Preparation and certification of two freshwater sediments certified reference materials for polycyclic aromatic hydrocarbons

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Two freshwater sediments certified reference materials (CRMs) for 16 polycyclic aromatic hydrocarbons (PAHs) have been developed by the Institute for Environmental Reference Materials (IERM) of Ministry of Environmental Protection (MEP) in China. The methodology for preparing the CRMs of PAHs in sediments is described in this paper. The collected natural sediment samples were air-dried, ground, homogenised, packed, sterilised and tested on stability and homogeneity. Homogeneity results showed that the between-unit variation was confirmed to be below 4.5% for each compound. Stability was assessed after storage of samples for 16 months at temperature less than 30°C and in shade. The certification of the natural sediment matrix CRMs for PAHs was based on the agreement of results using different analytical techniques including gas chromatography/mass spectrometry (GC/MS) and reversed-phase liquid chromatography (LC) by no less than eight collaborating laboratories including IERM. Results of the homogeneity showed that the calculated $u_{bb}'$ was 0.9–2.5% for environmental river standard-4 (ERS-4) and 9–2.3% for environmental lake standard-1 (ELS-1), whereas stability results of total 16 PAHs indicated that the calculated $u_{rel,lts}$ was 4.2% for ERS-4 and 2.2% for ELS-1. Certified values of 16 PAHs in ERS-4 varied from 8.5 to 167 μg/kg and ranged from 0.036 to 2.8 mg/kg in ELS-1. The good comparability, together with the independent confirmation of the assigned mass fraction by using different methods, confirmed that the CRMs are suitable for the method validation and quality control in soil or sediments analysis.

Keywords: polycyclic aromatic hydrocarbons (PAHs); certified reference materials (CRMs); sediment; certification

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are serious and ubiquitous environmental contaminants with high mutagenicity, carcinogenicity and endocrine-disrupting effects \cite{1}. Under this consideration, the US Environmental Protection Agency (EPA) selected 16 PAHs for their ‘Priority Pollutant List’ \cite{2}, namely naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene. China also placed seven PAHs (namely naphthalene, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene) in the ‘Priority Pollutant List’ due to the persistence of these

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organic contaminants in sediments, which are considered as pollution indicators [3]. Therefore, monitoring the content level of PAHs in soil or sediment is particularly important.

To guarantee the reliability and comparability of analytical data, an intricate system of quality-assurance measures has to be put into effect in a laboratory. Reference materials and, in particular, certified reference materials (CRMs) are essential for achieving traceability and comparability of measurement results between laboratories and over time. Matrix CRMs are playing an increasingly important role in environmental monitoring in China. Various kinds of matrix CRMs are increasingly required. Because the kinds of CRMs developed in China are limited, many CRMs produced by foreign national metrology institutes are imported and used for environmental monitoring. For example, two sediment standard reference materials (SRMs) (SRM 1941b and SRM 1944) issued by the National Institute of Standards and Technology (NIST) have certified and reference mass fractions values for 24 PAHs [4,5]. Additionally, the Institute for Reference Materials and Measurements (IRMM) of European Commission, the National Metrology Institute of Japan (NMIJ) and the Laboratory of the Government Chemist (LGC) also issued sediment CRMs for PAHs [6–11]. However, CRMs developed in China are needed in some cases such as the content levels or patterns of the environmental pollutants or matrix type are different from those in other countries. Likewise, there is a lack of suitable reference material of sediment matrix for the proficiency testing schemes in China.

Therefore, the feasibility of the production of CRM for PAHs was evaluated at the Institute for Environmental Reference Materials (IERM) of Ministry of Environmental Protection (MEP). Recently, two freshwater sediments reference materials with different pollutant levels for the determination of representative PAHs have been prepared and certified by IERM. In this paper, the preparation and the certification of the two freshwater sediments CRMs for the determination of PAHs are described.

2. Experimental
IERM has a quality management system based on ISO Guide 34 [12] and ISO/IEC 17025 [13], which is accredited by the China National Accreditation Service for Conformity Assessment (CNAS). The certification of the CRMs for environmental monitoring has been carried out according to the technical requirements of ISO Guide 35 [14].

2.1. Material collection and preparation
The Yangtze River is the longest river in China which extends approximately 6400 km from the Qinghai–Tibet Plateau to the East China Sea. It is characterised by intense industrial and urban activity, especially in its lower reaches and estuaries in Eastern China. Nanjing is one of six major industrial cities located in the Eastern China, as well as the centre of petroleum processing and chemical manufacturing in this region [15]. Approximately 500 kg river sediment was collected from two sites (118°44′E and 32°05′N and 118°43′E and 32°05′N) in the Yangtze River at the mouth of the Nanjing Harbour in May 2008. The two sites were selected from six sites where samples were collected and examinated previously.

Taihu Lake is situated in the south of the Yangtze Delta, with a land area of 2338 km² and an average water depth of 1.9 m. It is one of the five largest freshwater lakes in China. Taihu Lake Basin has almost the highest population density in one of the most heavily industrialised areas in China [16]. The lake sediment was collected from three sites (120°13′E and 31°23′N, 120°06′E and 30°57′N, 120°13′E and 31°32′N) in Lake Taihu in June 2008.

The sediment materials were air-dried for two months at room temperature and in shade. After removing visible external objectives such as shells and grits, the materials were ground in
a ceramic ball mill. The pulverised materials were sieved by a 100 mesh stainless steel sieve and homogenised in a cone blender. The sediment powder was packaged in amber glass bottle and approximately 1500 bottles were produced (approximately 50 g/bottle). The bottled samples were sterilised by γ-ray irradiation from a 60Co source (20 kGy), and stored at temperature less than 30°C away from direct sunlight. The candidate reference material was named environmental river standard-4 (ERS-4) and environmental lake standard-1 (ELS-1).

2.2. Moisture and total organic carbon determination

The concentrations of the PAHs in ERS-4 and ELS-1 were given on a dry weight basis. The moisture content in ERS-4 and ELS-1 was determined by taking a portion of the material (typical 1–2 g) and drying it in an oven at 105°C for 6 h to attain constant mass. Three samples of each kind of CRMs were simultaneously determined at the time of the certification analyses in our lab. The means of moisture content in ERS-4 and ELS-1 were 1.3% and 0.6%, respectively. The mean contents of the total organic carbon in ERS-4 and ELS-1 were 1.1% and 0.6%, respectively.

2.3. Determination of PAHs

Pesticides residue grade dichloromethane (DCM) and n-hexane (J.T. Baker) were used for extraction step. Guarantee grade sodium sulphate anhydrous (Tianjin Jinke Institute of Fine Chemicals) and silica gel (Merck) were used for purification. The standard solution of 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene) in DCM: methanol (1:1) at a concentration of 2000 μg/ml was obtained from Supelco. A mixture of seven deuterated PAHs including naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, pyrene-d10, benzo[a]pyrene-d12 and benzo[ghi]perylene-d12 in DCM: methanol (1:1) with a concentration of 200 μg/ml from Cambridge was used as surrogate solution. 13C6-labelled hexachlorobenzene (HCB) from IERM in hexane with a concentration of 100 μg/ml and benz[a]anthracene-d12 (Cambridge) in n-hexane with a concentration of 200 μg/ml were used as internal standards.

ERS-4 and ELS-1 were analysed for 16 PAHs (namely naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene) considered of primary environmental concern according to the US EPA. Analysis of the 16 PAHs was performed using gas chromatography/mass spectrometry (GC/MS) in homogeneity and stability study. It was notable that all the analytical results and PAHs values in CRMs were not corrected with moisture content.

Before extraction, samples were spiked with 10 μl surrogate standard with a concentration of 10 μg/ml (diluted concentration) for indicating recovery, which was a mixture containing seven deuterated PAHs (naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, pyrene-d10, benzo[a]pyrene-d12 and benzo[ghi]perylene-d12). Five grams of the subsample of sediment was extracted with Soxhlet extraction using 250 ml n-hexane/DCM (1:1) for 24 h. Treated copper powder was then added to the extracts to remove elemental sulphur. The extract was quantitatively transferred onto a column containing 7 g silica gel and eluted with 20 ml n-hexane to remove the non-polar constituents, which were discarded, and then eluted with 50 ml 30% DCM in n-hexane. The elute was then concentrated to less than 1 ml. Prior to injection, 100 μl 13C6-labelled HCB and 50 μl benz[a]anthracene-d12 were added as internal standards.
standards and diluted with n-hexane to 1 ml. $^{13}$C$_6$-labelled HCB was used for calculating the contents of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Benz[a]anthracene-d$_{12}$ was used for calculating the contents of benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene. The recovery of the PAHs analysed in this study was in the range of 65.8–90.6% (naphthalene-d$_8$, 67.5%; acenaphthylene-d$_8$, 65.8%; phenanthrene-d$_{10}$, 74.4%; fluoranthene-d$_{10}$, 88.7%; pyrene-d$_{10}$, 90.6%; benzo[a]pyrene-d$_{12}$, 84.1%; and benzo[ghi]perylene-d$_{12}$, 85.9%).

The 16 PAHs were analysed by GC coupled with MS, operating in the electron impact mode (EI, 70 eV). The separation was performed on a 30 m DB-5MS-column (30 m × 0.25 mm i.d. × 0.25 µm). Oven temperature programme started at 80°C, held for 1 min, then up to 170°C at 20°C/min, held for 3 min, then up to 200°C at 5°C/min, held for 3 min, and finally to 280°C at 2.5°C/min and held for 2 min. Injection volume was 1.0 µl in splitless mode with 45 s splitless period. Carrier gas was helium (1.0 ml/min) and the temperatures of the injector, transfer line and ion source were 310°C, 280°C and 230°C, respectively. Data acquisition was performed under selected ion monitoring (SIM) mode. A DB-17MS-column (30 m × 0.25 mm × 0.25 µm) was used for separating benzo[b]fluoranthene and benzo[j]fluoranthene. And an Rxi-XLB-column (30 m × 0.25 mm × 0.25 µm) was used for separating chrysene and triphenylene. Additionally QA/QC (quality assurance and quality control) measures included running a procedural blank, replicate and sediment CRM (SRM 1944). A procedural blank was processed along with each batch of up to 15 samples to demonstrate freedom from cross-contamination. With the exception of naphthalene, levels of other individual PAHs in procedural blanks were less than three times their MDL (method detection limit). The replicate samples were analysed in the laboratory along with regular sample, as another quality control tool to ensure valid results. The values of replicate samples agree within 10% of their average value. In addition, a CRM purchased from NIST was analysed, and the analysis results of PAHs were in the scope of the reference values.

2.4. Homogeneity assessment set-up

For ERS-4, homogeneity was tested on 15 units selected by a stratified random samplings scheme covering the whole batch, and three subsamples were analysed in each unit. For ELS-1, homogeneity was tested on 25 units selected by a stratified random samplings scheme covering the whole batch, and three subsamples were analysed in each unit. Analyses for the 16 PAHs were performed on each subsample according to the above described method. Measurement sequences were randomised to be able to minimise possible trends both in the filling sequence and in the analytical sequence.

The homogeneity was evaluated by one-way analysis of variance (ANOVA) as described by ISO Guide 35. The between-bottle standard deviation ($s_{bb}$) and within-bottle standard deviation ($s_{wb}$) were calculated. A possible inhomogeneity is expressed as the uncertainty due to the between-bottle inhomogeneity of the material ($u_{bb}$) and is quantified as $u_{bb} = s_{bb} = \sqrt{MS_{among} - MS_{within}}$, where $MS_{among}$ mean squares between-bottle from an ANOVA; $MS_{within}$, mean squares within-bottle from an ANOVA. In the case of $MS_{among} < MS_{within}$ (indication that the study set-up and/or the method repeatability was not sufficiently good), the maximum heterogeneity that could be hidden by the method variability. Then, the influence of analytical variation on the standard deviation between units $t_{bb}'$ was calculated and the larger value between $s_{bb}$ and $t_{bb}'$ was used for the estimates of inhomogeneity. The $u_{bb}'$ was calculated as $u_{bb}' = \sqrt{MS_{within} / n} \sqrt{2 / v_{MS_{within}}}$, where $n$ is the number of replicates per bottle and $v_{MS_{within}}$ represents the degrees of freedom of $MS_{within}$. 

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2.5. **Stability assessment set-up**

Judging from similar materials issued from other organisations such as NIST SRM 1941b and SRM 1944, the expiry date of the CRMs was given to be 10 years after the date of certification if they were stored at temperatures less than 30°C and away from direct sunlight [17]. Therefore, ERS-4 and ELS-1 samples were stored at temperature less than 30°C and in shade. The long-term stability test will be monitored at regular intervals and changes in the values will also be provided to users if they are significant.

Samples were analysed duplicate samples from three randomly selected bottles from the whole batch stored for 0, 4, 8, 12 and 16 months. A linear regressions model was performed for processing data, namely assuming component values (Y) of time (X) varying linear equation as

\[
Y = b_0 + b_1X,
\]

where \(b_0\) and \(b_1\) are the regression coefficients, then the estimated standard deviation of \(b_1\) is given by

\[
S(b_1) = \frac{s}{\sqrt{\sum_{i=1}^{n} (X_i - \bar{X})^2}}
\]

where \(s^2 = \frac{\sum_{i=1}^{n} (Y_i - b_0 - b_1X_i)^2}{n-2}\)

\(t_{\text{cal}}\) is given by

\[
t_{\text{cal}} = \frac{|b_1|}{S(b_1)}
\]

The long-term instability is estimated as \(u_{\text{uls}} = S(b_1) \times t\), with \(u_{\text{uls}}\) being the uncertainty of long-term instability and \(t\) denoting the chosen duration.

At a 95% confidence level, in the case of \(t_{\text{cal}} \leq t_{0.95, n-2}\), the components are stable.

3. **Results and discussion**

3.1. **Homogeneity assessment**

The results of the homogeneity evaluations are shown in Table 1. As can be seen in Table 1, between-bottle variation (\(s_{bb}\) or \(u_{bb}'\)) was confirmed to be below 4.5% for each of the PAHs and its average was below 2%, proving the suitability of the materials as CRMs. No statistically significant difference between bottles and within bottles was observed for the PAHs at the 5.0 g sample size. Therefore, the material was assumed to be homogeneous.

3.2. **Stability assessment for PAHs**

The uncertainties of stability during storage are listed in Table 2. As can be seen in Table 2, for ERS-4, values of \(t_{\text{cal}}\) for 15 PAHs were smaller than \(t_{0.95, n-2}\), except value of \(t_{\text{cal}}\) for fluorene was smaller than \(t_{0.99, n-2}\). For ELS-1, values of \(t_{\text{cal}}\) for 16 PAHs were smaller than \(t_{0.95, n-2}\). During the 16-month monitoring period, no significant changes in mass fractions for the 16 PAHs were detected in the two freshwater sediments. The stability will be further monitored at regular intervals.

3.3. **Material characterisation**

3.3.1. **Technical evaluation**

In order to assign PAHs values for sediment CRMs, 11 laboratories were organised to attend twice interlaboratory comparisons for PAHs in sediment organised by IERM. The 11
laboratories with long-standing experience had recently demonstrated their ability to carry out accurate PAHs determinations through participating twice in interlaboratory comparisons. All participation laboratories were accredited to ISO 17025 or China Metrology Accreditation. Fulfilment of quality management requirements ensured that the technical standard had been maintained from the time of demonstration of competence to the actual measurement.

Eleven laboratories including IERM were selected to cover different extraction and quantification methods. A short summary of the methods is given in Table 3. Before the start of the measurements, a workshop was organised in order to discuss the details of the measurement protocols and deal with potential misunderstandings.

As can be seen in Table 3, the general approach for the value assignment of the PAHs in both ERS-4 and ELS-1 consisted of combining results from analyses using a variety of different extraction techniques and solvents, clean-up procedures and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction (SE) and pressurised liquid extraction (PLE) using DCM or n-hexane–DCM mixture or DCM–acetone mixture or n-hexane–acetone mixture, clean-up of the extracts using solid-phase extraction (SPE) or gel permeation chromatography (GPC), followed by: (1) GC/MS analysis of the PAH fraction on three stationary phases of different selectivity, that is, a 5% phenyl-substituted methylpolysiloxane phase, a 50% phenyl-substituted methyl phase, a nonpolar proprietary 100% dimethylpolysiloxane phase; (2) HPLC-UV/FLD or HPLC-DAD/FLD or HPLC-FLD analysis of the PAHs, and (3) UPLC-DAD/FLD analysis of the PAHs.

Each laboratory was requested to perform six independent measurement series. Measurement sequences consisted of a complete calibration line, determination of a method blank, recovery experiments, measurement of a quality control sample and of the candidate CRM samples. All relevant data, such as method description, method-performance characteristics and final measurement results, had to be submitted by the participants using a standardised

### Table 1. Results of the homogeneity study for ERS-4.

| PAHs                  | ERS-4          | ELS-1          |
|-----------------------|----------------|----------------|
|                       | Average mass fractions $W_B$ (μg/kg) | Average mass fractions $W_B$ (μg/kg) |
|                       | $s_{bb}$ (%) | $u_{bb}$ (%) | $s_{bb}$ (%) | $u_{bb}$ (%) |
| Naphthalene           | 72.2          | 2.4           | 87.1          | 4.2           |
| Acenaphthylene        | 10.7          | 1.3           | 74.0          | n.c.          |
| Acenaphthene          | 14.5          | 1.7           | 162.0         | 1.6           |
| Fluorene              | 31.2          | 1.6           | 317.4         | 0.7           |
| Phenanthrene          | 145.7         | 1.1           | 2487          | 2.2           |
| Anthracene            | 22.5          | 1.4           | 330.3         | n.c.          |
| Fluoranthene          | 173.5         | 1.1           | 2843          | n.c.          |
| Pyrene                | 138.9         | 1.3           | 1988          | n.c.          |
| Benzo[a]anthracene    | 62.5          | 2.3           | 872.4         | 0.6           |
| Chrysene              | 88.1          | 0.9           | 774.3         | 0.8           |
| Benzo[b]fluoranthene  | 92.1          | 1.4           | 741.5         | n.c.          |
| Benzo[k]fluoranthene  | 44.9          | 1.7           | 431.6         | 2.1           |
| Benzo[a]pyrene        | 76.4          | 2.4           | 584.6         | 0.6           |
| Indeno[1,2,3-cd]pyrene| 72.7          | 2.1           | 556.5         | n.c.          |
| Dibenzo[a, h]anthracene| 22.2         | 2.5           | 133.8         | 2.1           |
| Benzo(ghi)perylene    | 86.4          | 1.9           | 535.6         | n.c.          |

Note: n.c., cannot be calculated as the mean-squared error between bottles is less than the mean-squared error within bottles.
| PAHs          | Average mass fractions $W_B$ (μg/kg) | RSD (%) | $b_0$ (μg/kg) | $b_1$ (μg·month/kg) | $S_{(b_1)}$ (%) | $u_{rel,lhs}$ (%) | $t_{cal}$ (%) | Average mass fractions $W_B$ (μg/kg) | RSD (%) | $b_0$ (μg/kg) | $b_1$ (μg·month/kg) | $S_{(b_1)}$ (%) | $u_{rel,lhs}$ (%) | $t_{cal}$ (%) |
|--------------|-------------------------------------|---------|--------------|-------------------|----------------|------------------|---------------|-------------------------------------|---------|--------------|-------------------|----------------|------------------|---------------|
| Naphthalene  | 69.7                                | 9.4     | 69.4         | 0.028             | 0.597          | 0.05            | 13.7          | 72.1                                | 20.3    | 67.4         | 0.588             | 1.294          | 0.45            | 28.7          |
| Acenaphthylene| 8.8                                 | 21.0    | 7.2          | 0.203             | 0.121          | 1.68            | 22.0          | 68.2                                | 13.8    | 76.0         | -0.972            | 0.651          | 1.49            | 15.3          |
| Acenaphthene | 13.7                                | 7.2     | 13.1         | 0.075             | 0.078          | 0.96            | 9.1           | 170.3                               | 6.3     | 169.6        | 0.090             | 0.971          | 0.09            | 9.1           |
| Fluorene     | 30.5                                | 3.7     | 29.2         | 0.160             | 0.048          | 3.37            | 2.5           | 308.7                               | 4.5     | 296.1        | 1.575             | 0.880          | 1.79            | 4.6           |
| Phenanthrene | 155.1                               | 3.6     | 155.3        | -0.019            | 0.509          | 0.04            | 5.2           | 2579.2                              | 2.9     | 2550.3       | 3.609             | 6.456          | 0.56            | 4.0           |
| Anthracene   | 20.4                                | 9.7     | 18.6         | 0.220             | 0.129          | 1.70            | 10.2          | 342.8                               | 5.2     | 329.9        | 1.613             | 1.350          | 1.20            | 6.3           |
| Fluoranthene | 171.6                               | 5.7     | 177.8        | -0.785            | 0.770          | 1.02            | 7.2           | 2747.0                              | 6.6     | 2917.1       | -21.26            | 11.15          | 1.91            | 6.5           |
| Pyrene       | 136.2                               | 6.3     | 140.1        | -0.484            | 0.738          | 0.66            | 8.7           | 1965.9                              | 5.6     | 2087.6       | -15.21            | 4.903          | 3.10            | 4.0           |
| Benz[a]anthracene | 71.3  | 12.5    | 63.6         | 0.96              | 0.591          | 1.62            | 13.3          | 829.1                               | 6.0     | 800.0        | 3.642             | 4.045          | 0.90            | 7.8           |
| Chrysene     | 81.7                                | 8.1     | 84.9         | -0.41             | 0.553          | 0.74            | 10.8          | 766.9                               | 5.4     | 742.9        | 3.000             | 3.379          | 0.89            | 7.0           |
| Benzo[b]fluoranthene | 101.7 | 6.4     | 102.0        | -0.034            | 0.591          | 0.06            | 9.3           | 728.7                               | 2.1     | 734.6        | -0.741            | 1.342          | 0.55            | 2.9           |
| Benzo[k]fluoranthene | 41.7  | 11.3    | 42.8         | -0.138            | 0.422          | 0.33            | 16.2          | 423.9                               | 3.6     | 431.2        | -0.920            | 1.274          | 0.72            | 4.8           |
| Benzo[a]pyrene  | 75.0  | 6.8     | 76.4         | -0.17             | 0.454          | 0.37            | 9.7           | 607.1                               | 3.9     | 597.5        | 1.198             | 2.069          | 0.58            | 5.5           |
| Indeno[1,2,3-cd]pyrene | 72.4  | 4.0     | 71.9         | 0.063             | 0.260          | 0.24            | 5.7           | 561.4                               | 4.4     | 567.4        | -0.746            | 2.224          | 0.34            | 6.3           |
| Dibenzo[a, h]anthracene | 20.2  | 11.7    | 19.2         | 0.125             | 0.202          | 0.62            | 16.0          | 131.0                               | 6.4     | 131.0        | -0.002            | 0.769          | 0.00            | 9.4           |
| Benzo[ghi]perylene | 86.0  | 6.1     | 84.0         | 0.242             | 0.455          | 0.53            | 8.5           | 538.5                               | 4.0     | 547.2        | -1.080            | 1.842          | 0.59            | 5.5           |
| Total 16 PAHs | 1155.8                             | 2.9     | 1155.4       | 0.045             | 3.026          | 0.01            | 4.2           | 12840.7                             | 1.9     | 13045.7      | -25.62            | 17.30          | 1.48            | 2.2           |

Note: (1) At the 95% confidence level, 3 degrees of freedom, $t_{0.95,3} = 3.18$; at the 99% confidence level, freedom 3, $t_{0.99,3} = 5.84$; (2) according to the 16-month validity calculation, $u_{rel,lhs} = u_{16}/average mass fraction \times 100$; RSD, relative standard deviation.
Table 3. Overview of analytical approach for certification of PAHs in ERS-4 and ELS-1.

| Lab No. | Extraction | Clean-up | Analysis technique | Chromatographic column |
|---------|------------|----------|--------------------|------------------------|
| LAB01   | Soxhlet extraction with \(n\)-hexane/DCM (volume ratio 1:1) for 24 h | Silica solid-phase extraction (SPE) cartridge | GC-MS | DB-5MS (30 m × 0.25 mm × 0.25 µm) |
|         |            |          |                    | DB-17MS (30 m × 0.25 mm × 0.25 µm) |
| LAB02   | Pressurised liquid extraction with \(n\)-hexane/DCM (volume ratio 1:1) | Florisil SPE cartridge | GC-MS | DB-1MS (30 m × 0.25 mm × 0.25 µm) |
|         |            |          |                    | VF-17MS (30 m × 0.25 mm × 0.25 µm) |
| LAB03   | Soxhlet extraction with DCM/acetone (volume ratio 1:1) for 24 h | Silica SPE cartridge | HPLC-UV/FLD | Waters PAH \(C_{18}\) (250 mm × 4.6 mm, 5 µm), polymeric \(C_{18}\) phase |
| LAB04   | Soxhlet extraction with \(n\)-hexane/DCM (volume ratio 1:1) for 24 h | Silica SPE cartridge | HPLC-DAD/FLD | Waters PAH \(C_{18}\) (250 mm × 4.6 mm, 5 µm), polymeric \(C_{18}\) phase |
| LAB05   | Pressurised liquid extraction with \(n\)-hexane/DCM (volume ratio 1:1) | Silica SPE cartridge | GC-MS | DB-5MS (30 m × 0.25 mm × 0.25 µm) |
|         |            |          |                    | DB-17MS (30 m × 0.25 mm × 0.25 µm) |
| LAB06   | Soxhlet extraction with \(n\)-hexane/DCM (volume ratio 1:1) for 20 h | Silica SPE cartridge | HPLC-UV/FLD | ZORBAX Eclipse PAH (100 mm × 4.6 mm, 1.8 µm) |
| LAB07   | Auto Soxhlet extraction with DCM for 6 h | None | GC-MS | DB-5MS(30 m × 0.25 mm × 0.25 µm) |
|         |            |          |                    | VF-17MS (30 m × 0.25 mm × 0.25 µm) |
| LAB08   | Pressurised liquid extraction with DCM/acetone (volume ratio 1:1) | Silica SPE cartridge | HPLC-DAD/FLD | Waters PAH \(C_{18}\) (250 mm × 4.6 mm, 5 µm), polymeric \(C_{18}\) phase |
| LAB09   | Pressurised liquid extraction with DCM/acetone (volume ratio 4:1) | Gel permeation chromatography (GPC) | HPLC-FLD | Waters PAH \(C_{18}\) (250 mm × 4.6 mm, 5 µm), polymeric \(C_{18}\) phase |
| LAB10   | Pressurised liquid extraction with DCM/acetone (volume ratio 1:1) | Silica SPE cartridge | GC-MS | DB-5MS (30 m × 0.25 mm × 0.25 µm) |
|         |            |          |                    | DB-17MS (30 m × 0.25 mm × 0.25 µm) |
| LAB11   | Pressurised liquid extraction with hexane/acetone (volume ratio 1:1) | GPC | UPLC-DAD/FLD | Waters acquity UPLC BEH RP18 (150 mm × 2.1 mm, 1.7 µm) |

Note: DCM, dichloromethane; GC-MS, gas chromatography-mass spectrometry; HPLC, high performance liquid chromatography; UPLC, ultrahigh performance liquid chromatography; UV, ultraviolet; FLD, fluorescence detector; DAD, diode array detector.
report. The mean results and RSDs (in parenthesis) from each of the 11 participating labs are shown in Tables S1 and S2.

There was no obvious difference between Soxhlet extraction and PLE. PLE has been widely used in analysis organic contaminants in environmental-matrix samples. Analytical results of acenaphthylene were different because of interferences and lower sensitivity of HPLC-FLD. The analytical results and the standard deviations of the GC/MS analyses (five sets of results) and HPLC/UPLC analyses (six sets of results) for two sediment CRMs are summarised in Tables S1 and S2. The mean of accepted means and between-laboratory standard deviations obtained by GC-MS and LC methods are shown in Figure 1. Most of the results from GC-MS agreed with the LC results, exhibiting the good comparability. In addition to the good agreement among each other, evidence was obtained that the results obtained by GC-MS were confirmed by results from non-GC-based methods, such as HPLC or UPLC.

3.3.2. Statistical evaluation

Results accepted on technical grounds were subjected to a further statistical evaluation (Table 4).

It was checked whether the data sets followed approximately normal distributions and whether variances for each compound were homogeneous. Grubbs test was applied to evaluate within-laboratory parallel data. Outliers of variance in between-laboratory were detected using the Cochran test. Outliers of average in between-laboratory were detected using the Dixon test. Generally, the outliers detected from Grubbs test were retained. In case of RSD of within-laboratory parallel data was smaller than 15%, the stragglers and outliers from Cochran test were retained. The outliers (the 95% confidence interval) detected from Dixon test were removed.

The regression analysis (Figure 2) showed a significant increase of absolute within-laboratory standard deviation with increasing compound mass fraction, while the relative within-laboratory

| PAHs                | Average mass fractions (µg/kg) | RSD (%) | \( \mu_{\text{rel,char}} \) (%) | ERS-4 |          | Average mass fractions (µg/kg) | RSD (%) | \( \mu_{\text{rel,char}} \) (%) | ELS-1 |
|---------------------|--------------------------------|---------|---------------------------------|-------|---------|--------------------------------|---------|---------------------------------|-------|
| Naphthalene         | 11 51.1                         | 28.7    | 8.7                             | 11    | 59.9    | 19.6                           | 5.9     |
| Acenaphthylene      | 8 8.5                           | 28.3    | 10.0                            | 8     | 36.4    | 78.1                           | 27.6    |
| Acenaphthene        | 11 11.5                         | 19.7    | 5.9                             | 11    | 147     | 19.6                           | 5.9     |
| Fluorene            | 11 24.5                         | 15.3    | 4.6                             | 11    | 272     | 11.6                           | 3.5     |
| Phenanthrene        | 11 150                          | 6.7     | 2.0                             | 11    | 2542    | 12.3                           | 3.7     |
| Anthracene          | 11 18.6                         | 19.0    | 5.7                             | 11    | 313     | 13.2                           | 4.0     |
| Fluoranthene        | 11 167                          | 6.0     | 1.8                             | 11    | 2805    | 6.9                            | 2.1     |
| Pyrene              | 11 136                          | 13.9    | 4.2                             | 11    | 1940    | 8.2                            | 2.5     |
| Benz[a]anthracene   | 10 77.5                         | 15.5    | 4.9                             | 10    | 788     | 8.1                            | 2.6     |
| Chrysene            | 11 87.4                         | 14.9    | 4.5                             | 11    | 795     | 8.3                            | 2.5     |
| Benzo[b]fluoranthene| 10 110                          | 11.2    | 3.5                             | 10    | 718     | 9.6                            | 3.0     |
| Benzo[k]fluoranthene| 11 41.8                         | 12.7    | 3.8                             | 11    | 389     | 9.9                            | 3.0     |
| Benzo[a]pyrene      | 11 76.4                         | 8.6     | 2.6                             | 11    | 621     | 9.1                            | 2.8     |
| Indeno[1,2,3-cd]pyrene| 11 74.6                        | 9.2     | 2.8                             | 11    | 583     | 11.6                           | 3.5     |
| Dibenzo[p,h]anthracene| 11 19.1                        | 21.4    | 6.5                             | 10    | 120     | 16.9                           | 5.3     |
| Benzo[ghi]perylen| e 9 82.4                         | 4.3     | 1.4                             | 9     | 550     | 4.4                            | 1.5     |

Note: \( p \), number of accepted sets of results.
Figure 1. Comparison of mean results from GC-MS, HPLC and UPLC methods for ERS-4 (a) and ELS-1 (b) from the 11 laboratories. Error bars are the standard deviations among laboratories.

(Naph, Naphthalene; Acnpl, Acenaphthylene; Acnpn, Acenaphthene; Flre, Fluorene; Phen, Phenanthrene; Anth, Anthracene; Flth, Fluoranthene; Pyre, Pyrene; BaA, Benz[a]anthracene; Chry, Chrysene; BbF, Benzo [b]fluoranthene; BkF, Benzo[k]fluoranthene; BaP, Benzo[a]pyrene; IcdP, Indeno[1,2,3-cd]pyrene; DahA, Diben[a,h]anthracene; BghiP, Benzo[ghi]perylene.)

Figure 2. Regression analysis of within-laboratory standard deviation.
standard deviation decreased slightly but not significantly with increasing compound mass fraction. The various RSDs therefore can be combined into a single data set [18].

Finally, the number of effective data set was not less than eight groups. The certified values of 16 PAHs were calculated as the average of the laboratory results after removing outliers. The uncertainty of characterisation was calculated as \( u_{\text{char}} = \frac{s}{\sqrt{p}} \), with \( s \) being the standard deviation of data set means and \( p \) denoting the number of laboratories.

3.3.3. **Uncertainty assessment**

The standard uncertainty of the two CRMs included collaborating characterisation uncertainty (\( u_{\text{char}} \)), between-bottle inhomogeneity uncertainty (\( u_{\text{bb}} \)) and long-term instability uncertainty (\( u_{\text{lts}} \)). Because no systematic change in mass fractions was detected during the 16-month monitoring period, short-term instability uncertainty (\( u_{\text{lts}} \)) had not been tested. Therefore, the expanded uncertainty (\( U \)) of the certified property value was calculated as

\[
U = k \times \sqrt{u_{\text{bb}}^2 + u_{\text{lts}}^2 + u_{\text{char}}^2}
\]

where \( U \) is the expanded uncertainty, \( k \) is the coverage factor (usually set to \( k = 2 \), which approximates a 95% confidence level), \( u_{\text{bb}} \) is the uncertainty due to the inhomogeneity of the material, \( u_{\text{lts}} \) is the uncertainty due to the instability of the material and \( u_{\text{char}} \) is the uncertainty in the characterisation of the property value. The relative uncertainty components for 16 PAHs in ERS-4 and ELS-1 are listed in Table 5. The largest uncertainty (the controlling factor) for each PAH was \( u_{\text{lts}} \) for ERS-4 and ELS-1, and \( u_{\text{char}} \) of each PAH for ERS-4 was similar compared to ELS-1.

| PAHs                  | Relative \( u_{\text{char}} \) (%) | Relative \( u_{\text{bb}} \) (%) | Relative \( u_{\text{lts}} \) (%) | Relative \( u_{\text{CRM}} \) (%) | Relative \( u_{\text{char}} \) (%) | Relative \( u_{\text{bb}} \) (%) | Relative \( u_{\text{lts}} \) (%) | Relative \( u_{\text{CRM}} \) (%) |
|-----------------------|------------------------------------|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|----------------------------------|----------------------------------|-----------------------------------|
| Naphthalene           | 8.7                                | 2.4                              | 13.7                             | 16.4                             | 5.9                               | 4.2                              | 28.7                             | 29.6                              |
| Acenaphthylene        | 10.0                               | 2.5                              | 22.0                             | 24.3                             | 27.6                              | 2.0                              | 15.3                             | 31.6                              |
| Acenaphthene          | 5.9                                | 1.7                              | 9.1                              | 11.0                             | 5.9                               | 1.6                              | 9.1                              | 11.0                              |
| Fluorene              | 4.6                                | 1.6                              | 2.5                              | 5.5                              | 3.5                               | 1.5                              | 4.6                              | 6.0                                |
| Phenanthrene          | 2.0                                | 1.8                              | 5.2                              | 5.9                              | 3.7                               | 2.2                              | 4.0                              | 5.9                                |
| Anthracene            | 5.7                                | 1.6                              | 10.2                             | 11.8                             | 4.0                               | 1.1                              | 6.3                              | 7.5                                |
| Fluoranthene          | 1.8                                | 1.6                              | 7.2                              | 7.6                              | 2.1                               | 1.4                              | 6.5                              | 7.0                                |
| Pyrene                | 4.2                                | 1.3                              | 8.7                              | 9.7                              | 2.5                               | 1.1                              | 4.0                              | 4.8                                |
| Benz[a]anthracene     | 4.9                                | 2.3                              | 13.3                             | 14.4                             | 2.6                               | 0.9                              | 7.8                              | 8.3                                |
| Chrysene              | 4.5                                | 0.9                              | 10.8                             | 11.7                             | 2.5                               | 1.0                              | 7.0                              | 7.5                                |
| Benzo[b]fluoranthene  | 3.5                                 | 1.4                              | 9.3                              | 10.0                             | 3.0                               | 1.2                              | 2.9                              | 4.3                                |
| Benzo[k]fluoranthene  | 3.8                                 | 1.7                              | 16.2                             | 16.7                             | 3.0                               | 2.1                              | 4.8                              | 6.0                                |
| Benzo[a]pyrene        | 2.6                                 | 2.4                              | 9.7                              | 10.3                             | 2.8                               | 1.4                              | 5.5                              | 6.3                                |
| Indeno[1,2,3-cd]pyrene| 2.8                                 | 2.1                              | 5.7                              | 6.7                              | 3.5                               | 2.0                              | 6.3                              | 7.5                                |
| Diben[a,h]anthracene  | 6.5                                 | 2.5                              | 16.0                             | 17.4                             | 5.3                               | 2.1                              | 9.4                              | 11.0                               |
| Benzo[ghi]perylenel   | 1.4                                 | 1.9                              | 8.5                              | 8.8                              | 1.5                               | 1.9                              | 5.5                              | 6.0                                |

\( u_{\text{CRM}} \) is the standard uncertainty of the content of the 16 PAHs in the CRM.
### 3.3.4. Value assignment and comparison with other sediment CRMs

The unweighted mean of laboratory means were assigned as certified values for 16 PAHs for both ERS-4 and ELS-1. It was worth noting that the certified values were based on 8 or more than 8 valid data sets received from the participants. In addition, the relative uncertainty components received by each participant should be less than 30%. If not, the indicative values for PAHs would be assigned. Finally, the certified values and their uncertainties for 16 PAHs were obtained, which are shown in Table 6, and the certified or reference values of other available sediment CRMs are summarised in Table 7.

From Table 7, the levels and uncertainties of PAHs in ERS-4 are lower than two samples of NIST, and the levels in ELS-1 are similar with SRM 1941b, lower than SRM 1944 of NIST, while uncertainties are a little bit higher than SRM 1941b, similar with SRM 1944 of NIST. The values of PAHs in ERS-4 and ELS-1 were at the microgram per kilogram level. Their levels are much lower than those in other CRMs except NMIJ CRM 7307-a (Figure 3). These PAH values are comparable to those found in environmental samples. Therefore, the two CRMs can meet the demands for environmental monitoring and interlaboratory comparison.

### 4. Conclusions

The two freshwater sediments CRMs for PAHs were the first developed in China, which represents the more highly characterised natural-matrix CRM with respect to PAHs in China. The certified concentrations, which reflect today’s environmental concentrations, were established by interlaboratory comparison and through technical and statistical evaluation of the results. The two reference materials have been approved by General Administration of Quality Supervision, Quarantine of the People’s Republic of China in November 2011 as Certified Reference Material and the appropriate serial numbers are GSB 07-2787-2011 and GSB 07-2788-2011. The two freshwater sediments CRMs for PAHs successfully developed will play an increasing important role for soil, sediment and sludge environmental monitoring in China.

#### Table 6. Certified values for 16 PAHs in IERM CRM ERS-4 and ELS-1 (μg/kg).

| PAHs                        | Certified value | U_{CRM} (k = 2) | Certified value | U_{CRM} (k = 2) |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|
| Naphthalene                 | 51              | 17              | 60              | 36              |
| Acenaphthylene              | 8.5             | 4.1             | 36              | 23              |
| Acenaphthene                | 11.5            | 2.5             | 147             | 33              |
| Fluorene                    | 24.5            | 2.7             | 272             | 33              |
| Phenanthrene                | 150             | 18              | 2540            | 300             |
| Anthracene                  | 18.6            | 4.4             | 313             | 48              |
| Fluoranthene                | 167             | 26              | 2800            | 390             |
| Pyrene                      | 136             | 27              | 1940            | 189             |
| Benz[a]anthracene           | 78              | 23              | 788             | 130             |
| Chrysene                    | 87              | 21              | 795             | 120             |
| Benzo[b]fluoranthene        | 110             | 23              | 718             | 63              |
| Benzo[k]fluoranthene        | 42              | 15              | 389             | 48              |
| Benzo[a]pyrene              | 76              | 16              | 621             | 79              |
| Indeno[1,2,3-cd]pyrene      | 75              | 11              | 583             | 88              |
| Dibenz[a,h]anthracene       | 19.1            | 6.7             | 120             | 27              |
| Benzo[ghi]perylene          | 82              | 15              | 550             | 66              |

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Table 7. Comparison of ERS-4 and ELS-1 with other sediment CRMs (µg/kg).

| PAHs               | NIST SRM 1941b 2002 | NIST SRM 1944 1999 | IRMM BCR CRM 535 1997 | LGC LGC6188 2000 | NMIJ CRM 7307-a 2009 | IERM ERS-4 2011 | IERM ELS-1 2011 |
|--------------------|---------------------|--------------------|-----------------------|-------------------|----------------------|------------------|------------------|
| Naphthalene        | 848 ± 95            | 1650 ± 310         | –                     | 220 ± 110          | –                    | 51 ± 17          | 60 ± 36          |
| Acenaphthylene     | (53.3 ± 6.4)        | –                  | –                     | –                 | (1)                  | –                | –                |
| Acenaphthene       | (38.4 ± 5.2)        | (570 ± 30)         | –                     | 70 ± 20            | –                    | 11.5 ± 2.5       | 147 ± 33         |
| Fluorene           | 85 ± 15             | (850 ± 30)         | –                     | 120 ± 40           | 5.98 ± 1.08          | 24.5 ± 2.7       | 272 ± 33         |
| Phenanthrene       | 406 ± 44            | 5270 ± 330         | –                     | 1040 ± 300         | 24.46 ± 3.96         | 150 ± 18         | 2540 ± 300       |
| Anthracene         | 184 ± 18            | 1770 ± 330         | –                     | 360 ± 110          | 3.59 ± 1.14          | 18.6 ± 4.4       | 313 ± 48         |
| Fluoranthene       | 651 ± 50            | 8920 ± 320         | –                     | 1790 ± 350         | 25.11 ± 2.52         | 167 ± 26         | 2800 ± 390       |
| Pyrene             | 581 ± 39            | 9700 ± 420         | 2520 ± 180            | 1480 ± 500         | 22.24 ± 3.54         | 136 ± 27         | 1940 ± 189       |
| Benz[a]anthracene  | 335 ± 25            | 4720 ± 110         | 1540 ± 100            | 830 ± 180          | 7.15 ± 0.92          | 78 ± 23          | 788 ± 130        |
| Chrysene           | 291 ± 31            | 4860 ± 100         | –                     | 830 ± 160          | 8.39 ± 0.74          | 87 ± 21          | 795 ± 120        |
| Benzo[b]fluoranthene | 453 ± 21           | 3870 ± 420         | 2290 ± 150            | 820 ± 190          | 24.87 ± 7.72         | 110 ± 23         | 718 ± 63         |
| Benzo[k]fluoranthene | 225 ± 18          | 2300 ± 200         | 1090 ± 150            | 500 ± 80           | 5.28 ± 1.46          | 42 ± 15          | 389 ± 48         |
| Benzo[a]pyrene     | 358 ± 17            | 4300 ± 130         | 1160 ± 100            | 650 ± 140          | 4.57 ± 0.53          | 76 ± 16          | 621 ± 79         |
| Indeno[1,2,3-cd]pyrene | 341 ± 57           | 2780 ± 100         | 1560 ± 140            | 370 ± 140          | 5.61 ± 2.13          | 75 ± 11          | 583 ± 88         |
| Dibenzo[a,h]anthracene | 53 ± 10           | 424 ± 69           | –                     | 130 ± 50           | 0.92 ± 0.44          | 19.1 ± 6.7       | 120 ± 27         |
| Benzo[ghi]perylene | 307 ± 45            | 2840 ± 100         | –                     | 360 ± 130          | 6.76 ± 1.89          | 82 ± 15          | 550 ± 66         |

Note: The results are expressed as the certified or reference concentration ± the expanded uncertainty. Values in parentheses are the reference values.
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