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# A new marine sediment certified reference material (CRM) for the determination of persistent organic contaminants: IAEA-459.


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# Sediment CRMs

- Sediments : relevant matrix for monitoring the water compartment (WFD)
  - ✓ Long-term trend assessment

- There is a noticeable lack of natural sediment CRMs for Persistent Organic Pollutants (POPs) in marine sediments with very low concentrations (µg $kg^{-1}$)
  - ✓ New Marine Sediment CRM for persistent organic contaminants with low concentrations

- Polychlorinated biphenyls (ΣPCBs~50 µg $kg^{-1}$ dry weight)
- Chlorinated pesticides (ΣDDTs ~ 9 µg $kg^{-1}$ dry weight)
- Polybrominated diphenyl ethers (ΣPBDEs ~10 µg $kg^{-1}$ dry weight)
- Polycyclic aromatic hydrocarbons (Σparent PAHs ~ 680 µg $kg^{-1}$ dry weight)

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# Sediment quality guidelines for POPs in marine sediments compared to concentrations of IAEA-459

| | | ISQG[a] & TEL[b] & FEQG[c] | IAEA-459 |
|---|---|---|---|
| PCBs and OCs pesticides | Total PCBs | 21.5[a,b] | 55 |
| | p-p'-DDE | 2.07[a,b] | 3.6 |
| | p-p'-DDD | 1.22[a,b] | 3 |
| | p-p'-DDT | 1.19[a,b] | 1.32 |
| | Lindane | 0.32[a,b] | 0.182 |
| | Heptachlor epoxide | 0.60[a] | 0.15 |
| | Dieldrin | 0.71[a] | 0.1 |
| PAHs | Acenaphtene | 6.71[a] | 1.8 |
| | Acenapthylene | 5.87[a] | 3.2 |
| | Anthracene | 46.9[a] | 6 |
| | Benzo(a)anthracene | 74.8[a] | 19.3 |
| | Benzo(a)pyrene | 88.8[a] | 22.7 |
| | Chrysene | 108[a] | 27.5 |
| | Dibenz(a,h)anthracene | 6.22[a] | 6.6 |
| | Fluoranthene | 113[a] | 37.3 |
| | Fluorene | 21.2[a] | 4.7 |
| | 2-Methylnapthalene | 20.2[a] | 15.5 |
| | Napthalene | 34.6[a] | 20.9 |
| | Phenanthrene | 86.7[a] | 33.9 |
| | Pyrene | 153[a] | 46.3 |
| | Σ16 PAHs | 656[a] | 355 |
| PBDEs | total triBDE | 44[C] | 0.1[d] |
| | total tetraBDE | 39[C] | 0.005[d] |
| | BDE 99 | 0.4[C] | 0.12[d] |
| | BDE 100 | 0.4[C] | 0.0145[d] |
| | hexaBDE | 440[C] | 0.06[d] |
| | decaBDE | 19[C] | 5.4[d] |

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# CRM PRODUCTION PROCESS

**produced according to the guidelines of ISO Guide 34:2009**

- ❑ select the material
- ❑ prepare the units (e.g. bottles)
- ❑ labelling
- ❑ measure homogeneity
- ❑ measure stability
- ❑ characterization study
- ❑ assignment of reference values

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# Origin of the material

- Collected in Han River estuary, South Korea.
- This sediment was freeze-dried, ground and sieved at 125 µm.
- The sieved sediment was homogenized by mixing it in a stainless steel rotating homogenizer for three weeks.
- Then, aliquots of about 50 g were packaged into cleaned amber glass bottles with aluminium screw caps, labelled IAEA-459 and sealed with Teflon tape.



Credit: (Jpbarras at English Wikipedia)

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# Homogeneity assessment

**The between-bottle homogeneity:**

- **DDTs**
- **PCBs**
- **PBDEs**
- **parent PAHs**

**10 bottle units randomly selected and analysed under repeatability conditions.**

$u_{c,bb}$ is the combined uncertainty of the between-unit experiment expressed as the uncertainty on a single unit

**The within–bottle homogeneity**

- **DDTs**
- **PCBs**
- **PBDEs**
- **parent PAHs**

**6 determinations in one bottle**

$s_{meas}$ is the intrinsic variability of the method ($s_{method}$) divided by the square root of n, the number of replicates per unit;

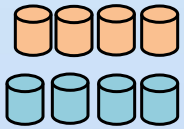
$$s^2_{bb} = u^2_{c,bb} - s^2_{meas}$$ **ANOVA-like approach**

$s_{bb}$ is the estimate of between bottle variation in the material, named $u_{hom}$

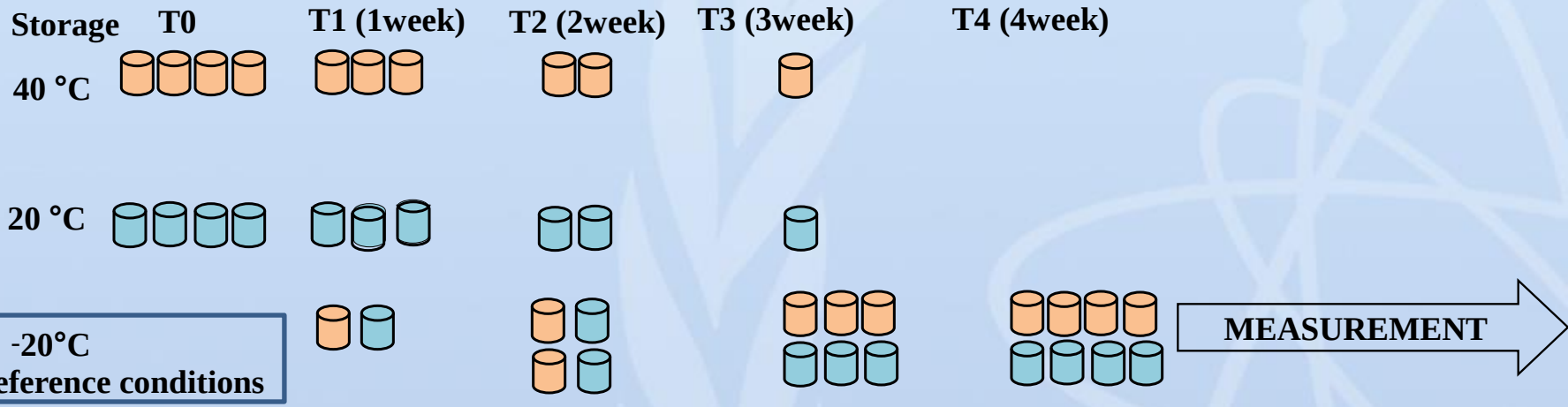
**$U_{hom}$ <11% for the certified analytes**

# Short-term stability test

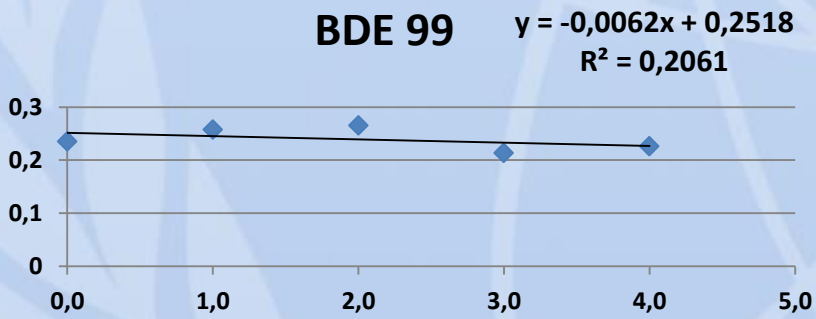
- 4 Bottles at 40 °C
- 4 Bottles at 20 °C



**Isochronous design over 4 weeks**




- ❑ No slope for each selected analyte was detected that differed significantly from zero.
- ❑ Uncertainty associated with short term stability under transport conditions was taken as zero.



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# Characterization study

**PARTICIPATING LABORATORIES**

| | |
|---|---|
| Ontario Ministry of the Environment and Climate change | CANADA |
| CNEAC | CHINA |
| Molecular Science Institute (ISM), Talence | FRANCE |
| IFREMER-DCN/RBE/BE/LBCO, Nantes | FRANCE |
| Federal Maritime and Hydrographic Agency, Hamburg | GERMANY |
| ISPRA, Laboratory of Organic Pollutants | ITALY |
| ISPRA – Istituto Superiore per la Ricerca e la Protezione Ambientale | ITALY |
| South Sea Institute, KORDI | KOREA |
| PI Center for ecotoxicological Research | MONTENEGRO |
| Institute of Marine Research (Havforskninginstituttet) | NORWAY |
| A.N. Severtsov Inst. Ecological & Evolution | RUSSIAN FEDERATION |
| Centre for Environment, Fisheries and Aquaculture Science | UNITED KINGDOM |
| IAEA | MONACO |

- Laboratories of demonstrated competence
- Selected based in results of previous interlaboratory comparisons
- Formal accreditation was not mandatory but meeting the requirements of ISO/IEC 17025

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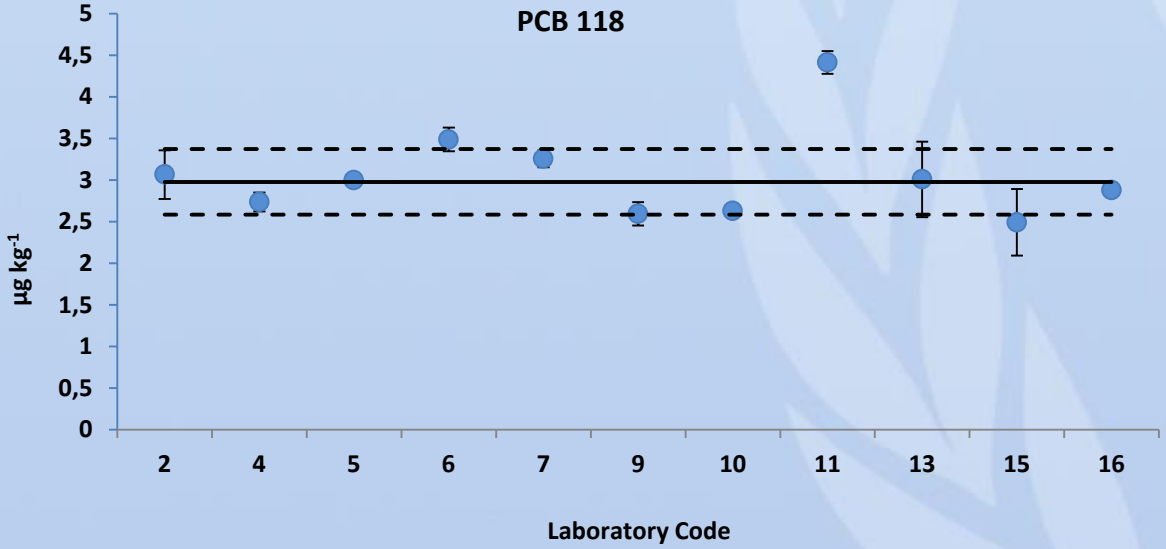
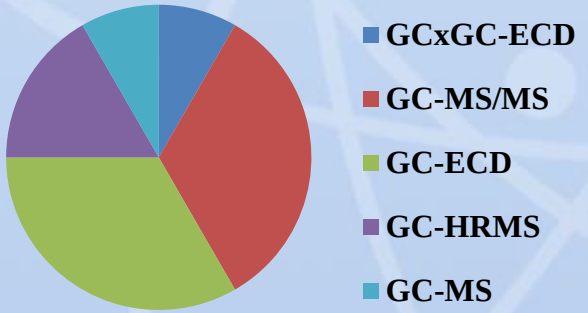
# Characterization-PCBs

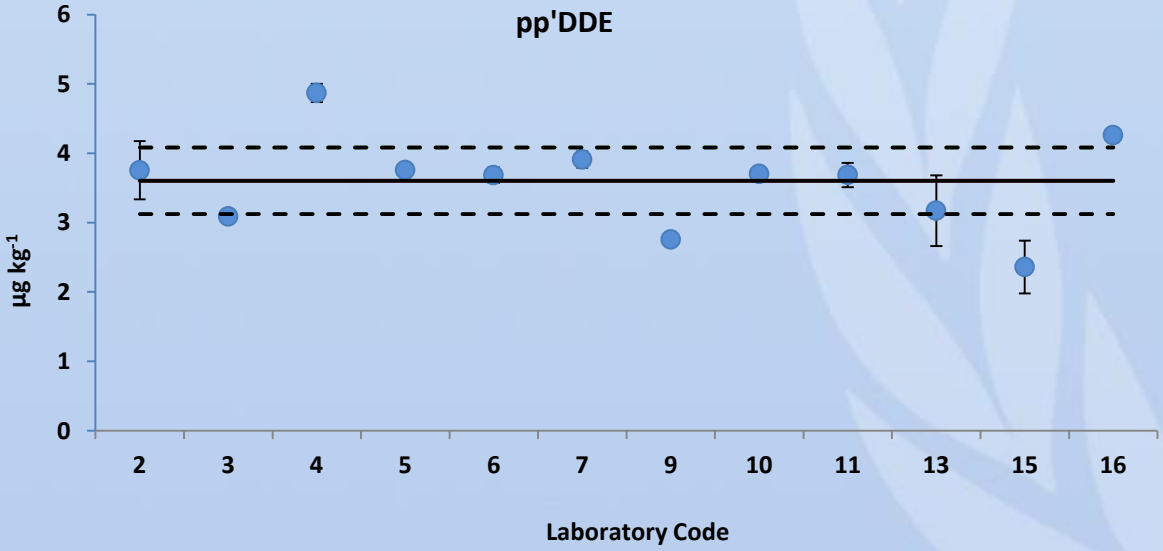
| Extraction | Solvent | Cleanup | Fractionation | Equipment |
|---|---|---|---|---|
| PSE | DCM/n-Hexane | Silica | none | GC x GC-ECD |
| Sohxlet | DCM/n-Hexane | Concentrated $H_2SO_4$ | Multilayer silica gel columns | GC-MS/MS |
| Microwave | DCM | Copper and Silica acidified wih sulfuric acid | no | GC-ECD |
| ASE | DCM | GPC & silica/alumina & sulphuric acid | HPLC | GC-HRMS |
| Microwave | Acetone/hexane | Silica & GPC | none | GC-MS/MS |
| Microwave | Hexane/acetone 90:10 | Concentrated $H_2SO_4$ & copper | none | GC-MS/MS |
| Sohxlet | DCM/n-Hexane | Silica | | GC-ECD |
| ASE | DCM:n-hexane (1:1) | Copper | ABN silica 7,5 g | GC-MS |
| ASE | Toluene:methanol(9:1) | Acid/basic silica | none | GC-HRMS |
| Sohxlet | Other | | | GC-MS/MS |
| Microwave | DCM/n-Hexane | | Florisil | GC-ECD |
| Microwave | DCM/n-Hexane | Copper | Florisil | GC-ECD |

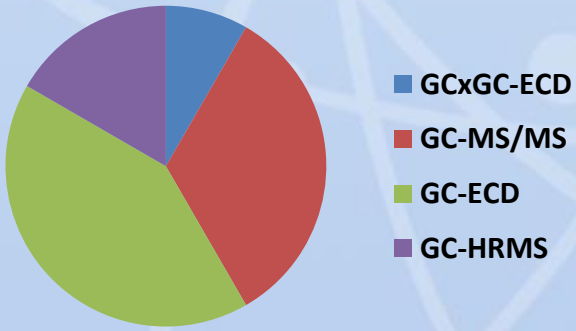


# Characterization-OCS pesticides

| Extraction | Solvent | Cleanup | Fractionation | Equipment |
|---|---|---|---|---|
| PSE | DCM/n-Hexane | Silica | none | GC x GC-ECD |
| Sohxlet | DCM/n-Hexane | Concentrated H2SO4 | Multilayer silica gel columns | GC-MS/MS |
| Microwave | DCM | Copper and Silica acidified wih sulfuric acid | none | GC-ECD |
| ASE | DCM | GPC & silica/alumina & sulphuric acid | HPLC | GC-HRMS |
| Microwave | Acetone/hexane | Silica & GPC | none | GC-MS/MS |
| Microwave | Hexane/acetone 90:10 | Concentrated H2SO4 & copper | none | GC-MS/MS |
| Sohxlet | DCM/n-Hexane | Silica | | GC-ECD |
| ASE | DCM:n-hexane (1:1) | Copper | ABN silica 7,5 g | GC-ECD |
| ASE | Toluene:methanol(9:1) | Silica or acid/basic silica | none | GC-HRMS |
| Sohxlet | Other | | Other | GC-MS/MS |
| Microwave | DCM/n-Hexane | | Florisil | GC-ECD |
| Microwave | DCM/n-Hexane | Copper | Florisil/SPE | GC-ECD |



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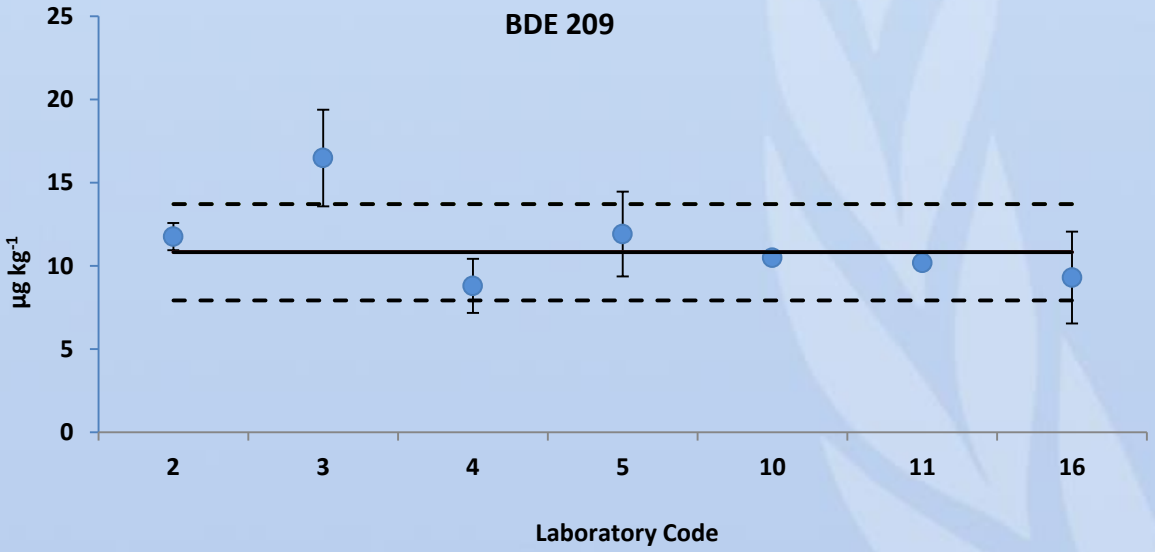
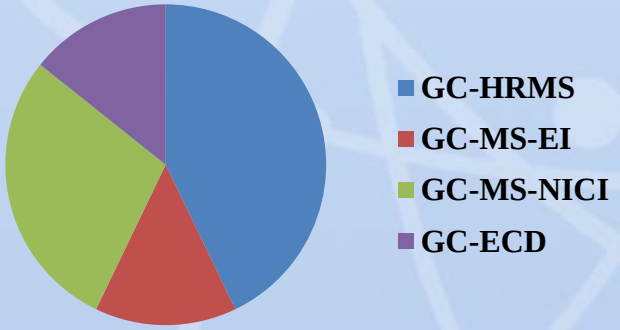
# Characterization-PBDEs

| Extraction procedure | Solvent | Cleanup | Fractionation | Equipment |
|---|---|---|---|---|
| Sohxlet | Toluene | Silica multilayer | Alumina | GC-HRMS |
| Soxhlet | Hex:DCM(1:1) | Sulphuric acid | Multilayer silica/florisil | GC-MS-EI |
| Microwave | DCM | Copper and Silica acidified wih sulfuric acid | no | GC-MS-NICI |
| ASE | DCM | GPC & silica/alumina & sulphuric acid & HPLC | no | GC-HRMS |
| ASE | DCM:n-hexane (1:1) | Copper | ABN silica 7,5 g | GC-MS-NICI |
| ASE | Toluene:methanol(9:1) | Acid/basic silica | no | GC-HRMS |
| Microwave | Hex:DCM(1:1) | Copper | Florisil | GC-ECD |



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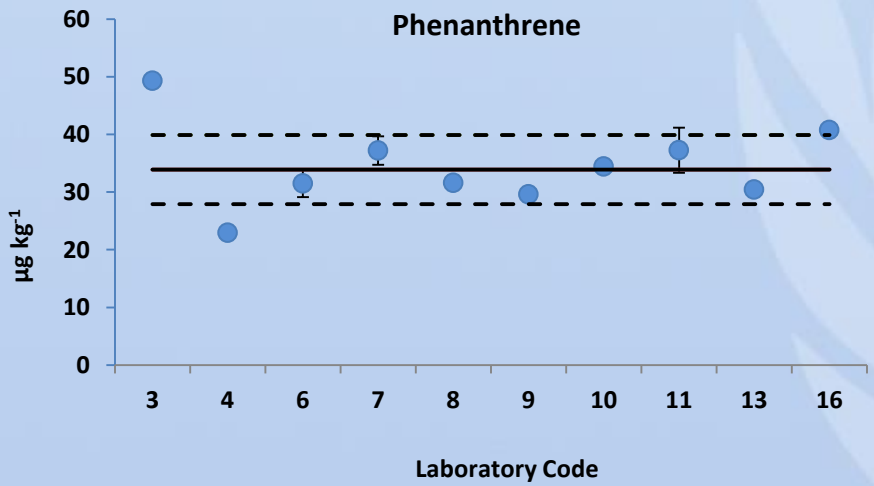
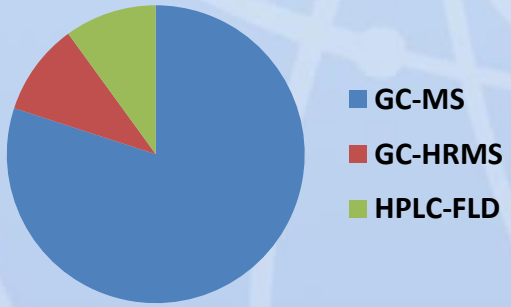
# Characterization-PAHs

| Extraction | Solvent | Cleanup | Fractionation | Equipment |
|---|---|---|---|---|
| ASE | DCM-Hexane | Florisil | none | GC-MS |
| Microwave | Dichloromethane | Copper/alumina | Silica | GC-MS |
| Microwave | Acetone-hexane | Silica/GPC | none | GC-MS/MS |
| Sonication | MeOH-acetonitrile | none | none | HPLC-FLD |
| Sohxlet | DCM-Hexane | Silica&alumina | GPC | GC-MS |
| Sohxlet | DCM-Hexane | none | Silica&alumina | GC-MS |
| ASE | DCM-hexane | Copper/silica | none | GC-MS |
| ASE | Toluene:MEOH (9:1) | Silica | none | GC-HRMS |
| Saponification & LLE | MEOH/pentane | Alumina | none | GC-MS |
| Microwave | Dichloromethane/n-Hexane | Copper | Silica:cyano SPE | GC-MS |



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# Determination of assigned values and uncertainties

- **The robust statistics approach:**
  - The robust average and robust standard deviation calculated using the Algorithm A:
    - ✓ Annex C.1 from the ISO standard 13528

**Iterative process**

$x^*$=median $x_i$ ($i$= 1, 2,., $p$)

**The robust standard deviation**

$s^*$= 1.483 median $|x_i - x^*|$ ($i$= 1, 2,., p)

**The final "cut-off" values used in the robust algorithm was estimated as: $\delta = 1.5\ s^*$**

## UNCERTAINTIES

$$u_{char} = 1.25 \times \frac{s^*}{\sqrt{p}}$$ ISO 13528

**Where:**

**$s^*$ is the robust standard deviation**

**p is the number of participating laboratories.**

# Uncertainty of the Assigned Value ($U_{CRM}$)

$U_{CRM}$ uncertainty of the average concentration after storage for time T and after transport

$$U_{CRM}\,[\%] = k * (u^2_{char} + u^2_{hom} + u^2_{stab} + u^2_{short})^{1/2}$$

$u_{char}$ uncertainty value characterization measurement

$u_{hom}$ uncertainty bottle to bottle variation, homogeneity

$u_{stab}$ uncertainty long term stability

$u_{short}$ uncertainty short term stability (transport)

K =2 for a confidence level of 95%

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# Certification procedure

**The robust mean of the laboratory means was assigned as certified value,**

- **for those compounds where the assigned value was derived from at least five datasets**
- **from at least two different analytical techniques**
- **and its relative expanded uncertainty was less than 40 % of the assigned value.**

❖ ***Assigned mass fraction values that did not fulfill the criteria of certification are considered information values***

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# Metrological Traceability and Commutability

**The methods used by all participating laboratories were validated by using matrix standard reference materials (CRMs) from:**

- **NIST: (SRM1941b, SRM 1944),**
- **IAEA (IAEA-408, IAEA-159)**
- **QUASIMEME proficiency tests (MS3 polycyclic aromatic hydrocarbons in sediment, MS2 chlorinated organics in sediment).**

- ❑ **values reported by participants are based on calibration standard solutions of known purity, issued by accredited commercial companies with documented unbroken chain of calibrations,**
  - ❑ **assigned values derived from combining the individual results are traceable to International System of Unis (SI).**
- ❑ **the agreement between the results generated by different analytical methodologies ensures the comparability of the measurement results and shows commutability of the material.**

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# Conclusions

**Combination of different data sets from at least two different analytical techniques has allowed the assignment of certified concentrations**

- **22 PCBs**
- **6 OC pesticides**
- **5 PBDEs**
- **18 PAHs**

**following the recommendation of ISO Guide 35**

- ❑ **CRM 459 a valuable sediment reference material for use in the validation of analytical methods for the determination of a great number of POPs listed at the Stockholm Convention as well as other persistent and priority substances (PSs), such as PAHs included within the environmental monitoring programs.**

- ❑ **These target compounds in the reference material are very close to the environmental quality standards (EQS).**

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# Acknowledgements

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| South Sea Institute, KORDI | KOREA |
| PI Center for ecotoxicological Research | MONTENEGRO |
| Institute of Marine Research (Havforskninginstituttet) | NORWAY |
| A.N. Severtsov Inst. Ecological & Evolution | RUSSIAN FEDERATION |
| Centre for Environment, Fisheries and Aquaculture Science | UNITED KINGDOM |
| IAEA | MONACO |

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**THANK YOU FOR YOUR ATTENTION!**