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Article

Interlaboratory Comparison of Quantifying Hydrocarbons and Trace Elements in Sediment Samples from a Tropical Estuary

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The Marine and Environmental Studies Laboratory at PUC-Rio, in partnership with the PETROBRAS R&D Center (Brazil), conducted an interlaboratory comparison of aliphatic and aromatic hydrocarbons and trace element determinations. The goal of this study was to produce a homogeneous and stable material and obtain consensus concentration values for its use as a reference material (RM) for sediments from tropical regions. The prepared material is adequate for use as a reference material because it has remained stable (Test F, ANOVA, $p < 0.05$) since its preparation in 2007. In this study, several alkylated polycyclic aromatic hydrocarbon (PAH) compounds were included, and the resulting dispersion was the same order of magnitude as the parental PAH (16 PAH USEPA).

Keywords: reference material, interlaboratory study, petroleum hydrocarbon, trace elements

Introduction

Polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, and other aliphatic hydrocarbons, have been used as indicators of oil and incomplete combustion residues in the marine environment. In addition, PAHs are considered as contaminants of special concern due to the carcinogenic and mutagenic properties of some of its components.[1,2] Metals and metalloids are components that occur naturally in the environment. In addition, metals and metalloids have historically been released in the environment due to human activities. Unlike organic pollutants, which can be degraded into less harmful components through biological or chemical processes, trace elements are non-degradable. Thus, trace elements can accumulate in sediments and act as sources of natural or anthropogenic disturbances. The effects of metal pollution in the environment can be substantial and long lasting. More importantly, toxic metals can enter the food chain and adversely affect humans when contaminated seafood is consumed.[3]

The process of quantifying organic and inorganic trace substances is complex because they are present in environmental matrices at low concentrations and include a broad spectrum of components or species that must be identified and quantified individually. In addition, environmental matrices are complex and require the use of careful procedures and methods with very low detection limits. Thus, laboratory intercomparisons represent an essential method for validating methods and verifying the accuracy of results. Accuracy and precision are critical when analyzing hydrocarbons and trace-metals in environmental samples when assessing and monitoring coastal and/or ocean environments.

As in many other countries, laboratories in Brazil depend on reference materials (RMs) prepared in North America, Europe or Japan to apply such quality control. In addition to the inherent barriers for importing them, these RMs are based on the matrices of temperate climates and often have geochemical characteristics that differ from those of tropical regions.

The goal of this study was to establish the capacity of Brazil for producing reference materials for petroleum hydrocarbons and trace elements in an environmental matrix, specifically from a tropical region. In addition, this study describes and evaluates the steps that were taken to obtain the reference material SED001. Once prepared and established,

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the consensus values of these materials can be made available to universities, research centers and commercial laboratories. The prepared sediment sample (SED 001) was distributed to several regional and international laboratories in February 2008. The procedures used for preparing this material were based on ISO Guide 35[4] and Villeneuve *et al*.[5] The preparation steps for the reference material included the selection of a sampling site containing sediments with the characteristics of interest (presence of hydrocarbons and trace-elements at detectable quantities), particulate size reduction, homogenization and distribution in glass bottles (the three last steps were performed by CETEM Mineral Technology Center, RJ, Brazil).

The aim of this study was to produce a reference material that could be used for calibrating analytical procedures for quantifying petroleum hydrocarbons and trace elements. To accomplish this task, the participants were requested to report the individual *n*-alkane contents, the isoprenoids pristane and phytane contents, the total resolved and unresolved aliphatic contents, and the individual polycyclic aromatic hydrocarbon contents (16 Environmental Protection Agency (EPA)-priority PAHs: naphthalene (N), acenaphthylene (Acen), acenaphthene (Ace), fluorene (F), phenanthrene (Ph), anthracene (Ant), fluoranthene (Fl), chrysene (Ch), pyrene (P), benzo(*a*)pyrene (BaP), benz(*a*)anthracene, (BaAnt), benzo(*b*)fluoranthene (BbFl), benzo(*k*)fluoranthene (BkFl), indeno(1,2,3-*c*,*d*)pyrene (IP), dibenz(*a*,*h*)anthracene (DBAnt), benzo(*ghi*)perylene (BghiPe); and also, perylene (Pe), dibenzothiophene (DBT), benzo(*e*)pyrene (BeP); the five series of alkylated homologues: naphthalenes (C1N, C2N, C3N and C4N), fluorenes (C1F, C2F and C3F), phenanthrenes (C1Ph, C2Ph, C3Ph and C4Ph), dibenzothiophenes (C1DBT, C2 DBT and C3DBT), chrysenes (C1Ch and C2Ch) and pyrenes (C1P and C2P)).

For trace elements, the participant laboratories were requested to report the individual metal concentrations using three different digestion methods: (*i*) 1.0 mol L^{-1} HCl – a milder extraction that provides almost all bioavailable elements;[6] (*ii*) EPA 3050b[7] (concentrated HNO_3 treatment) – which does not allow total digestion but also releases bioavailable elements; and (*iii*) EPA 3052[8] (HNO_3 + HF) – which performs total digestion. The targeted elements included Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Sb, Ba, Hg and Pb. The trace elements were chosen based on their environmental importance and the interests of the petroleum industry. Three different methods were provided so that each laboratory could perform the trace element determination using at least one method.

The requested methodology for determining hydrocarbons and trace elements would be established based on the routines of the respective participating laboratories.

Experimental

Sample preparation

A sufficiently large amount of sediment (130 kg wet weight) was collected from Guanabara Bay, Rio de Janeiro, after screening the initial sampling site (coordinates: –43.087910 and –22.765130). The material was collected using a Van Veen sampler in containers that were previously decontaminated using acetone and dichloromethane. The collected material was stored in a refrigeration unit until the beginning of the process steps. To this batch, the following preparation procedures were applied: freeze-drying, grinding, and sieving through a 75 µm stainless steel sieve. The fraction smaller than 75 µm was homogenized in a stainless steel rotating drum (200 L), followed by stepwise separation and packing using a stainless steel rotating separator with 12 collectors. The obtained aliquots contained approximately 40 g of sediments. These aliquots were stored in glass bottles with aluminum screw caps and sealed with Teflon tape.

Homogeneity test

The homogeneity of the material was initially assessed by determining the concentrations of the hydrocarbons (n = 10) and trace elements (n = 13) in the sediment samples from different glass bottles. The F test was used to evaluate the homogeneity between the different bottles and within each bottle (analysis of variance (ANOVA); software SPSS 8.0).[4] A preliminary PAH analysis was conducted at the Laboratory of Marine and Environmental Studies (LABMAM) using EPA method 8270D (gas chromatography-mass spectrometry (GC-MS)). In contrast, the trace element determinations were performed at the Laboratory of Atomic Spectrometry (LABSPECTRO) using EPA method 3050 (inductively coupled plasma-optical emission spectrometry (ICP-OES)). All samples were analyzed in triplicate. Both laboratories are part of the Department of Chemistry at PUC-Rio.

Stability study

Several determinations were performed following the production of the sediment samples (n = 6) to assess the stability of the sediment material (SED 001). The results showed that the material is stable under actual conditions regarding the tested compounds (F test, ANOVA, $p < 0.05$).

Moisture content

The initial moisture content established for the material was 3.95 ± 0.05% (n = 10). With time, the moisture contents were determined from aliquots of the lyophilized material by drying in an oven at 105 ºC to a constant weight. Currently, the moisture content is 4.00 ± 0.05%.

Information regarding the shipping and data return

In February 2008, 42 bottles of sediment sample (SED 001) were distributed to laboratories that responded positively to the invitation letters, which were forwarded to 100 labs. In addition, a sample description and general instructions for analysis were included.

This study followed the structure suggested by Carvalho *et al*.[9] Participants were requested to analyze hydrocarbons and trace metals by using the current techniques and methods that were applied in their laboratories. In addition, participants were also requested to perform three separate determinations for each analyte and to include a short description of their methods with the results (extraction, clean up, gas chromatographic conditions, etc.). For this purpose, a reporting form was attached to the information sheet. The concentrations were reported as net values (i.e., after correcting based on a blank, moisture content, etc.), with as many significant figures as justified by the precision of the method. For each group of targeted substances, the participants were requested to report the average weights of the samples that were taken for analysis, the moisture content, the methods used to confirm the identities of the compounds, the calculations used for the results, a summary of the quality control procedures that were routinely employed in the laboratory, the arithmetic mean value and the relative standard deviations (in percentage) of their determinations.

Results and Discussion

Homogeneity test

The results and the statistical analyses (F test (ANOVA); SPSS 8.0 applied for evaluating the homogeneity) indicated that the SED 001 could be considered as homogeneous between the bottles and within each bottle. The material did not show any significant inhomogeneity ($F = MSB / MSW < F_{crit}$ for $\alpha = 5\%$, where MSB and MSW are the mean squares between and within-bottles, respectively).[4] Tables 1 and 2 show the preliminary results for the trace elements and hydrocarbons (mean and standard deviation (SD)), respectively.

Stability study

Several determinations were performed following the production of the sediment samples (n = 10) to assess the stability of the material (SED 001). Table 3 shows the results produced by LABMAM between 2007 and 2014 for some analytes. The results showed that the material is stable under actual conditions (F test, ANOVA, $p < 0.05$). The bottles were stored in the laboratory at a temperature of 21.0 ± 1.0 °C.

Table 1. Trace element results of the homogeneity test. Mean values (triplicate) from each vial are expressed in mg kg^{-1}, dry weight

Bottle × analyte	Mg	Al	Mn	Fe	Cu	Ba	Ti	Pb
SED 012	12379	26283	644	32143	50	141	45	4332
SED 014	11857	25237	617	30961	51	140	46	4334
SED 091	11746	25012	614	30647	51	141	45	4311
SED 115	11912	25389	620	31027	52	141	45	4333
SED 134	11996	25422	627	31250	49	141	45	4390
SED 204	11913	25727	618	30924	49	142	46	4522
SED 212	11746	25392	612	30665	49	145	45	4340
SED 259	11700	25040	608	30392	50	145	46	4240
SED 343	11591	25008	604	30263	49	144	45	4300
SED 344	11863	25392	615	30750	51	141	45	4540
SED 347	11832	25172	617	30795	52	143	46	4371
SED 453	11601	24551	604	30068	50	142	45	4361
SED 493	11767	24920	614	30537	51	140	45	4368
Mean	11839	25273	616	30802	50	142	45	4365
SD	201.6	422.3	10.3	516.6	1.1	1.7	0.5	82.9

Table 2. Results of the homogeneity test for PAH. Mean values (triplicate) from each vial are expressed in μg kg^{-1}, dry weight

Bottle × analyte	SED 30	SED 91	SED 139	SED 204	SED 259	SED 343	SED 374	SED 453	SED 508	SED 551	Mean	SD
N	3.5	2.3	3.5	4.5	2.9	6.9	4.7	4.9	3.4	3.3	4.0	1.3
Acen	20.9	17.7	24.3	21.3	22.2	23.5	25.2	19.8	16.1	17.1	20.8	3.1
Ace	2.8	1.7	3.0	4.4	2.6	3.0	3.5	2.8	2.1	2.6	2.8	0.7
F	11.4	9.6	12.6	14.6	14.9	17.0	15.6	14.2	11.5	11.0	13.2	2.4
Ph	26.0	24.8	27.9	28.0	28.5	31.2	39.0	30.5	28.0	21.6	28.5	4.6
Ant	17.7	17.3	19.4	20.1	21.0	22.8	22.3	21.2	18.8	14.7	19.5	2.5
Fl	52.0	46.5	59.8	47.6	49.3	49.5	62.0	46.0	38.3	40.3	49.1	7.5
Ch	143.3	142.6	165.2	164.6	168.6	173.0	173.6	142.4	124.0	113.8	151.1	21.1
P	122.6	129.8	140.4	144.5	147.5	152.2	149.1	132.7	128.6	85.1	133.2	19.6
BaP	183.3	163.2	221.4	158.1	190.8	193.7	222.0	148.8	131.3	141.4	175.4	31.9
BaAnt	105.0	98.1	121.0	129.9	131.3	138.7	130.1	114.5	97.4	76.9	114.3	19.6
BbFl	213.5	207.2	261.5	211.4	210.8	251.8	264.0	187.7	163.2	148.3	211.9	39.2
BkFl	65.1	57.8	78.1	71.5	71.3	82.9	82.3	59.7	52.2	48.1	66.9	12.3
IP	89.7	77.5	106.6	85.3	91.0	92.2	108.6	70.1	71.0	62.0	85.4	15.4
DBAnt	41.8	35.9	50.1	39.7	45.7	41.4	50.3	31.6	33.5	29.3	39.9	7.4
BghiPe	102.3	87.1	121.4	98.5	104.7	106.3	124.0	80.4	81.6	64.0	97.0	18.8
Pe	70.0	57.5	84.4	74.2	77.2	86.1	90.6	61.0	54.3	59.4	71.5	13.1

Table 3. Results of the stability study for PAH, data analyses and sample size. Values are expressed in μg kg^{-1}, dry weight

Data analyses	Apr 07 (n = 10)	May 07 (n = 5)	Aug 07 (n = 10)	Sep 07 (n = 5)	Aug 08 (n = 5)	Feb 11 (n = 3)	Sep 12 (n = 3)	Oct 12 (n = 3)	Jan 13 (n = 10)	Jan 14 (n = 3)	Mean	SD
Acen	23.2	31.5	22.9	22.5	24.5	18.0	19.9	18.3	27.7	19.2	22.8	4.3
DBT	9.3	11.3	9.2	9.0	9.7	6.1	8.0	8.6	8.2	6.4	8.6	1.5
Ph	31.3	38.3	31.2	35.4	29.7	27.9	26.8	35.4	33.8	29.0	31.9	3.7
Ant	21.4	27.0	21.4	20.0	18.6	12.8	13.5	12.2	16.9	16.0	18.0	4.6
Fl	54.9	69.1	54.2	69.6	51.9	74.3	64.1	72.1	82.7	69.3	66.2	9.9
P	145.9	164.0	145.9	144.6	160.9	122.1	139.5	169.6	106.8	153.0	145.2	19.1
BaAnt	125.7	144.2	124.7	123.7	119.9	82.7	81.8	66.1	91.3	76.0	103.6	26.8
Ch	167.0	215.3	166.4	189.1	175.8	114.3	44.5	49.9	59.0	109.0	129.0	62.4
BbFl	236.1	276.2	231.0	297.8	195.1	129.6	117.1	161.8	153.2	93.1	189.1	69.4
BkFl	74.3	92.5	73.1	74.8	54.5	62.2	37.9	48.8	78.0	38.4	63.5	18.2
BeP	149.8	198.0	146.5	187.9	206.7	131.4	119.7	185.6	136.5	138.1	160.0	31.3
BaP	196.0	259.7	192.5	276.0	178.7	108.2	82.3	98.0	107.1	146.2	164.5	67.9
Pe	79.7	108.6	78.6	98.0	57.9	62.0	38.0	35.6	59.0	18.7	63.6	28.3
IP	95.1	117.9	93.9	134.0	115.3	117.2	76.0	89.1	75.1	94.6	100.8	19.4
DBAnt	44.3	56.6	44.0	52.7	56.2	59.2	37.3	53.7	38.6	47.8	49.0	7.8
BghiPe	107.7	128.4	106.7	126.7	128.4	112.7	75.7	105.6	71.9	100.1	106.4	20.0

Data summary

Forty two laboratories agreed to participate, and only 27 laboratories returned their results. Of these laboratories, 8 provided data for both hydrocarbons and trace elements, 11 only provided results for hydrocarbons, and 8 only provided results for trace elements. Each laboratory was identified by a code number to preserve anonymity. The analytical methods that were used by the participants for petroleum hydrocarbon analysis, including the pre-treatment of the sample and the GC conditions, are given in Table 4. For trace elements (Table 5), the methods of quantification used by the laboratories ICP-OES, atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and neutron activation analysis (INAA).

Statistical evaluation

Results were considered acceptable when they were obtained from laboratories that reported a minimum of three replicates. The laboratories that only reported one or two replicates were disregarded. The range, mean, and standard deviation values for each analyte were based on the reported laboratory means. Next, the outliers were removed using Grubbs test, and the range, mean and standard deviation were recalculated.

To determine the laboratory performances, z-scores[10,11] were calculated according to the following equation:

$$z = (x_i - x_a) / s_b \quad (1)$$

where x_i is the mean of the reported analyte concentrations in the samples from each laboratory; x_a is the assigned value (a mean value of the acceptable results in the intercomparison run); and s_b is the target standard deviation.[10] The z-score is based on the properties of a normal distribution. These values express the performance of each laboratory and its deviation relative to the average results. The performance is considered acceptable if $/z/ < 2$. The measurement is regarded as out of control when $/z/ > 3$. This score represents a simple method for providing each participant with a normalized performance score for bias. This procedure has been accepted as a standard procedure by ISO/IUPAC.[12-14] In addition, this calculation accounted for the variations of repeatability (which estimate the variation in a single laboratory over a short period of time) and reproducibility (which estimate the variations of the measurements between the laboratories).[10]

Criteria for assigning a reference material

Data for many of the analytes were sufficiently grouped to characterize the sediment samples as a reference material. The criteria used in the certification of petroleum hydrocarbon are presented by Villeneuve *et al.*[5] and Carvalho *et al.*,[9] i.e., (*i*) for a range of PAH concentrations. In this case, the relative uncertainty of the overall median does not exceed the following limits: > 10,000 µg kg^{-1} (30%), 1,000-10,000 µg kg^{-1} (50%), 100-1,000 µg kg^{-1} (60%), 10-100 µg kg^{-1} (80%) and < 10 µg kg^{-1} (100%). Furthermore, (*ii*) the overall mean is based on the data obtained by at least two different methods. (*iii*) The relative number of

Table 4. Summary of methods used for quantifying the petroleum hydrocarbons (aromatic and aliphatic compounds) in sediment sample SED 001

Methods	Laboratory code numbers
Extraction method	
Soxhlet	2[a]; 11; 13; 14; 15; 16; 17; 19
Microwave	3
Ultrasound	4; 5; 6; 7; 8; 9; 10
ASE	1; 2
Not indicated	12; 18
Solvents used	
Methanol/dichloromethane	5; 6
Dichloromethane	1; 2; 2[a]; 9; 10; 12; 14; 16; 19
Hexane/acetone	8; 13; 17
Hexane/toluene	4
Hexane/dichloromethane	3; 7; 11; 15
Cyclohexane/dichloromethane	18
Duration of extraction	
10 to 30 min	2; 6
4 to 8 h	2[a]; 11; 16; 17
24 h	14; 19
Not indicated	1; 3; 4; 5; 7; 8; 9; 10; 12; 13; 15; 18
Internal standards	
Mixture of deuterated PAH	All participants
Clean-up and/or fractionation of extracts	
Saponification/Si-Al	6; 19
Silica/alumina	1; 2; 2[a]; 8; 11; 12; 13; 17
Treatment with copper/Si-Al	3; 14; 15; 16
Florisil or HPLC	5; 18
None	7; 9; 10
Confirmation of identities	
GC-MS (polycyclic aromatic hydrocarbon)	All participants
GC-FID (aliphatic compound)	

[a] Laboratory that performed the determination using two methods. ASE: accelerated solvent extraction; HPLC: high-performance liquid chromatography; GC-FID: gas chromatography-flame ionization detector.

Table 5. Summary of the methods used for quantifying the elements in sediment sample SED 001. Laboratory code numbers and the instrumental methods used in each procedure

	1.0 mol L^{-1} HCl			EPA 3050			EPA 3052		
	ICP-OES	AAS	ICP-MS	ICP-OES	AAS	ICP-MS	ICP-OES	AAS	ICP-MS
Mg	10; 13	17	–	7; 9; 10; 13; 24; 25; 26	16; 17; 18	–	10; 13	17	–
Al	10; 13	17	–	7; 9; 10; 13; 24; 25; 26	16; 17; 18	–	10; 13	17	–
Ca	10; 13	17	–	7; 9; 10; 13; 24; 25; 26	16; 17; 18	–	10; 13	17	–
V	10; 13	–	22	7; 9; 10; 13; 24; 25; 26	16; 18	21; 22	10; 13	–	22
Cr	10; 13	17; 20	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18; 20	21; 22	10; 13	17; 20	22
Mn	10; 13	17	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18	21; 22	10; 13	17	22
Fe	10; 13	17	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18	21	10; 13	17	22
Co	10; 13	–	22	7; 8; 9; 10; 13; 24; 25; 26	16	21; 22	10; 13	–	22
Ni	8; 10; 13	–	22	7; 8; 9; 10; 13; 24; 25; 26	16; 18	21; 22	8; 10; 13	–	22
Cu	8; 10; 13	17; 20	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18; 20	21; 22	8; 10; 13	17; 20	22
Zn	8; 10; 13	17; 20	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18; 20	21; 22	8; 10; 13	17; 20	22
As	10; 13	–	22	7; 9; 10; 13; 24; 26	–	21; 22	10; 13	–	22
Se	10; 13	–	–	7; 9; 10; 13; 24; 26	–	21	10; 13	–	–
Sr	10; 13	–	–	7; 9; 10; 13; 24; 25; 26	–	21	10; 13	–	–
Ag	10	–	22	7; 9; 10; 24; 25; 26	16	22	10	–	22
Cd	10; 13	–	22	7; 9; 10; 24; 26	16	21; 22	10; 13	–	22
Sn	10; 13	–	22	7; 9; 10; 13; 24; 26	16	22	10; 13	–	22
Sb	10; 13	–	22	7; 9; 10; 13; 24; 26	16	22	10; 13	–	22
Ba	10; 13	–	22	7; 8; 9; 10; 13; 24; 25; 26	16; 18	21; 22	10; 13	–	22
Hg	–	–	–	7; 9; 25; 26	–	–	–	–	–
Tl	10; 13	–	22	9; 10; 13; 26	18	22	10; 13	–	22
Pb	8; 10; 13	17	22	7; 8; 9; 10; 13; 24; 25; 26	16; 17; 18	21; 22	8; 10; 13	17	22

laboratory means that were rejected as outliers did not exceed (a) 20% or (b) 50%. Finally, (*iv*) the overall mean was calculated based on the following number (or more) of laboratory means: (a) 10 or (b) 5. Based on these criteria, the certification classifications for aliphatic and aromatic hydrocarbons are provided in Tables 6 and 7, respectively, and can be defined as follows:

Class A: when all criteria are met; Class B: when criteria *i*, *ii*, *iii*b, and *iv*a or *i*, *ii*, *iii*a, and *iv*b are met; and Class C: when at least three laboratories give results that reasonably agree with each other.

These tables provide information regarding the final results, including the consensus values, the standard deviations, the numbers of participants who reported the concentrations of each substance, and the classification obtained by the analyte.[5]

For trace elements, the consensus values are presented in Table 8 for the three different digestion methods that were used (after verifying the outliers). We only considered the analytes for which at least three replicates were reported.

General remarks regarding the intercomparison of the hydrocarbons and trace elements

Overall, 19 laboratories provided data for hydrocarbons. Among these laboratories, only two did not report results for aliphatic compounds. Three of these laboratories only sent one analysis result and were excluded from the final evaluation. Generally, 64% of the laboratories indicated at least one outlier when determining the aliphatic hydrocarbon content, and 68% of the laboratories presented at least one outlier when determining the PAH content. Some laboratories did not report any correction for soil moisture content. The performance assessed by the z-score was satisfactory for all laboratories. Despite the large variability that is inherent to the intercomparison exercise, the typology of the *n*-alkanes and the PAH was

Table 6. Aliphatic compounds, dry weight basis. The results are expressed in µg kg^{-1}

Aliphatic hydrocarbons	Average value[a]	SD[b]	SD / %	N[c]	Outlier / %	Class
C12	141.0	110.7	79	7	30	C
C13	131.2	46.2	35	8	20	C
C14	177.1	61.9	35	11	–	B
C15	198.9	58.5	29	11	–	B
C16	178.7	69.8	39	13	–	C
C17	316.2	74.9	24	12	8	B
Pristane	179.1	67.3	38	11	8	B
C18	265.7	96.8	36	12	8	B
Phytane	244.6	111.0	45	12	8	B
C19	312.3	117.6	38	11	8	B
C20	338.3	135.1	40	13	–	B
C21	462.7	148.6	32	13	–	B
C22	479.0	199.4	42	13	–	B
C23	1128.9	353.1	31	13	–	B
C24	675.7	255.1	38	13	–	B
C25	2427.3	686.5	28	13	–	B
C26	703.6	298.5	42	13	–	B
C27	2911.0	928.1	32	13	–	B
C28	1035.8	439.2	42	13	–	B
C29	5098.5	1429.4	28	13	–	B
C30	702.0	146.4	21	11	15	B
C31	3144.0	1475.8	47	13	–	B
C32	569.8	291.8	51	13	–	B
C33	1639.5	875.2	53	11	8	B
C34	281.0	147.7	53	9	25	C
C35	666.8	336.7	50	10	9	B
C36	163.7	86.0	53	6	33	C
C37	196.3	114.4	58	8	11	C
C38	131.9	68.0	52	7	13	C
C39	152.5	79.9	52	8	–	C
C40	118.1	76.0	64	7	13	C

[a]Average values are expressed on a dry weight basis; [b]standard deviation; [c]number of accepted laboratory means that were used for calculating the recommended values and the standard deviation.

preserved. In Figures 1 and 2, both classes of compound are shown for the data obtained in this study. This result shows that the RM SED 001 is suitable for calibrating laboratory procedures that target the appraisal of hydrocarbon sources.

Overall, 13 laboratories presented results regarding the trace element concentrations in sediment sample SED 001. As expected, the results obtained for the trace elements using the different digestion methods showed a gradient that was related to the efficiency of the procedure. Milder digestion (with HCl)[6] resulted in lower concentrations than the samples analyzed by the two other methods, EPA method 3050B[7] (concentrated HNO_3 treatment) and EPA method 3052[8] (HNO_3 + HF). Similarly to the hydrocarbons, the z-scores for the metals were satisfactory. Three laboratories (or 25%) reported outlier values for the methods using 1 mol L^{-1} HCl, 15% reported outlier values when using EPA method 3050B, and 33% reported outliers when using EPA method 3052. Figure 3 shows some of these results.

Comparison of SED 001 with other materials

Table 9 shows the results and standard deviations that were obtained in the current study (SED 001) and those reported for two commercial reference materials (NIST 1941b[14] and IAEA-435[15]). The data variability observed in this study was in the same range as the variabilities reported for other materials prepared by specialized groups in this area. In fact, the reference materials are classified into two groups, reference materials (RMs) and certified reference materials (CRMs). In the second group, the traceability chain is much larger and should generally present lower variability.

Very few reference materials report alkylated compound contents. In this study, the results obtained for alkylated PAH are of similar quality to those reported for the 16 PAHs. In addition, no increase in variation was observed due to the limited availability of commercial standards for alkylated compounds and due to the different approaches used to determine their concentrations (Table 10). Exceptions occurred for the lighter alkylated PAHs, such as alkyl naphthalene and alkyl phenanthrene, which presented higher variation. In addition, the higher molecular mass homologues tended to show larger variability, which was potentially derived from the growing uncertainty in defining the area in the ion chromatogram when transitioning from C_0 to C_n compounds.

Table 11 shows the results for trace elements in the current study (SED 001 by EPA 3052 method[8]) and of other commercial reference materials (NIST 8704,[16] NIST 695,[17] and IAEA-433[18]). The range of the results for the reference material (SED 001) was 4.0 to 25%, which was higher than the range presented by NIST RM 8704 (from 3.0 to 8.0%), NIST 695 (from 0 to 4.0%) and IAEA 433 (5.0 to 12.0%).

A list of laboratories that participated in this study is presented in Table 12.

Table 7. Aromatic hydrocarbons, dry weight basis. The results are expressed in µg kg^{-1}

Aromatic hydrocarbons	Average value[a]	SD[b]	SD / %	N[c]	Outlier / %	Class
Naphthalene	21.1	14.6	69	14	18	C
2-Methyl naphthalene	40.9	28.6	70	9	25	B
1-Methyl naphthalene	25.4	14.0	55	9	18	B
C2-Naphthalene	95.5	44.6	47	9	18	B
C3-Naphthalene	80.2	39.4	49	9	18	B
C4-Naphthalene	65.2	37.6	58	9	–	C
Acenaphthylene	22.3	9.1	41	14	22	B
Acenaphthene	4.8	2.1	43	12	20	B
Fluorene	10.7	4.2	39	14	18	B
C1-Fluorene	23.0	12.2	53	7	13	C
C2-Fluorene	55.4	30.9	56	6	14	B
C3-Fluorene	99.3	57.5	58	5	17	C
Dibenzothiophene	11.4	4.7	41	9	18	B
C1-Dibenzothiophene	44.4	24.1	54	8	11	B
C2-Dibenzothiophene	185.5	106.0	57	7	13	B
C3-Dibenzothiophene	287.5	154.5	54	6	25	B
Phenanthrene	35.8	15.2	42	15	21	B
C1-Phenanthrene	78.7	39.0	49	8	11	B
C2-Phenanthrene	126.7	64.9	51	9	10	B
C3-Phenanthrene	247.7	138.7	56	8	20	B
C4-Phenanthrene	330.1	213.8	65	7	22	B
Anthracene	16.1	5.0	31	14	22	B
Fluoranthene	71.2	31.3	44	14	22	B
Pyrene	146.2	58.0	40	15	21	B
C1-Pyrene	329.5	215.8	65	9	18	B
C2-Pyrene	825.9	515.1	62	8	11	B
Benz(*a*)anthracene	97.4	44.8	46	15	17	B
Chrysene	137.1	70.0	51	15	21	B
C1-Chrysene	471.0	176.5	37	9	10	B
C2-Chrysene	1026.1	663.5	65	9	10	B
Benzo(*b*)fluoranthene	197.1	109.7	56	14	18	B
Benzo(*k*)fluoranthene	69.8	43.2	62	13	13	B
Benzo(*e*)pyrene	264.6	59.0	22	8	20	B
Benzo(*a*)pyrene	163.0	66.6	41	15	21	B
Perylene	74.5	13.2	18	9	25	B
Indeno(1,2,3-*c*,*d*)pyrene	125.2	59.9	48	15	21	B
Dibenz(*a*,*h*)anthracene	69.9	33.8	48	14	18	B
Benzo(*ghi*)perylene	146.4	51.9	35	14	22	B

[a]Average values are expressed on a dry weight basis; [b]standard deviation; [c]number of accepted laboratory means that were used in calculating the recommended values and the standard deviation.

Table 8. Trace elements, dry weight basis. The results are expressed in mg kg^{-1}

	1.0 mol L^{-1} HCl method					EPA methods 3050B or 3051					EPA method 3052				
	Average value[a]	SD[b]	SD / %	N[c]	Outlier / %	Average value[a]	SD[b]	SD / %	N[c]	Outlier / %	Average value[a]	SD[b]	SD / %	N[c]	Outlier / %
Mg	8576	3211	37	6	–	11319	3244	29	11	–	11338	1716	15	4	–
Al	7904	4936	62	6	–	35916	14135	39	11	–	64789	7314	11	5	–
Ca	5435	1925	35	5	–	5481	3075	56	10	–	7561	623	8	4	–
V	20.9	14.9	71	5	–	48.7	13.7	28	9	–	69.5	9.1	13	5	17
Cr	44.6	37.3	84	7	–	66.1	13.5	20	14	–	85.7	22.7	26	8	–
Mn	395.1	86.0	22	7	–	572.5	74.3	13	13	–	607.6	114.7	19	6	–
Fe	18739	10833	58	8	–	33519	5154	15	13	7	38146	3803	10	7	–
Co	3.4	2.8	83	7	–	6.5	2.0	30	11	–	11.2	3.7	33	6	–
Ni	8.6	4.5	53	7	–	18.6	3.8	20	11	–	24.0	3.8	16	5	–
Cu	25.4	15.1	59	9	–	47.9	7.3	15	12	8	54.3	8.7	16	6	14
Zn	123.4	46.3	38	10	–	152.8	21.3	14	14	7	183.4	25.0	14	8	–
As	4.3	2.6	60	6	–	6.2	3.3	53	8	11	9.4	2.4	26	6	14
Cd	0.4	0.2	40	4	20	0.9	0.7	74	8	–	–	–	–	–	–
Ba	23.7	16.4	69	6	14	55.4	16.4	30	11	15	236.5	86	36	5	–
Pb	29.9	4.1	14	7	12	37.2	9.2	25	13	–	41.3	4.3	10	4	–

[a]Average values are expressed on a dry weight basis; [b]standard deviation; [c]number of accepted laboratory means that were used in calculating the recommended values and the standard deviation.

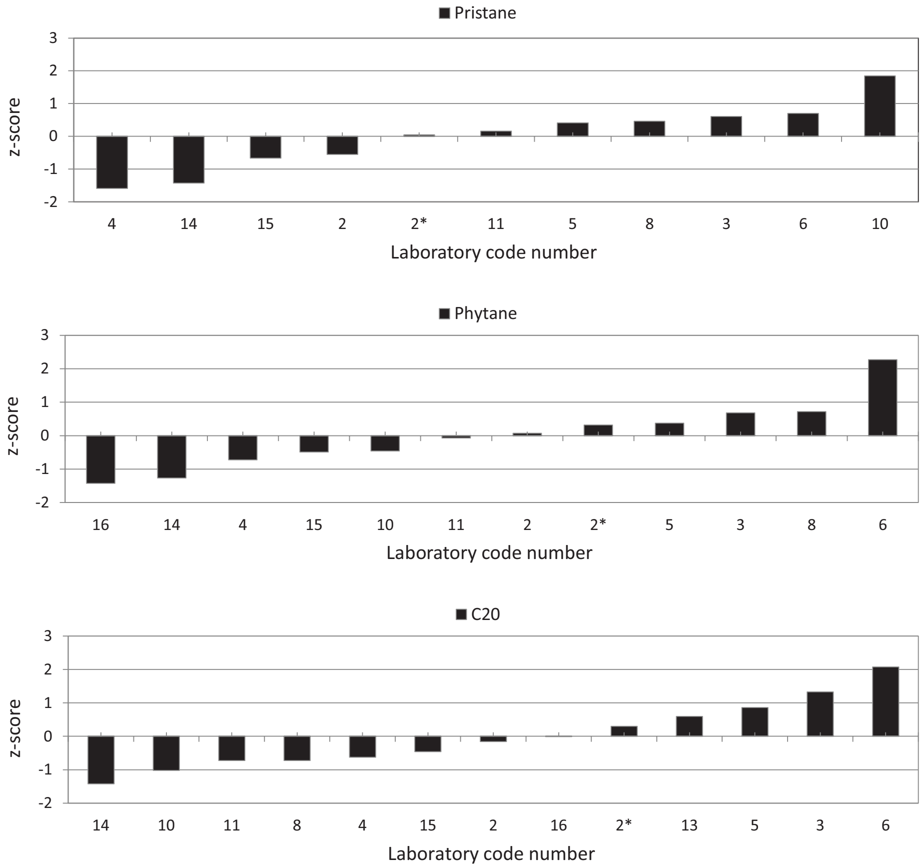

Figure 1. z-Scores for the aliphatic hydrocarbons in sediment sample SED 001. 2*: Laboratory that performed the determination using two methods.

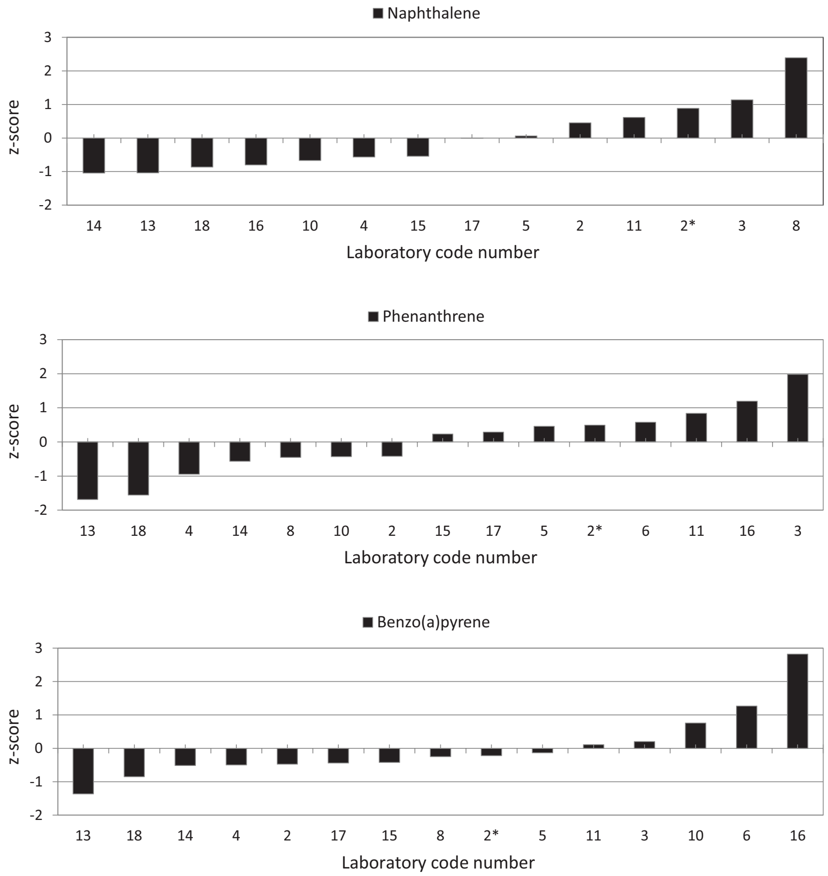

Figure 2. z-Scores for the aromatic hydrocarbons in sediment sample SED 001. 2*: Laboratory that performed the determination using two methods.

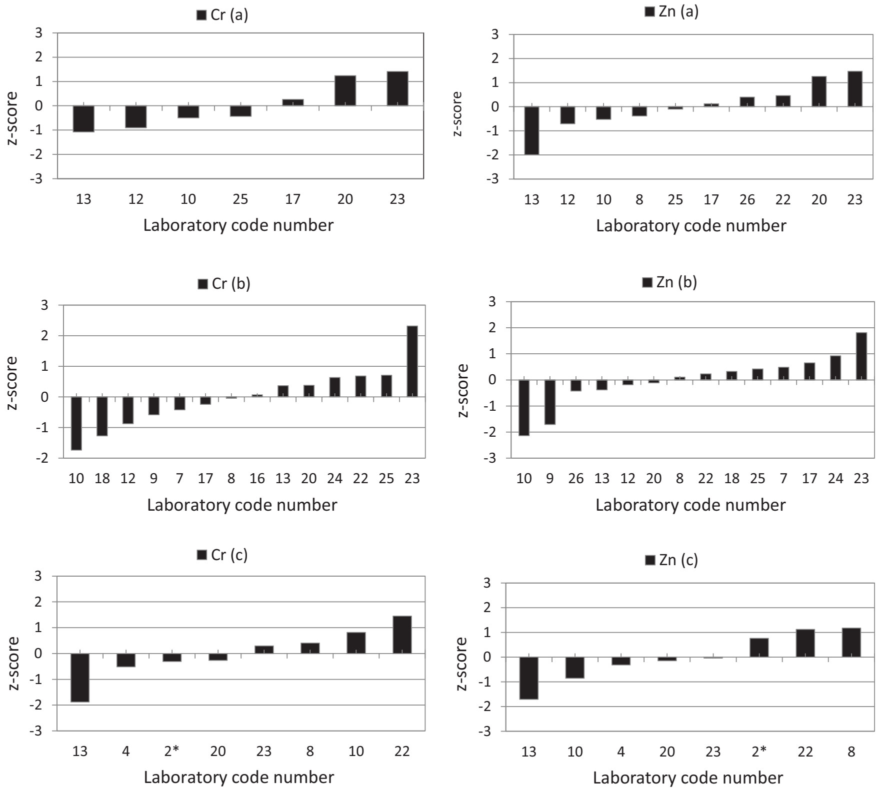

Figure 3. z-Scores for the trace-elements in sediment sample SED 001. Methods: (a) 1.0 mol L^{-1} HCl; (b) EPA 3050B or 3051 and (c) EPA 3052. Results obtained for Cr and Zn (n = 7, n = 14 and n = 8, respectively). 2*: Laboratory that performed the determination using two methods.

Table 9. Comparison of SED 001 with the other reference materials. The results are expressed in µg kg^{-1}

Compound	NIST 1941b		SED 001		IAEA-435	
	[ ]	SD	[ ]	SD	[ ]	SD
Naphthalene	848	95	21	14	7.8	6
Fluorene	85	15	11	4	1.6	1
Phenanthrene	406	44	36	15	8.4	5
Anthracene	184	18	16	5	7.9	10
Fluoranthene	651	50	71	31	3.9	4
Pyrene	581	39	146	58	11	15
Benz(*a*)anthracene	335	25	97	45	3.4	4
Chrysene	291	31	137	70	2.8	2.6
Benz(*b*)fluoranthene	453	21	197	110	1.8	2.1
Benz(*k*)fluoranthene	225	18	70	43	–	–
Benz(*e*)pyrene	325	25	265	59	23	28
Benz(*a*)pyrene	358	17	163	67	26	42
Perylene	397	45	75	13	–	–
Benz(*ghi*)perylene	307	45	146	52	0.89	0.65
Indeno(1,2,3-*c*,*d*)pyrene	341	57	125	60	2.2	2.6

Table 10. Results for the alkylated compounds in SED 001. The results are expressed in µg kg^{-1}

Compound	RM SED 001			NIST 1941b			QA05SED13[a]		
	[ ]	SD	n	[ ]	SD	n	[ ]	SD	n
2-Methyl naphthalene	41	29	9	276	53	8	223	116	9
1-Methyl naphthalene	25	14	9	127	14	8	98	24	8
C1-Fluorene	23	12	7	–	–	–	–	–	–
C2-Fluorene	55	31	6	–	–	–	–	–	–
C3-Fluorene	99	57	5	–	–	–	–	–	–
C1-Dibenzothiophene	44	24	8	–	–	–	–	–	–
C2-Dibenzothiophene	185	106	7	–	–	–	–	–	–
C3-Dibenzothiophene	288	154	6	–	–	–	–	–	–
C1-Phenanthrene	79	39	8	–	–	–	55	18	9
C2-Phenanthrene	127	64	9	–	–	–	–	–	–
C3-Phenanthrene	248	139	8	–	–	–	–	–	–
C4-Phenanthrene	330	218	7	–	–	–	–	–	–
C1-Pyrene	329	216	9	52	2	–	–	–	–
C2-Pyrene	826	515	8	–	–	–	–	–	–
C1-Chrysene	471	176	9	–	–	–	–	–	–
C2-Chrysene	1026	663	9	–	–	–	–	–	–

[a] Marine Sediment XIII.

Table 11. Comparison of SED 001 with other reference materials. The results are expressed in µg kg^{-1}

Metals	SED 001		NIST 8704		NIST 695		IAEA 433	
	[ ]	SD	[ ]	SD	[ ]	SD	[ ]	SD
V	70	9	94.6	4	122	3	160	11
Cr	86	22	–	–	–	–	136	10
Mn	608	114	544	21	–	–	316	16
Co	11	4	13.57	0.43	65.3	2.4	12.9	1.2
Ni	24	4	42.9	3.7	135	2	39.4	3.1
Cu	54	9	–	–	1225	9	30.8	2.6
Zn	183	25	408	15	–	–	101	8
As	9	2	–	–	200	5	18.9	1.8
Ba	236	86	413	13	–	–	268	32

Table 12. List of participants

Laboratory	Country	Results for
Analytical Solutions, RJ	Brazil	PAH /metal
Analytical Technology, SP	Brazil	PAH / metal
Bioagri Ambiental, SP	Brazil	PAH / metal
CEDRE	France	PAH
CONECO, FURG, RS	Brazil	PAH
Departamento de Geociências, Universidade de Aveiro	Portugal	PAH / metal
Departamento de Geologia e Recursos Naturais, Unicamp, SP	Brazil	Metal
Fisheries Research Services Marine Laboratory, Aberdeen	Scotland	PAH
Hidroquímica, FURG, RS	Brazil	Metal
Geochemical, MG	Brazil	PAH / metal
IAEA / MEL	Monaco	PAH / metal
Innolab, RJ	Brazil	PAH
Institute of Chemical and Environmental Research (ID / EA), Barcelona	Spain	PAH
Laboratório de Química Orgânica Marinha, Instituto Oceanográfico, USP, SP	Brazil	PAH
Laboratório de Análise por Ativação com Nêutrons, IPEN, SP	Brazil	Metal
Laboratório de Análises Ambientais, UFPR, PR	Brazil	PAH / metal
Laboratório de Biogeoquímica Ambiental / LBGqA, UFSCar, SP	Brazil	PAH / metal
Laboratório de Meio Ambiente, Centro de Tecnologia de Gás, CTGas, RN	Brazil	PAH / metal
Laboratório de Química, CENA USP, Piracicaba, SP	Brazil	Metal
LaGOM, UERJ, RJ	Brazil	PAH
LAQA, Tecpar, PR	Brazil	Metal
LQAO, CENPES-Petrobras, RJ	Brazil	PAH
Laboratório de Estudos Marinhos e Ambientais (LABMAM), PUC-Rio, RJ	Brazil	PAH
Labspectro, PUC-Rio, RJ	Brazil	Metal
SENAI-CIC/CETSAM, Laboratórios Ambientais, PR	Brazil	PAH
UFSC, SC	Brazil	Metal

Conclusions

The produced material is suitable for use as a reference material in processes that require routine quality control when analyzing hydrocarbons and trace elements in sediments. In general, the laboratories that participated in this program attained satisfactory performance, which was due to the large confidence intervals in some cases.

Each laboratory should examine their performance while considering the intended use of the analytical results. The laboratories that obtained results that were further away from the expected value should carefully check their analytical procedures.

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