEN, VITO and BOKU-Wien. The analytical techniques applied to establish the IMEP-21 reference values were ID-ICP-MS, ID-TIMS, k_0-NAA and GC-MS. IRMM coordinated the IMEP-21 certification campaign to establish the certified reference values for all the analytes under investigation. The IMEP-21 certification report summarises the organisatorial and technical details thereof. The results on the homogeneity and short term stability tests of the sewage sludge material are presented as well as the results of the reference measurements and the establishment of the reference values.

IMEP®

provides reference values with demonstrated traceability and demonstrated uncertainty, independent of the participants' results

invites participants to report results together with the best estimate of the expanded measurement uncertainty

enables result-oriented rather than procedure oriented evaluation of performance

demonstrates a degree of equivalence in measurement results on the international measurement infrastructure

IMEP®

Characteristics of IMEP®

Policy making and policy implementation aims at setting up a legal set of rules providing a maximum of consumer protection within healthy working and living environments and a prospering economy. In many cases implementation of international and national legislation is based on high quality chemical measurement results. Therefore laboratories need to be able to demonstrate that their measurement results are reliable, comparable and in compliance with legislation, international standards, and international recognition arrangements that support the free trade goal 'measured once, accepted everywhere'.

IMEP® is a publicly accessible metrological Interlaboratory Comparison scheme organised in support of EU policies. Therefore IMEP® is addressing different analytes in different matrices and not offering ILCs on a regular basis for a specific analyte and matrix. It intends to picture the state-of-the-practice in measurement capabilities of laboratories at a specific moment in time. IMEP® guarantees the confidentiality with respect to the identity of its participants and their reported result. .

Participants in IMEP® measure the analytes under investigation applying their routine measurement procedures and analytical techniques. In IMEP®, laboratories have always been invited to state uncertainty estimates for their reported results. Contrary to most regular proficiency testing schemes, the IMEP® measurement performance criteria are not only set relative to the reported value, but also to the reported measurement uncertainty. IMEP enables laboratories to assess their measurement performance and at the same time allows them to demonstrate their competence on a high quality level to accreditation, authorisation, and inspection bodies as well as to their regular customers. These specific features of the IMEP® programme make it a very valuable tool for international and European organisations or reference networks to verify measurement claims and monitoring the efficiency of multilateral arrangements

IMEP-21

IRMM launched IMEP-21 in Spring 2005 in view of support to the Council Directive 86/278/EEC of 12 June 1986. This directive sets rules for the use of sewage sludge in agriculture as to prevent harmful effects on the environment, and in particular on the soil. In this directive limit values for Cd, Cu, Hg, Ni Pb and Zn concentrations in sludge for use in agriculture are specified [1].

In the European Union, sludge policy varies depending on the degree of support that the recycling of sludge in agriculture has from the political level (Agricultural and/or Environment Ministries) and farmers' perception. Therefore the implementation of the Directive in national laws resulted in some cases in much lower defined maximum concentrations for metals. Furthermore limits for PCBs and PAHs congeners or the sum of congeners in sewage sludge are also set in some of these national legislations although they are not included in the Directive 86/278/EEC [2].

The directive 86/278/EEC is discussed to be revised. Lower levels for metals and most probably also upper levels for PCBs and PAHs concentrations might be included in the next revision, because of the extremely cancerogenic effect of some of the congeners, e.g. benzo(a)pyrene or benzo(b)fluoranthene [3].

Participants in IMEP-21 were therefore offered to measure the total amount content of 7 metals, 6 PCB congeners and 11 PAH congeners: Cd, Cr, Cu, Pb, Hg, Ni, Zn, PCB_28, PCB_52, PCB_101, PCB_118, PCB_153, PCB_180, sum_PCBs, anthracene, benz(a)anthracene, benz(a)pyrene, benz(b+k)fluoranthene, benzo(ghi)perylene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene, sum_PAHs. The IMEP-21 Certified Test Sample (CTS) needed therefore to be characterised for all the analytes listed above.

Collaboration with other organisations

The mission of IRMM is to promote a common European measurement system in support of EU policies, especially internal market, environment, health and consumer protection standards. IMEP® contributes to this by providing support to EU policies. By offering IMEP® to testing and calibration laboratories, IRMM supports the EU Member States by ensuring confidence in their national measurement system. IMEP® therefore enables to assess whether national measurement systems are in place to provide for an equivalent implementation of directives across an enlarged EU. To specific groups of laboratories this support can be organised in the frame of collaboration agreements or specific support programmes (IRMM's CARDS support)

IMEP-21 was organised in collaboration with the European Committee for Standardisation (CEN) upon approval of DG EuropAid, the Association of the European Geological Surveys (EuroGeoSurveys) Geoscientific Laboratory Network and the European Co operation for Accreditation (EA) [4, 5, 6, 7]. Measurement results in IMEP-21 were reported by 204 participants from 45 countries. Among those were 80 laboratories nominated by their NABs, 14 MEDA laboratories nominated by CEN via the Euromed quality programme and 9 laboratories nominated via the EuroGeoSurveys Geoscientific Laboratory Network.

The organisatorial details and the IMEP-21 participants' results are presented in the IMEP-21 participants' report, which is available via the IMEP web-site [8, 9].

IMEP-21 in support of the chemical measurement infrastructure

A direct way to support the chemical measurement infrastructure is to link, when possible, laboratories situated on the different levels of the international measurement infrastructure. This is realised by using samples from the same material batch in the various interlaboratory comparison programmes organised on the different levels. Over the past few years, the International Committee for Weights and Measures (CIPM), the guardian of the International Measurement System (the SI), has taken several initiatives to improve the equivalence of chemical measurements worldwide. In October 1999, IRMM and other National Metrology Institutes signed the Mutual Recognition Arrangement (MRA) [10]. The MRA enables National Metrology Institutes (NMIs) to demonstrate their measurement capability by participating in key comparisons and pilot studies.

The same sewage sludge material as used in IMEP-21 was also used for a key comparison and a pilot study on the metals of the Consultative Committee of Amount of Substance of the CIPM, (CCQM-K44 and CCQM-P70). Eight signatories of the MRA and 4 expert laboratories participated in CCQM-K44 & CCQM-P70. Results of this key comparison and the pilot study will be accessible via the Bureau International des Poids et Mesures (BIPM) web-site [11]. Hence the IMEP-21 certified reference values for the metals can be compared with the results of laboratories that represent their country at the international measurement structure level and vice versa.

Organisation of the certification campaign

Reference measurements are performed by institutes with internationally demonstrated and/or mutually recognised measurement capabilities. This also accounts for IRMM as a reference laboratory in IMEP-21. As signatory of the Mutual recognition agreement (MRA) IRMM has already successfully proven the measurement capabilities to measure trace elements in various matrices [12]. IRMM and IRMM/SCK-CEN participated previous to the establishment of the certified IMEP-21 reference values to the CCQM-K44 key comparison & CCQM-P70 pilot study where the same CTS was used and thus its measurement capabilities, to measure the metals under investigation in sewage sludge have been successfully confirmed by comparison to other NMIs and expert laboratories worldwide [11].

External institutes admitted to perform reference measurements on IMEP test materials have to comply with the stringent technical requirements as set in the call for expressions of interest published in 2004 in the Official Journal no. S 53 045071 of the European Communities [13]. A call for tender regarding homogeneity testing and certification measurements in the IMEP-21 sewage sludge test material was sent to all listed institutes that had met the criteria specified in the call for expressions of interest. Tenders were received from BAM (Federal Institute for Materials Research and Testing), VITO (Flemish Institute for technological research) and BOKU-WIEN (University of Natural Resources and Applied Life Sciences).

Subsequently the final list of reference laboratories in IMEP-21 was established (Table 1). The following staff is known to the authors to have contributed experimentally: E. Vassileva, C. Quétel, K. H. Grobecker, M. Bickel, A. Michiels, A. Bernreuther, S. Yazgan, P. Conneely, B. Sejeroe-Olsen, and O. Bercaru from IRMM. P. Vermaercke from SCK-CEN, T. Prohaska and S. Boulyga from BOKU-WIEN, J. Vogl, T. Win and R. Philipp from BAM, R. Van Cleuvenbergen, K. Tirez and M. Wevers from VITO.

The sewage sludge test material

The sludge material originates from different sewage plants in Italy and France and was provided by the Reference Materials (RM) unit. The blend material was air-dried at ambient temperature, further dried at 105 ^{o}C after crushing the lumps and large aggregates, and passed through a large Retsch hammer mill, equipped with tungsten carbide tools and a circular sieve with 2mm aperture. The obtained powder was passed over a 125 μm sieve and the fraction >125 μm discarded. The fraction <125 μm was homogenized for 2 weeks in a mixing drum. The material was then reprocessed in amber glass bottles each one containing ~ 40 g of material.

Initial screening

Four sewage sludge samples were subject to a semi-quantitative analysis. The total organic carbon content in this material was around 15%. The elemental concentrations were determined in a semi-quantitative analysis by ICP-QMS (Inductively Coupled Plasma-Quadrupole Mass Spectrometry). The analysis results of the 4 replicative samples were <10 %, indicating already at the screening stage good measurement reproducibility and homogeneity of the material. The range of metals amount content in this sewage sludge material was close to the limit concentration ranges as stated in the Council Directive 86/278/EEC [1]. The semi-quantitative screening on PCBs and PAHs congeners was performed by GC-MS (Gas Chromatography Mass Spectrometry). Indicative amount content values for 8 PCB and 12 PAH congeners were obtained. After investigation of the chromatograms interferences in the determination of PCB_138, PCB_170 and chrysene were observed in this material. Therefore it was decided not to include these congeners in the certification campaign for IMEP-21. Based on this initial screening the sewage sludge material was found to be appropriate to be certified as IMEP-21 CTS.

Table 1: IMEP-21 Reference laboratories

Logo	Address	Contact
	European Commission – Joint Research Centre Institute for Reference Materials and Measurements Isotope Measurement Unit Retieseweg 111 B-2440 Geel Belgium	http://www.irmm.jrc.be/imep/
	Studiecentrum voor Kernenergie Centre d'étude de l'énergie nucléaire Boeretang 200 2400 MOL Belgium e	http://www.sck.be
	Federal Institute for Materials Research and Testing Unter den Eichen 87 D-12205 Berlin Germany	http://www.bam.de
	VITO Flemish Institute for technological research Boeretang 200 BE- 2400 MOL Belgium	http://www.vito.be/
	Universität für Bodenkultur Wien University of Natural Resources and Applied Life Sciences Vienna, Austria /	http://www.boku.ac.at

Homogeneity characterisation

Minimum sample intake

For Cd, Hg and Pb solid sample Zeemann Atomic Absorption Spectrometry (SS-ZAAS) was carried out on 10 sub-samples, ~0.3mg each, of 10 sewage sludge bottles to determine the minimum sample intake. As a result the minimum sample intake of 0.2g sewage sludge was identified to yield in a measurement precision of 1%. Therefore it was recommended to the reference laboratories to use a minimum sample intake of 0.3g to achieve a measurement precision of 1% or better for all the analytes.

Homogeneity and short term stability

Since the IMEP-21 material was not intended to become a CRM (Certified Reference Material) the homogeneity testing, short term stability testing and the certification measurements were combined in the scope of the IMEP-21 certification campaign to be fit for purpose of material certification for an IMEP ILC. The design of the study was in such a way that part of the samples used in this certification campaign were stored for 4 weeks at 40^{o}C. This temperature represented the most probable temperature variation that could be expected during sample mailing and intermediate storage. In addition a few others sewage sludge bottles were stored for 4 weeks at 60 ^{o}C to check whether at that high temperature any significant trend for metals, PCBs and PAHs can be observed. The remainder of the sewage sludge batch was stored at room temperature. Only the MEP-21 coordinating team was aware which samples had been stored at higher temperatures. The reference laboratories measured these samples undisclosed. They were asked to treat all samples alike. With this combined design the measurement results reported by the reference laboratories do not only account for between unit variation, but also for possible variations according to temperature differences during transport or temporary storage before analysis.

Within, between bottle homogeneity and short term stability tests were carried out applying several analytical methods. For Cd, Hg, Pb and Zn tests were done by IRMM on 3 to 5 sub-samples from 3 to 5 bottles applying Isotope Dilution Mass Spectrometry (IDMS).

For Cu and Cr the homogeneity was assessed by SCK-CEN analysing 3 sub-samples from 10 bottles applying k_0-Neutron Activation Analysis (k_0-NAA). The homogeneity of Ni was determined by BOKU-WIEN, BAM and VITO. Each of these reference laboratories measured for Ni 3 sub-samples from 5 bottles applying either Isotope Dilution Mass Spectrometry (IDMS) or Atomic emission spectrometry (AES). Homogeneity and short term stability for PCBs and PAHs congeners were determined by BAM and VITO via assessment on 3 sub-samples from 5 bottles by means of Gas-chromatography-mass spectrometry (GC-MS).

Results from all these measurements were evaluated by a one-way analysis of variance ANOVA [14, 15, 16]. This allows the separation of the method variation (s_{wb}) from the experimental averages over one unit to obtain estimation for the real variation between units (s_{bb}). The measurement variation sets a lower limit u^{*}_{bb} to the between unit variance which depends on the mean squares between units, the number of replicate measurements per unit and the degrees of freedom of the mean squares between units. The uncertainty of homogeneity is consequently estimated as s_{bb} or in case of $s_{bb}<u^{*}_{bb}$ as u^{*}_{bb}.

Table 2 lists per analyte and per reference laboratory the between bottle variation (s_{bb} or u^{*}_{bb}, respectively), the variation resulting from the measurement variability (s_{wb}), the number of measured units, the number of replicate measurements and the analytical method. The between bottle variation was ranging from 0.3% - 1% for the metals and from 1% - 3% for the PCBs. No trend was observed for the samples that had been previously stored at higher temperature. The situation was slightly different for the PAHs. Again no trend was observed for the samples that had been previously stored at 40^{o}C, but for some of the PAH congeners a slight trend to lower concentrations was observed for the samples that had been stored for 4 weeks at 60^{o}C. This could also be seen in the fact that including the measurement results of these samples for some of the PAH congeners in the ANOVA analysis the between unit variation was greater than the variation that could be explained by the measurement variability.

Due to the fact that the IMEP-21 samples have been sent to all participants by courier express and that it is hardly probable that they were even exposed more than one day to a temperature above 40^0C, the homogeneity assessment for PAHs of the sewage sludge batch was done after excluding the results from the bottles that were stored on 60^0C. As a result the between bottle variation for the PAHs was ranging from 1% - 8%. Concluding the homogeneity and short term stability study, this material was found to be appropriate for the needs of this comparison.

Table 2 Result of the homogeneity and short term stability study of the IMEP-21 sewage sludge material

Analyte_ref. lab.	s_{wb} in %	s_{bb} or u^*_{bb} in %	no. of units	no. of replicate measurements	analytical method
Cadmium_IRMM	0.69	0.3	5	3	ID-ICP-MS
Chromium_SCK-CEN	1.06	0.45	10	3	k_0-NAA
Copper_SCK-CEN	2.5	0.84	10	3	k_0-NAA
Lead_IRMM	0.98	0.39	5	3	ID-ICP-MS
Mercury_IRMM	3.36	0.89	3	5	ID-ICP-MS
Nickel_BOKU-WIEN	1.66	0.68	5	3	ID-ICP-MS
Nickel_BAM	0.72	0.41	5	3	ID-TIMS
Nickel_VITO	0.9	0.32	5	3	ICP-AES
Zinc_IRMM	0.27	0.29	5	2	ID-ICP-MS
Zinc_SCK-CEN	0.85	0.45	10	3	k_0-NAA

Analyte_ref. lab.	s_{wb} in %	s_{bb} or u^*_{bb} in %	no. of units	no. of replicate measurements	analytical method
PCB_28_BAM	7.22	2.4	5	3	GC-MS
PCB_28_VITO	7.15	3.27	5	3	GC-MS
PCB_52_BAM	7.23	2.41	5	3	GC-MS
PCB_52_VITO	3.08	1.41	5	3	GC-MS
PCB_101_BAM	6.93	2.59	5	3	GC-MS
PCB_101_VITO	1.49	1.18	5	3	GC-MS
PCB_118_BAM	5.39	2.0	5	3	GC-MS
PCB_118_VITO	1.34	1.08	5	3	GC-MS
PCB_153_BAM	5.39	1.97	5	3	GC-MS
PCB_153_VITO	3.76	1.51	5	3	GC-MS
PCB_180_BAM	5.72	2.18	5	3	GC-MS
PCB_180_VITO	8.01	2.64	5	3	GC-MS

Analyte_ref. lab.	s_{wb} in %	s_{bb} or u^{*}_{bb} in %	no. of units	no. of replicate measurements	analytical method
Anthracene _BAM	25.26	8.51	5	3	GC-MS
Anthracene _VITO	7.03	7.10	5	3	GC-MS
Benz(a)anthracene _BAM	15.43	5.29	5	3	GC-MS
Benz(a)anthracene _VITO	3.95	4.41	3	3	GC-MS
Benz(a)pyrene _BAM	12.82	4.54	5	3	GC-MS
Benz(a)pyrene _VITO	4.29	2.03	3	3	GC-MS
Benz(b+k)fluoranthene _BAM	9.75	3.41	5	3	GC-MS
Benz(b+k)fluoranthene _VITO	5.34	2.51	3	3	GC-MS
Benzo(ghi)perylene _BAM	9.99	3.55	5	3	GC-MS
Benzo(ghi)perylene _VITO	10.58	4.73	3	3	GC-MS
Fluoranthene _BAM	6.17	2.55	5	3	GC-MS
Fluoranthene _VITO	5.72	5.10	3	3	GC-MS
Fluorene _BAM	10.13	3.71	5	3	GC-MS
Fluorene _VITO	2.22	1.04	3	3	GC-MS
Indeno(1,2,3-cd)pyrene _BAM	16.37	5.57	5	3	GC-MS
Indeno(1,2,3-cd)pyrene _VITO	6.22	2.66	3	3	GC-MS
Naphthalene _BAM	11.0	3.61	5	3	GC-MS
Naphthalene _VITO	8.77	3.73	3	3	GC-MS
Phenanthrene _BAM	7.25	2.46	5	3	GC-MS
Phenanthrene _VITO	6.54	3.65	3	3	GC-MS
Pyrene _BAM	5.21	1.79	5	3	GC-MS
Pyrene _VITO	4.23	5.06	3	3	GC-MS

Coordination

Each IMEP-21 reference laboratory received with the samples detailed technical specifications for homogeneity testing and certification, dry-mass correction, result reporting and uncertainty evaluation. To the external reference laboratories (see Table 1) these specifications were attached as Annex to the legal contract. The reference laboratories were given 10 weeks from the entry into force of the contract to perform the measurements and to report back to the IMEP-21 coordinator at IRMM. The objective was to obtain from the replicate measurements performed by the external reference laboratories two or three independent reference measurement values per analyte. IRMM and IRMM/SCK-CEN had previously to this certification campaign successfully proven their measurement capabilities for Cd, Cr, Cu, Hg Pb and Zn in the same sewage sludge material via participation in the CCQM-K44 key comparison & CCQM-P70 pilot study [11]. Therefore for those analytes no additional external reference measurements were requested.

Technical specifications

The technical specifications included:

- o A list of all analytes with indicative concentration levels
- o The number of measurements per unit and the measurement sequence
- o Instructions on permitted certification methods
- o Instructions for the dry-mass correction and digestion of the sewage sludge
- o Requirements for result reporting
- o Requirements for uncertainty evaluation

The technical requirements were the following:

Measurement sequence

15 measurements on 5 sewage sludge bottles need to be carried out for each of the analytes. Per sample bottle 3 independent measurements (independent digestions, extractions, clean-up, independent calibration for every single measurement, spread over at least two days) are required. Each bottle has a sample code and the measurements need to be performed in the order as indicated in the instruction documents that are sent together with the samples.

Certification method

The certification method of choice should be preferably a definite/primary method (e.g. isotope dilution mass spectrometry) or an internationally agreed measurement procedure [17]. Other analytical methods such as k_0-NAA are also permitted. For PCBs and PAHs analysis the method of choice should be preferably GC-MS with isotopically labelled analogues for internal standards/surrogates. GC-ECD is also permitted.

Digestion/extraction

For the analysis of metal amount content, different digestion methods and instrumentation, employing various combinations of acids can be used. The aim is to digest the sewage sludge material completely as total mass fractions are to be determined (not only leachable fractions). Should this fail, the analyte content in the residue should be measured in order to estimate the correction needed and its uncertainty contribution. Different methods for extraction and clean-up can be used for PCBs and PAHs analysis. Minimum sample intake should be 0.3g for metals as well as for PCBs, PAHs analysis!!

Dry-mass correction

The sewage sludge will absorb ambient moisture at typical laboratory temperature and humidity conditions. Therefore the sample bottle should only be opened immediately before weighing aliquots for the analysis. For correction of the measured values to dry mass, water content measurements should be made on a separate portion of the same material with a mass of 0.5 ± 0.1g. The material should be dried before weighing for 24 hours in a ventilated oven at 105 ± 2 ^{o}C. The weighing has to be carried out after the sample has reached thermal equilibrium at room temperature in a desiccator, recommended time about 20 min. The loss of mass corresponds to the “dry-mass correction factor” that should be applied. The reported results of the reference laboratories for the measured water content in the sewage sludge are listed in Table 3.

In addition the water content of the sewage sludge material was also determined at IRMM by Karl-Fischer titration. No significant difference was observed.

Table 3 Reported values for water content determination and dry-mass correction

Reference laboratory.	Water content in %	Dry-mass correction factor g (dry mass)/g (sample)
BAM	4.72 ± 0.06	0.9528 ± 0.0006
BOKU-WIEN	4.96 ± 0.11	0.9504 ± 0.0011
IRMM	5.64 ± 0.2	0.9436 ± 0.002
SCK-CEN	5.64 ± 0.4	0.9436 ± 0.0036
VITO	3.5 ± 2.1	0.965 ± 0.021

Result reporting

An excel spreadsheet is provided for reporting results and is obligatory to be used. In addition a detailed description of the measurement procedure is required. Measurement results must be provided with a report in English describing the analytical method, sample intake, sample preparation, dry mass determination, the calibration strategy, reagents including standards (with lot numbers) used and the order and time of the measurements, the sample it refers to and the particular digestion, extraction, clean-up method and detection method.
The results for the metals must be expressed as mg/kg mass fractions; the results for the PCBs and PAHs congeners as ng/g mass fractions and refer to dry mass. The dry mass content must be reported, too.

Uncertainty reporting

The uncertainty statement should be evaluated and presented according to the principles outlined in, e.g. Guides for Quantifying Measurement Uncertainty (GUM) issued by the International Organisation for Standardisation (ISO, 1993) and/or EURACHEM (1995) [18, 19]. This implies that each laboratory replying to the tender should report together with the measurement result a complete uncertainty budget according to the following requirements:

- state your measurement equation
- identify all significant sources of uncertainty
- state your input quantities
- include factors related to sample treatment in your measurement equations
- describe the applied evaluation process and type of assumed distribution for your uncertainty estimation
- quantify uncertainty components and convert them to standard uncertainties
- calculate the combined standard uncertainty u_c
- present an expanded uncertainty U with the coverage factor k=2

Analytical methods and techniques

In Table 4 the analytical protocol and instrumental techniques are listed as applied by the reference laboratories for the respective analytes.
The methods applied were:

- Isotope dilution mass spectrometry (IDMS) using quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) or thermal ionisation mass spectrometry (TIMS). IDMS is based on the measurement of isotope amount ratios. A known amount of sample with known isotopic composition of the element/compound is mixed with a material (spike) where the element/compound of interest is present in a different isotopic composition. Once isotopic homogeneity has been established for the mix (blend), minor losses in the subsequent sample preparation do not affect the result. The unknown concentration is evaluated from measurements of the induced blend ratio.

- Gas chromatography with isotopically labelled analogues for internal standards/surrogates was used to separate organic components before the mass spectrometric measurement (GC-MS)

- NAA is based on gamma spectrometry measurements of samples irradiated with neutrons in a nuclear reactor. The capture of a neutron in a stable isotope may lead to the immediate emission of a γ-ray and the formation of a γ -emitter isotope to be monitored. Classical NAA is based on comparison of activities of the unknown sample and a known standard co-irradiated under similar conditions. This approach eliminates the need for accurate determination of neutron fluxes and detector calibration. The required measurements are the relative specific γ-emission of the activity products in the sample and in the standard, measured in the same counting position. The major drawback is the need of one standard per element concentration to be determined. The k_0 standardisation NAA method allows the determination of elemental concentrations in the sample without the use of mono- or multi-element calibrators.

- ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometer) uses ICP (inductively coupled plasma) to produce excited atoms that emit electromagnetic radiation at a wavelength characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Table 4 Analytical methods and instrumental techniques

Analyte_ref. lab.	Digestion method / Acid mixture	analytical method	instrumental technique
Cadmium_IRMM	Cold pre-digestion step (>4 hours) with mixture H_2O_2 + HNO_3+HF followed by 2 steps microwave oven digestion	IDMS	ICP-QMS
Chromium_SCK-CEN	-	NAA	k_0-NAA
Copper_SCK-CEN	-	NAA	k_0-NAA
Lead_IRMM	Cold pre-digestion step (>4 hours) with mixture H_2O_2 + HNO_3+HF followed by 2 steps microwave oven digestion	IDMS	ICP-QMS
Mercury_IRMM	Cold pre-digestion step (>4 hours) with mixture H_2O_2 + HNO_3+HF followed by 2 steps microwave oven digestion (incl. add HCl)	IDMS	ICP-QMS
Nickel_BOKU-WIEN	HNO_3+H_2O_2 microwave digestion after cooling followed by HNO_3+HF microwave digestion	IDMS	HR-ICP-MS
Nickel_BAM	microwave digestion with HNO_3 +H_2O_2, followed by microwave digestion with H_2F_2+HNO_3 H_2O	IDMS	TIMS
Nickel_VITO	microwave digestion with HNO_3 +H_2O_2+ H_2O followed by microwave digestion with H_3BO_3	AES	ICP-AES
Zinc_IRMM	Cold pre-digestion step (>4 hours) with mixture H_2O_2 + HNO_3+HF followed by 2 steps microwave oven digestion	IDMS	ICP-QMS
Zinc_SCK-CEN	-	NAA	k_0-NAA

Analyte_ref. lab.	Extraction / clean-up	internal standards	instrumental technique
PCBs_BAM	extraction: ASE (accelerated solvent extraction) with cyclohexane, 100 ^{0}C, 140 bar, 2 cycles; clean up: solid phase extraction chromatography, aromatic sulfonic acid + silica gel column, elution with cyclohexane	^{13}C-labeled isotopes as internal standards, added volumetrically before extraction	GC-MS
PCBs_VITO	extraction: soxhlet with n-hexane/acetone clean up: solid phase extraction chromatography, 2 g of silica/NaOH 1N 33%, 10 g of silica/H2SO4 44% and ca. 2 cm of sodium sulfate, elution with n-hexane	internal standards: individual 40 µg/ml solutions of 7 ^{13}C-labelled congeners added before extraction	GC-MS
PAHs_BAM	extraction: ASE (accelerated solvent extraction) with toluene, 100 ^{0}C, 140 bar, 2 cycles clean up: solid phase extraction chromatography, silica gel column, elution with toluene, concentration of the eluate to 1ml	deuterated isotopes as internal standards, added gravimetrically before extraction	GC-MS
PAHs_VITO	extraction: soxhlet with n-hexane/acetone clean up: solid phase extraction chromatography, 1 g of alumina, 3g of silica and ca. 1 cm of sodium sulfate, elution with n-hexane/dichloromethane	deuterated PAHs (16 EPA compounds) added before extraction	GC-MS

IMEP-21 Certified Reference value

The IMEP philosophy is that the best possible values will serve as IMEP reference values, obtained from well-understood measurement processes in a complete transparent way. Based on the values reported by the reference laboratories the IRMM assigns an 'IMEP-21 reference value' to the analytes in the test materials. This is the actual certification process, which leads to the issuing of a material certificate [8]. Each test material is then referred to as a 'certified test sample' (CTS).

The reported replicative measurement results of the reference laboratories were used to establish the IMEP-21 certified reference values. The certified reference values for the majority of the analytes was obtained by combining the measurement result from two external reference laboratories. Since IRMM and SCK-CEN demonstrated by means of participation in CCQM comparisons their excellent measurement capability for Cd, Cu, Cr, Hg and Pb and Zn in this sewage sludge material, there was no need to request additional measurements from external reference laboratories for these analytes [11]. In case measurements from two reference laboratories were available, the average had been taken as the estimate of the certified reference values for the analyte. The associated uncertainty was calculated by combining the individually uncertainties. In case results from 2 reference laboratories did not agree within the stated uncertainties, an additional contribution was added that just covers the between-laboratory variation. All calculations are done using the software GUM Workbench [20, 21].

Results of the certification campaign

The results derived from the replicate measurements and the reported analytical protocol of the respective reference laboratories are given in Table 5 to Table 23 with the respective IMEP-21 certified reference value. In addition these results are displayed graphically in Figure 1 to Figure 19. As mentioned in the previous paragraph the results for Cd, Cu, Cr, Hg and Pb were only measured by IRMM or/and SCK-CEN since they took part in the CCQM comparison.

Inorganic analytes

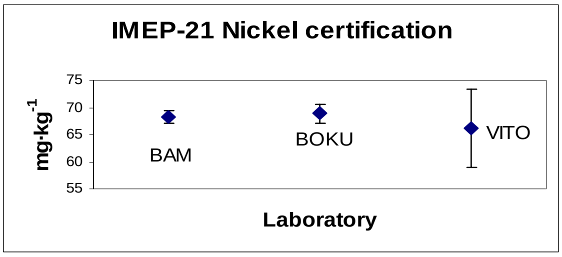
For Cd, Hg and Pb the IMEP-21 reference value was derived from the ID-ICP-MS measurements carried out by IRMM. Cr and Cu were derived from the measurements performed by SCK-CEN using k_0-NAA (Table 24).

Three reference laboratories reported results for Ni. BAM applied ID-TIMS, BOKU applied ID-ICP-MS and VITO applied ICP-AES. The results all agree within their uncertainties, but the ICP-AES result has a considerable larger uncertainty compared to the two IDMS results. Therefore the ICP-AES result was omitted in the calculation of the reference value for Ni, but can be seen as a confirmation of the 2 IDMS results.

Table 5 Reported measurement values and IMEP-21 reference value for nickel

Institute	value in mg·kg^{-1}	expanded uncertainty in mg·kg^{-1} U, k=2
BAM	68.22	1.12
BOKU	68.86	1.69
VITO	66.128	7.2
IMEP-21 ref. value	68.5	1.0

Figure 1 Graphical display of reference measurement values for nickel

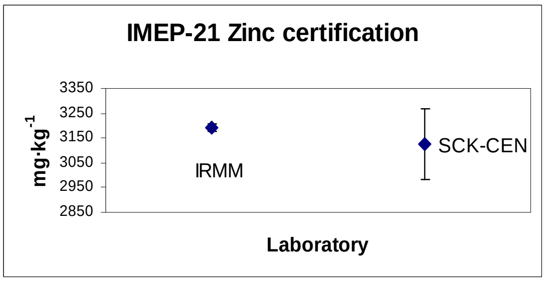


Since there was only one IDMS result available for Zn, the reference value was derived combining the results from the k_0-NAA measurements carried out by SCK-CEN with the results from the ID-ICP-MS, despite the difference in uncertainty.

Table 6 Reported measurement values and IMEP-21 reference value for zinc

Institute	value in mg·kg^{-1}	expanded uncertainty in mg·kg^{-1} *U*, *k*=2
IRMM	3193.06	14.39
SCK-CEN	3126	144
IMEP-21 ref. value	3160	72

Figure 2 Graphical display of reference measurement values for zinc



Organic analytes

The PCB congeners were measured by BAM and VITO, both institutes applying GC-MS with isotopically labelled standards (Table 4).
The results for the PBCs are listed in the following Tables. For PCB_28 congener the largest contribution due to inhomogeneity was observed (see Table 2) the uncertainty of the reference value accounts for this and is larger than for the other PCB congeners.

Table 7 Reported measurement values and IMEP-21 reference value for PCB_28

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	56.9	5.0
VITO	39.59	6.33
IMEP-21 ref. value	48.2	9.0

Figure 3 Graphical display of reference measurement values for PCB_28

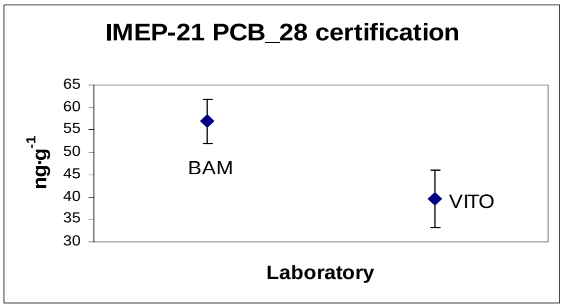


Table 8 Reported measurement values and IMEP-21 reference value for PCB_52

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	96.1	8.34
VITO	88.41	4.49
IMEP-21 ref. value	92.3	4.7

Figure 4 Graphical display of reference measurement values for PCB_52

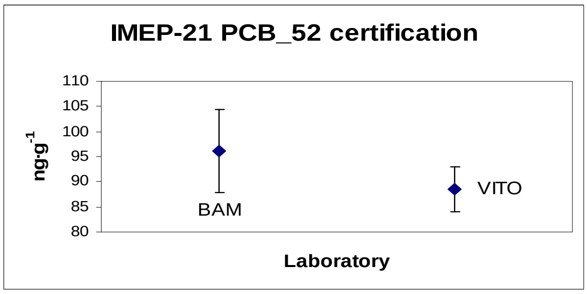


Table 9 Reported measurement values and IMEP-21 reference value for PCB_101

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	117.9	11
VITO	124.1	8.38
IMEP-21 ref. value	121	6.9

Figure 5 Graphical display of reference measurement values for PCB_101

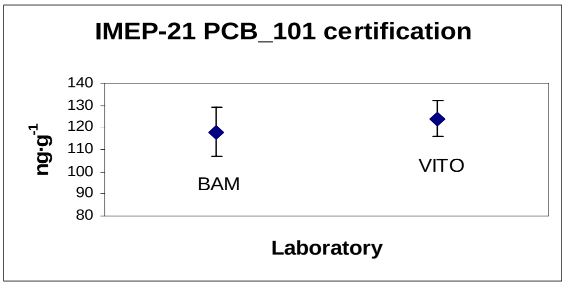


Table 10 Reported measurement values and IMEP-21 reference value for PCB_118

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	84.5	6.09
VITO	90.24	5.58
IMEP-21 ref. value	87.4	4.1

Figure 6 Graphical display of reference measurement values for PCB_118

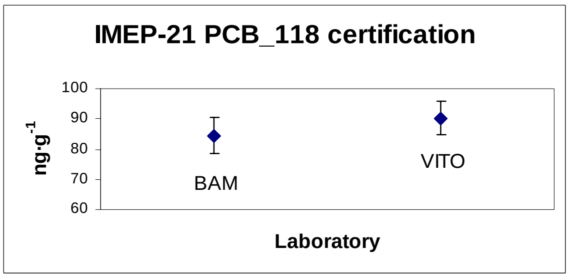


Table 11 Reported measurement values and IMEP-21 reference value for PCB_153

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	207.4	14.73
VITO	198.6	10.76
IMEP-21 ref. value	203	9.1

Figure 7 Graphical display of reference measurement values for PCB_153

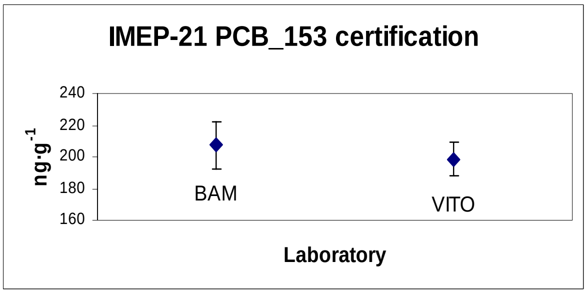
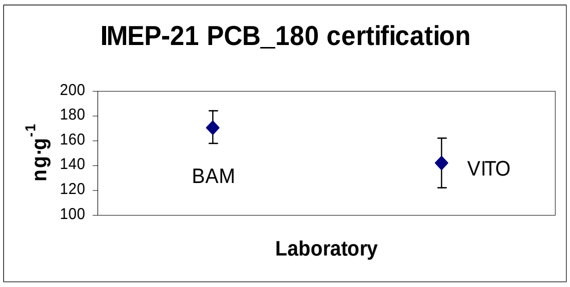


Table 12 Reported measurement values and IMEP-21 reference value for PCB_180

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	170.9	13.4
VITO	142.6	20
IMEP-21 ref. value	157	12

Figure 8 Graphical display of reference measurement values for PCB_180



The PAH congeners were also measured by BAM and VITO, both institutes applying GC-MS with isotopically labelled standards (Table 4). The results for the PAHs are listed in the following Tables. As mentioned in the paragraph on homogeneity testing, a slight trend to lower concentrations of some of the PAHs was observed for the samples that had been stored for 4 weeks at 60°C prior to the measurements. This effect was taken into account and is reflected in the larger uncertainties of the reference values for benz(a)pyrene, fluorene and naphthalene (see also Table 2).

Table 13 Reported measurement values and IMEP-21 reference value for anthracene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	122	32
VITO	86	15.5
IMEP-21 ref. value	104	18

Figure 9 Graphical display of reference measurement values for anthracene

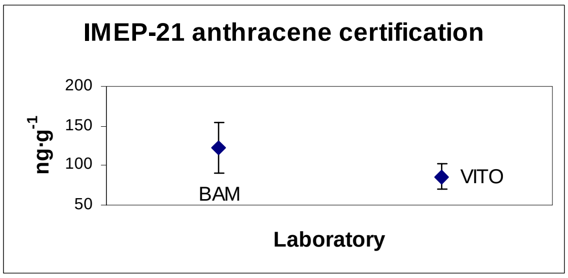


Table 14 Reported measurement values and IMEP-21 reference value for benz(a)anthracene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	435	82.86
VITO	337.6	74.3
IMEP-21 ref. value	386	56

Figure 10 Graphical display of reference measurement values for benz(a)anthracene

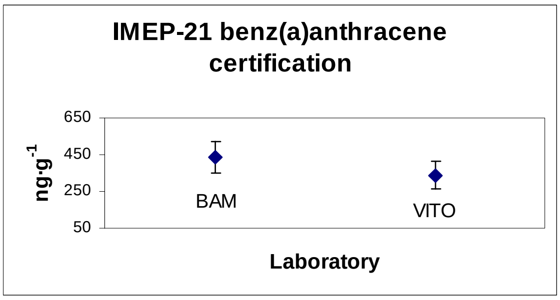


Table 15 Reported measurement values and IMEP-21 reference value for benz(a)pyrene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	447	73
VITO	319	35.1
IMEP-21 ref. value	383	91

Figure 11 Graphical display of reference measurement values for benz(a)pyrene

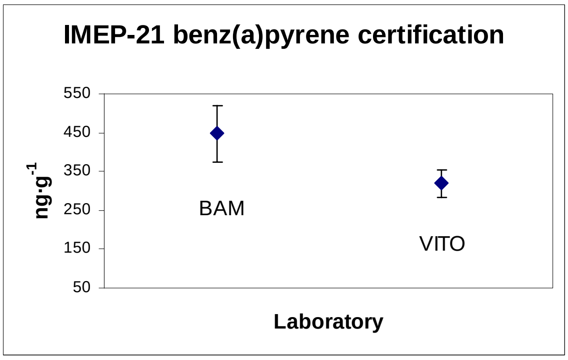


Table 16 Reported measurement values and IMEP-21 reference value for benz(b+k)fluoranthene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	1240	151.94
VITO	988.4	283.28
IMEP-21 ref. value	1110	160

Figure 12 Graphical display of reference measurement values for benz(b+k)fluoranthene

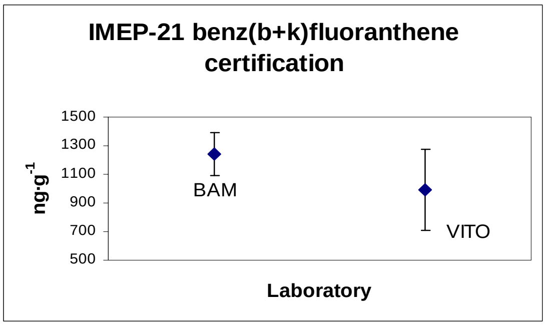


Table 17 Reported measurement values and IMEP-21 reference value for benzo(ghi)perylene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} U, k=2
BAM	528	67.43
VITO	487	94.27
IMEP-21 ref. value	508	58

Figure 13 Graphical display of reference measurement values for benzo(ghi)perylene

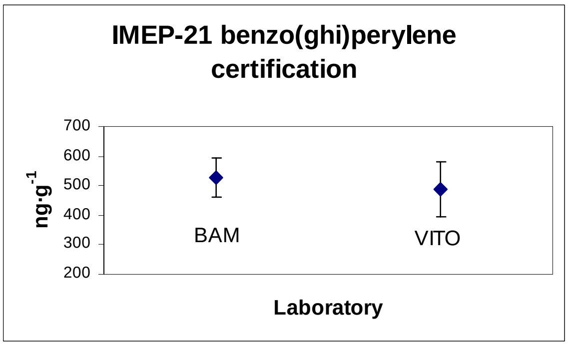


Table 18 Reported measurement values and IMEP-21 reference value for fluoranthene.

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} U, k=2
BAM	984	90.21
VITO	847	88.76
IMEP-21 ref. value	916	63

Figure 14 Graphical display of reference measurement values for fluoranthene

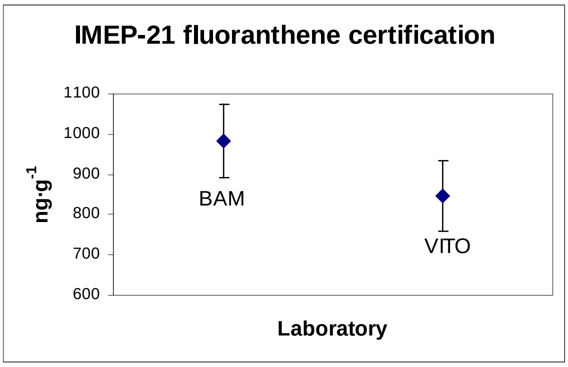


Table 19 Reported measurement values and IMEP-21 reference value for fluorene

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} U, k=2
BAM	108	14.41
VITO	72.59	13.07
IMEP-21 ref. value	90	22

Figure 15 Graphical display of reference measurement values for fluorene

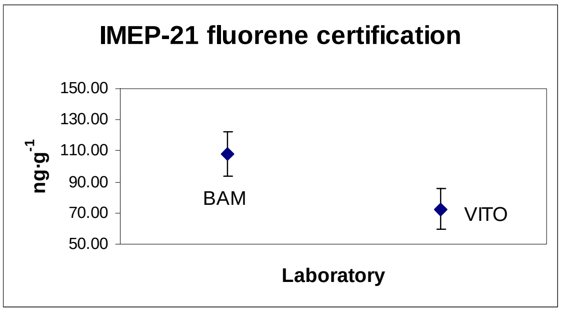


Table 20 Reported measurement values and IMEP-21 reference value for indeno(1,2,3-cd)pyrene

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} U, k=2
BAM	444	89
VITO	296.1	77
IMEP-21 ref. value	370	54

Figure 16 Graphical display of reference measurement values for Indeno(1,2,3-cd)pyrene

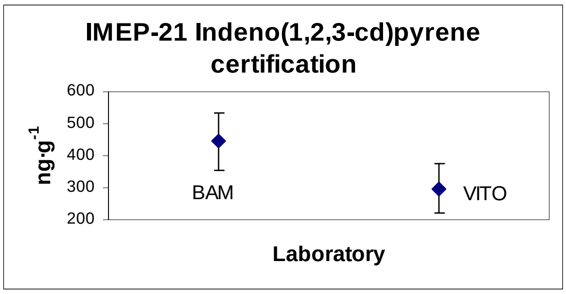


Table 21 Reported measurement values and IMEP-21 reference value for naphthalene

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	168	21.38
VITO	64.29	12.22
IMEP-21 ref. value	116	27

Figure 17 Graphical display of reference measurement values for naphthalene

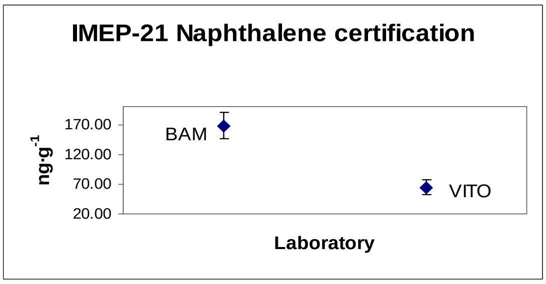


Table 22 Reported measurement values and IMEP-21 reference value for phenanthrene

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	865	76.68
VITO	626.8	113.90
IMEP-21 ref. value	746	77

Figure 18 Graphical display of reference measurement values for phenanthrene

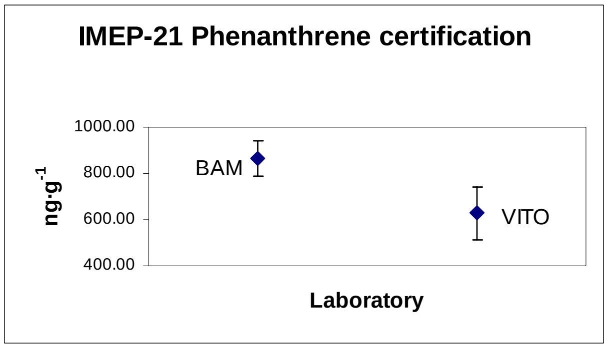
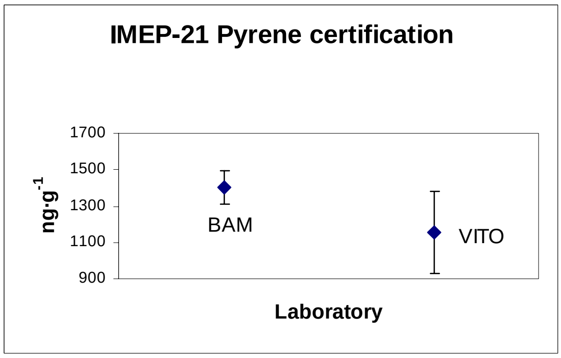


Table 23 Reported measurement values and IMEP-21 reference value for pyrene

Institute	value in ng·g^{-1}	expanded uncertainty in ng·g^{-1} *U*, *k*=2
BAM	1401	90.33
VITO	1155.30	224.31
IMEP-21 ref. value	1280	120

Figure 19 Graphical display of reference measurement values for pyrene



All the IMEP-21 certified reference values are listed in Table 24.

Table 24: IMEP-21 Certified reference values

analyte	certified value in $mg \cdot kg^{-1}$	expanded uncertainty in $mg \cdot kg^{-1}$ *U*, *k*=2
Cadmium	19.23	0.24
Chromium	209	10
Copper	843	40
Lead	619.8	8.7
Mercury	9.03	0.36
Nickel	68.5	1.0
Zinc	3160	72

analyte	certified value in $ng \cdot g^{-1}$	expanded uncertainty in $ng \cdot g^{-1}$ *U*, *k*=2
PCB_28	48.2	9.0
PCB_52	92.3	4.7
PCB_101	121.0	6.9
PCB_118	87.4	4.1
PCB_153	203.0	9.1
PCB_180	157	12
Sum_PCBs	709	20

analyte	certified value in $ng \cdot g^{-1}$	expanded uncertainty in $ng \cdot g^{-1}$ *U*, *k*=2
Anthracene	104	18
Benz(a)anthracene	386	56
Benz(a)pyrene	383	91
Benz(b+k)fluoranthene	1110	160
Benzo(ghi)perylene	508	58
Fluoranthene	916	63
Fluorene	90	22
Indeno(1,2,3-cd)pyrene	370	54
Naphthalene	116	27
Phenanthrene	746	77
Pyrene	1280	120
Sum_PAHs	6010	260

Summary and Conclusions

In IMEP-21 24 inorganic and organic analytes were certified for their total amount content via measurements carried out by reference laboratories that complied with the technical requirements of providing demonstrated traceability and uncertainty of their measurement values. The overall result for the analytes under investigation in IMEP-21 is very satisfactory, despite the observed matrix intrinsic inhomogeneity of a few of the PAHs. IMEP-21 proves once more that the IMEP metrological tool is a complete transparent process. It supports routine laboratories by providing independent reference values. Therefore they can assess the quality of their results on an international forum by comparing their measurement results to those reference values. This is of major importance in cases when the certified reference value would not coincide with a consensus value derived from the participants' results [8]. In this sense, IMEP complements the regular and sector-specific proficiency testing (PT) and external quality assessment (EQA) schemes. IMEP enables laboratories to assess their measurement performance and at the same time allows them to demonstrate their competence on a high quality level to accreditation, authorisation, and inspection bodies as well as to their regular customers.

Furthermore the same sewage sludge material was used for comparisons of international metrology organisations (CCQM) [11]. The advantage of this approach is that an efficient use of test material is made, contributing and supporting the establishment of the international measurement infrastructure. This means supporting NMIs in disseminating their measurement capabilities to field laboratories and at the same time allowing field laboratories to compare their results with the results of laboratories that represent their country at the international measurement structure.

Acknowledgements

Special thanks to F. Ulberth, A. Held, A. Bernreuther and T. Linsinger from the RM unit for their support in providing the suitable sewage sludge sample and in the design of the homogeneity study. The authors acknowledge furthermore the input of all the scientists who contributed to the reprocessing and characterisation of the sewage sludge material : - E. Vassileva, C. Quétel, K. H. Grobecker, M. Bickel, A. Michiels, A. Bernreuther, S. Yazgan, P. Conneely, B. Sejeroe-Olsen, O. Bercaru from IRMM. Particularly we would like to thank our collaborators from other institutes B. Magnusson and Mathias Johansson from SP, P. Vermaercke from SCK-CEN, T. Prohaska and S. Boulyga from BOKU-WIEN, J. Vogl, T. Win and R. Philipp from BAM, R. Van Cleuvenbergen, K. Tirez and M. Wevers from VITO.

Furthermore the assistance of all IMEP team members, particularly our MILC experts, S. Bynens and E. Garlick, and of our former IMEP team member C. Harper is warmly acknowledged. In addition our colleagues form the MSU L. Huysmans, E. Dalle Molle and P. Hesemans made huge efforts to help us in complying with the administrative requirements for this ILC.

List of abbreviations

AES	Atomic emission spectrometry
BAM	Bundesanstalt für Materialforschung und –prüfung (Berlin, Germany)
BOKU	Universität für Bodenkultur Wien
BIPM	Bureau International des Poids et Mesures (Paris, France)
CARDS	Community Assistance for Reconstruction, Development and Stabilisation
CCQM	Comité Consultatif pour la Quantité de Matière
CEN	European Committee for Standardisation
CIPM	International Committee for Weights and Measure
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRMs	Certified Reference Materials
CTS	Certified Test Sample
EA	European Co-operation for Accreditation
EC	European Commission
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
EuroGeoSurveys	The Association of the European Geological Surveys
GC-MS	Gas Chromatography Mass Spectrometry
GUM	Guide for expression for Uncertainty in Measurement
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IMEP®	International Measurement Evaluation Programme
ILC	Interlaboratory Comparison
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
MRA	Mutual Recognition Agreement
NAA	Neutron Activation Analysis
NAB	National Accreditation Body
PT	Proficiency Testing Scheme
SCK-CEN	Studiecentrum voor Kernenergie- Centre d’étude de l’énergie nucléaire
SS-ZAAS	Solid Sample Zeemann Atomic Absorption Spectrometry
TIMS	Thermal Ionisation Mass Spectrometry
VITO	Flemish Institute for technological research

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European Commission

EUR 22243 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements –
IMEP-21 Trace Elements, PCBs and PAHs in Sewage Sludge Certification Report
Authors:Y.Aregbe, S. Bynens, L. Van Nevel, I. Verbist, P. Robouch and P.D.P. Taylor
Luxembourg: Office for Official Publications of the European Communities
2006 – 25 pp. – 21 x 29.7 cm
Scientific and Technical Research series

Abstract

The International Measurement Evaluation Programme (IMEP®) is an Interlaboratory Comparison (ILC) scheme in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). It is founded, owned and co-ordinated by the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate-General Joint Research Centre.

The aim of this interlaboratory comparison programme is to picture objectively the degree of equivalence and the quality of chemical measurements. Contrary to most other external quality assessment schemes, participating laboratories in IMEP® can compare their measurement results and uncertainty statements with external certified reference values, obtained completely independent from the participants' result. These reference values are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. Participants in IMEP® use their routine analytical procedures to measure the IMEP-certified test sample (CTS). Therefore they can assess the quality of their results on an international forum by comparing their values to the IMEP-reference values. IMEP supports quality assurance work at routine level and stresses, particularly, the educational aspect. In this way, IMEP complements the regular and sector-specific proficiency testing (PT) and external quality assessment (EQA) schemes.

The European Union promotes the use of sewage sludge as fertilizer in agriculture. The Council Directive 86/278/EEC of 12 June 1986 sets rules for the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. In this directive limit concentration ranges of metals in sewage sludge are laid down. In national legislation the concentration ranges for metals can be set below these limits. Furthermore limits for Polychlorinated Biphenyls (PCBs), and Polycyclic Aromatic Hydrocarbons (PAHs) congeners in sewage sludge are set in some of the national legislations. The directive 86/278/EEC is discussed to be revised and lower levels for metals and most probably also upper levels for PCBs and PAHs concentrations will be included. Participants in IMEP-21 were offered to measure the total amount content of 7 metals, 6 PCB congeners and 11 PAH congeners: Cd, Cr, Cu, Pb, Hg, Ni, Zn, PCB_28, PCB_52, PCB_101, PCB_118, PCB_153, PCB_180, sum_PCBs, anthracene, benz(a)anthracene, benz(a)pyrene, benz(b+k)fluoranthene, benzo(ghi)perylene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene, sum_PAHs.

IMEP-21 was organised in collaboration with The European Committee for Standardisation (CEN) upon approval of DG EuropAid, the Association of the European Geological Surveys (EuroGeoSurveys) Geoscientific Laboratory Network and the European Co operation for Accreditation (EA). In IMEP-21 3228 measurement results on 26 analytes were reported by 204 participants from 45 countries. Amongst those were participants nominated by CEN, EuroGeoSurvey and by national accreditation bodies (NABs) but also laboratories from Western Balkan countries (IRMM's CARDS support), new member states and other countries participated in MEP-21.

Reference measurements in IMEP are performed by institutes with internationally demonstrated and/or mutually recognised measurement capabilities. The institutes involved in establishing the IMEP 21 certified reference values were IRMM, BAM, SCK-CEN, VITO and BOKU-Wien. The analytical techniques applied to establish the IMEP-21 reference values were ID-ICP-MS, ID-TIMS, k0-NAA and GC-MS. IRMM coordinated the IMEP-21 certification campaign to establish the certified reference values for all the analytes under investigation. The IMEP-21 certification report summarises the organisatorial and technical details thereof. The results on the homogeneity and short term stability tests of the sewage sludge material are presented as well as the results of the reference measurements and the establishment of the reference values.