Accuracy and precision of selected analytical methods used in marine geochemical studies

MSc Katarzyna Koziorowska, PhD Karol Kuliński, Prof. Janusz Pempkowiak

Institute of Oceanology Polish Academy of Sciences in Sopot, Marine Chemistry and Biochemistry Department

Accuracy and precision are two particularly important parameters in marine geochemical studies, because the sample preparation procedures for measurements are, most often, elaborated and complex, consisting of a sequence of several operations. This increases the risk of errors occurring or overlooking contamination of the processed sample. Moreover, the measured components (analytes) are often found in very low concentrations, comparable to the limits of detection of the methods used. This intensifies the problems and difficulties in obtaining correct and reliable results. A set of procedures that lead to the quantification of analytical errors is commonly described as quality control (QC). QC most often includes establishing accuracy, which describes the difference between a result of a measurement and the true (or expected) value of a given property (e.g. concentration of an analyte in the sample), and precision, which indicates the degree to which the results of the measurements are reproducible (Potts, 2012; Schoene et al., 2013) [9, 10].

Studies on the cycling of elements in the surface spheres of the Earth have gained in significance since a direct link between greenhouse gases concentration in the atmosphere and climate change was established. Both, the concentrations of carbon and nitrogen and the amounts of the elements stored in specific reservoirs are of primary importance in this respect. Marine sediments are especially interesting, since it is believed that they are an important sink of organic and inorganic matter including carbon and nitrogen deposited from the water column. A significant part of the deposited organic matter is buried in subsurface sediments, which excludes biogenic elements, from contemporary cycling. Thus, the burial of organic matter directly limits the productivity of ecosystems and, indirectly, the concentration of the atmospheric CO_2 and its negative consequences (Schubert and Calvert, 2001; Smith et al., 2015; Stein and Macdonald, 2004) [11, 12, 13]. However, if the results of the measurements are to be used, for example, in numerical biogeochemical models that focus on predicting the effect of possible climate warming, the measurements must be highly accurate. Therefore it is of the utmost importance that both the accuracy and the precision of the measuring methods are verified. Quality control characteristics are also required to establish the statistical significance of the differences between and among data sets characterizing different compartments and components of the environment.

Most of the studies assess the precision and the accuracy of the measurements. In addition, quality control includes blank samples, limits of detection, limits of quantification and sensitivity of the used methods in relation to both the quality of the samples and the concentrations of the analysed components. Uncertainty often indicates statistically significant differences between averages, or, the lack of such significance. Typically, on every few or a few dozen samples, one or more control samples are analysed, to assess the precision given as a relative standard deviation. Additionally, most often, certified reference materials are analysed, in order to determine accuracy – called commonly as the recovery rate.

Despite its importance, geochemical studies often lack QC e.g. limits of detection and accuracy and precision of analytical methods used, even if uncertainty or accuracy values are necessary for the proper interpretation of the results, e.g. when the measured concentrations are very low or differences between the results are small. Thus the aim of this study was to determine the accuracy and the precision of the analytical methods used to estimate the basic properties of surface sediments. The following sediment properties were measured: (i) moisture (measured using two methods: drying in an oven at 105°C and freeze-drying), (ii) organic matter – loss on ignition at 450°C, (iii) concentrations of total carbon (C_{tot}), organic carbon (C_{org}), total nitrogen (N_{tot}) as well as the isotopic composition of these three ($\delta^{13}C_{tot}$, $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$, respectively), (iiii) concentrations of metals: copper (Cu), lead (Pb), cadmium (Cd), manganese (Mn), calcium (Ca), iron (Fe), magnesium (Mg), zinc (Zn) and (iv) ^{210}Pb activity concentrations.

METHODS

Sampling

A single, typical sample of fine grained marine surface sediment was selected for analysis. The sample was taken during the cruise of s/y Oceania, in the Norwegian Sea (73.50 N, 19.33 E), and more specifically near the border with the Barents Sea. This area is located on the continental shelf of the European Arctic, which is currently a centre of many activities in the field of engineering and geochemistry, especially in the context of studies related to the global carbon cycle and large constructions.

Immediately after it was collected, the sediment sample was transferred to a polyethylene bag and frozen at -20°C until analysed. In the laboratory the sample was, first, defrosted and homogenized, then five representative sub-samples were taken for the purpose of the various analyses as described in paragraphs 2.2 – 2.6. Additionally, each analytical procedure included the so called blank sample – a sample deprived of actual sediment matrix which was treated similarly to other samples. The results of the blank samples were also used to calculate the limits of detection and the limits of quantification. Additionally, certified reference materials (CRM) with known composition were analysed to assess the accuracy of the methods used. All the measurements were performed in the Marine Biogeochemistry Laboratory at the Institute of Oceanology of the Polish Academy of Sciences in Sopot, Poland (http://www.iopan.gda.pl/BGeochem/index_pl.html).

Moisture measurements

The moisture was measured using two methods: drying in an oven (ED53, BINDER) at 105°C for 24 h, and freeze-drying (Labconco, Freezone). The samples were weighed before and after drying and freeze drying, then moisture was calculated using the following formula:

$$W = \frac{m_m - m_s}{m_m} \cdot 100\%$$

where:
W – moisture [%],
m_m – wet sediment weight [g],
m_s – dry sediment weight [g].

Loss on ignition (*LOI*)

Approximately 200 mg of dry sediment was weighed (0.01 mg accuracy) to a pre-weighted porcelain crucible. Next, crucibles with the sediment were combusted in a muffle furnace at a temperature of 450°C for 8 hours. Then *LOI* was calculated using the following formula:

$$LOI = \frac{m_{sp} - m_p}{m_{sp}} \cdot 100\%$$

where:
LOI – loss on ignition [%],
m_{sp} – sediment weight before combusting [g],
m_p – sediment weight after combusting [g].

Carbon and nitrogen elemental and stable isotopes analyses

Concentrations of total carbon (C_{tot}), organic carbon (C_{org}), total nitrogen (N_{tot}), total and organic carbon stable isotopes composition ($\delta^{13}C_{tot}$ and $\delta^{13}C_{org}$) and total nitrogen stable isotopes composition ($\delta^{15}N_{tot}$) were analysed in an Elemental Analyser Flash EA 1112 Series combined with an Isotopic Ratio Mass Spectrometer IRMS Delta V Advantage (Thermo Electron Corp., Germany). Details of these measurements are described by Kuliński et al. (2014) [5]. In short, about 30 mg (0.001 mg accuracy) of freeze-dried and homogenized sediments were weighed into silver capsules. The samples used for measurements of organic carbon concentration and stable isotopes composition were additionally soaked with 2M hydrochloric acid to remove carbonates and dried at 60°C for 24 h (the procedure was repeated four times). The quantitative measurements were calibrated against certified reference materials (marine sediments – Flußsediment) provided by HEKAtech GmbH (Germany). The isotopic composition of total carbon ($\delta^{13}C_{tot}$), organic carbon ($\delta^{13}C_{org}$) and total nitrogen ($\delta^{15}N_{tot}$) was measured using laboratory working pure reference gases (CO_2 and N_2) calibrated against IAEA standards: CO-8 and USGS40 for CO_2 and N-1 and USGS40 for N_2. The results of $\delta^{13}C_{tot}$, $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$ are given in the conventional delta notation, i.e., versus PDB for $\delta^{13}C_{tot}$, $\delta^{13}C_{org}$ and versus air for $\delta^{15}N_{tot}$, as parts per thousand (‰). The calculations were performed according to the following equation:

$$\delta X \, (‰) = \left[\frac{R_{sample}}{R_{standard}} - 1 \right] \cdot 1000$$

where:
X – ^{13}C or ^{15}N,
R – the ratio of $^{13}C/\,^{12}C$ or $^{15}N/\,^{14}N$.

Metals concentrations analyses

The concentration of various metals was measured using two instruments: an Inductively Coupled Plasma Mass Spectrometer (ICPMS) for copper, lead and cadmium and an Atomic Absorption Spectrophotometer (AAS) for manganese, calcium, iron, magnesium and zinc. Metal concentrations measurements were carried out in a solution obtained after wet digestion of pre-weighted samples according to the procedure described by Walkusz et al. (1992) [16]. The sediment material was freeze-dried and weighed (about 500 mg, 0.1 mg accuracy) prior to digestion with concentrated 14 M nitric acid, 23 M hydrofluoric acid and 12 M perchloric acid in volume ratios 7:7:1. Various salts present in the dry residue were converted to chlorides through evaporation with concentrated – 12 M and dissolved – 1 M, hydrochloric acid. Then, depending on the measured element, the samples were appropriately diluted (10, 100 and 1000 times). After the measurements, the concentrations have been recalculated and expressed per mass unit (g) of dry sediment. The accuracy of the method was assessed based on the analysis of two certified reference materials – marine sediments (IAEA 433 obtained from the International Atomic Energy Agency, Vienna, Austria and JMS1 obtained from MBH Analytical Ltd, Bernet, UK).

^{210}Pb analyses

^{210}Pb activity concentration measurements were carried out according to the procedure described by Zaborska et al. (2007) [18], and Pempkowiak (1991) [8]. First, 200 mg of dry and homogenous material was spiked with ^{209}Po chemical yield tracer and digested using 12 M hydrofluoric acid (3 ml) and concentrated perchloric acid (2 ml). Next, ^{210}Po and ^{209}Po were spontaneously deposited on silver disks. After deposition the disks were analysed for isotopes of polonium in a multi-channel analyser (Canberra) equipped with a Si/Li detector. The activity concentrations of ^{210}Po in the sediment samples were calculated based on chemical recovery by comparing the measured and spiked activities of ^{209}Po. Quality control was based on the measurement of blanks, standard sediments (IAEA-300 and IAEA-326 obtained from the International Atomic Energy Agency, Vienna, Austria) and spiked samples to verify the recovery and the efficiency of detection.

Statistical analyses

The results obtained were assessed using the following statistical methods: the Dixon test (Q-test) – to eliminate results burdened with gross errors from the data set, averages and medians – to assess representative values of the measured properties, standard deviations (SD) and relative standard deviations (RSD)

– to assess precision, the recovery rate – to establish accuracy. The statistical significance of differences of two- or multi-component data sets was established using the t-Student test and/or ANOVA.

RESULTS

The results of the measurements are presented in Table 1. The underlined values mark results burdened with gross errors, as indicated by the Dixon test (Q-test). The occurrence of the gross errors is, most likely, caused by the inhomogeneity of the analysed material. Estimated statistical parameters such as averages, SDs or RSDs have been calculated without taking into account the underlined results.

The results indicate that the analysed sediment has typical characteristics for samples collected in the polar regions (Koziorowska et al., 2016; Kuliński et al., 2014; Zaborska et al., 2008) [4, 5, 19]. For example total nitrogen concentration in the sample amounted to 0.156 ± 0.003% (Table 1), which is well in the range of nitrogen contents of 0.04% to 0.31%, that have been reported before (Knies et al., 2007; Schubert and Calvert, 2001) [2, 11]. The results for the biogenic elements (C_{tot}, C_{org}, $\delta^{13}C_{tot}$, $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$) are also in the range of values obtained by other authors (Knies et al., 2007; Kędra et al., 2012; Winkelmann and Knies, 2005) [2, 6, 17]. The concentrations of metals: Cu, Pb, Cd, Mn, Ca, Fe, Mg and Zn were equal to 18.9 ± 0.9 µg g⁻¹, 14.6 ±1.8 µg g⁻¹, 0.29 ± 0.02 µg g⁻¹, 246.6 ± 10.5 µg g⁻¹, 10.3 ± 0.5 mg g⁻¹, 34.2 ± 0.8 mg g⁻¹, 14206.5 ± 212.6 µg g⁻¹ and 74.6 ± 0.4 µg g⁻¹, respectively (Table 2). These metal concentrations do not differ significantly from the results reported by other authors in the area of Svalbard (Frankowski and Zioła-Frankowska, 2014) [1], the White Sea (Koukina and Vetrov, 2013) [3] and the Barents Sea (Zaborska et al., 2008) [19]. The ²¹⁰Pb average activity concentration was estimated at 42.6 ± 4.0 Bq kg⁻¹. Several reports (Koziorowska et al., 2016; Szczuciński et al., 2009; Zaborska et al., 2008) [4, 14, 19], indicate activity concentrations of this radio-nuclide similar to the ones obtained in this study. The sample is also characterized by relatively high moisture (64.67 ± 0.13% or 63.76 ±1.45% – depending on the used method), most likely due to large contents of the fined fraction and organic matter.

Table 1. The results of the sub-samples analysis: moisture, loss on ignition (LOI), concentrations of: total nitrogen (N_{tot}), total carbon (C_{tot}), organic carbon (C_{org}), stable isotopes composition of total nitrogen ($\delta^{15}N_{tot}$), total carbon ($\delta^{13}C_{tot}$) and organic carbon ($\delta^{13}C_{org}$). Gross errors – underlined values

Subsample	Moisture [%]		LOI [%]	N_{tot} [%]	C_{tot} [%]	C_{org} [%]	$\delta^{15}N_{tot}$ [‰]	$\delta^{13}C_{tot}$ [‰]	$\delta^{13}C_{org}$ [‰]
	drying	freezedrying							
1	64.58	63.18	5.44	0.156	1.644	1.303	5.37	-18.31	-21.48
2	64.67	64.59	5.35	0.159	1.627	1.315	5.61	-17.87	-22.42
3	64.58	61.47	5.46	0.157	1.657	1.334	5.40	-18.27	-22.82
4	64.88	64.87	5.53	0.157	1.624	1.078	5.50	-18.28	-23.30
5	64.64	64.71	5.43	0.152	1.589	1.290	5.04	-18.02	-22.98
Average	64.67	63.76	5.44	0.156	1.628	1.310	5.38	-18.15	-22,60
SD*	0.13	1.45	0.06	0.003	0.026	0.019	0.21	0.20	0,70
RSD [%]**	0.19	2.28	1.19	1.776	1.585	1.427	4.0	1.08	3,1

* SD – standard deviation

** RSD [%] – relative standard deviation

Table 2. The results of the analysis of metals in the sub-samples: concentrations of copper (Cu), lead (Pb), cadmium (Cd), manganese Mn), calcium Ca), iron (Fe), magnesium (Mg), zinc (Zn) and ²¹⁰Pb activity concentration. Gross errors – underlined values

Subsample	Mn	Zn	Fe	Mg	Ca	Cu	Pb	Cd	²¹⁰Pb
	µg g⁻¹		mg g⁻¹			µg g⁻¹			Bq kg⁻¹
1	256.4	69.5	33.70	13.4	10.92	16.6	11.6	0.29	39.0
2	280.5	74.1	33.55	15.2	10.56	18.0	15.9	0.27	38.7
3	269.2	74.9	33.81	14.5	8.98	19.6	14.1	0.32	43.2
4	254.9	75.0	34.89	13.4	9.99	18.2	15.5	0.26	48.6
5	261.8	74.3	35.31	13.2	9.84	19.8	16.0	0.29	43.4
Average	264.6	74.6	34.25	13.9	10.33	18.9	15.4	0.29	42.6
SD*	10.5	0.4	0.79	0.9	0.50	0.9	0.8	0.02	4.0
RSD [%]**	4.0	0.6	2.31	6.3	4.86	5.0	5.5	8.0	9.5

* SD – standard deviation

** RSD [%] – relative standard deviation

DISCUSSION

Accuracy and precision of the analytical methods used

Determination of moisture and organic matter concentrations

The results of the analysis indicate that moisture content is similar for both methods used (drying and freeze-drying) and amounts to 64.64% ± 0.13% (SD) and 63.76 ± 1.45% (SD), respectively. The results do not differ in statistically significant manner. However, drying in an oven at 105°C is characterized by much better precision than freeze-drying (RSD equal to 0.19% and 2.28%, respectively), possibly due to the insufficient time of freeze-drying to facilitate the removal of moisture. A relatively high precision has also been achieved for the assessment of loss on ignition, where the relative standard deviation amounts to 1.2% – most likely due to the simple analytical procedure, a non-existent blank and a large loss of mass in comparison to the sensitivity of the balance used.

Concentrations and isotopic compositions of carbon and nitrogen

The results show that the precision of the analyses of total carbon, organic carbon and total nitrogen was high as the relative standard deviations were equal to 1.58% (RSD), 1.43% (RSD) and 1.78% (RSD), respectively. In addition, the accuracy of the method was determined using certified reference materials (marine sediments) provided by HEKAtech GmbH (Germany) with a known concentration of total carbon and nitrogen (C = 45.0 mg g^{-1} and N = 3.68 mg g^{-1}). Three sub-samples of reference material were analysed, the results amounted to 44.7 ± 0.8 mg g^{-1} for total carbon and 3.71 ± 0.06 mg g^{-1} for total nitrogen. This gives a recovery rate equal to 99.6% for carbon and 100.8% for nitrogen, indicating an exceptional accuracy of this analysis, and confirms the high precision of the measurements. The isotopic compositions of total nitrogen and both total and organic carbon were determined with working pure reference gases (CO$_2$ and N$_2$) calibrated against IAEA standards. The relative standard deviations were estimated at 4.0% for $\delta^{15}N_{tot}$,

1.08% for $\delta^{13}C_{tot}$ and 3.1% for $\delta^{13}C_{org}$. The lower precision of the organic carbon isotopic composition results compared to $\delta^{13}C_{tot}$ could be caused by the presence of residual carbonates in the analysed material, despite quadruple acidification and drying of the samples with hydrochloric acid to remove carbonates.

Analyses of the heavy metals concentrations

The results of the metal concentrations analyses indicate that elements measured in AAS are characterized by high precision, as the relative standard deviations were estimated at 4.0% for Mn, 4.9% for Ca, 2.3% for Fe, 1.5% for Mg and 0.6% for Zn. While, the values of RSD for copper, lead and cadmium, measured in ICPMS, amounted to 5.0%, 5.5% and 8.0%, respectively. However, when comparing the precision of both these analytical methods, one should keep in mind, the spread of the measured concentrations. The concentrations range from 0.26 to 19.8 µg g^{-1} (Cu, Pb, Cd) and 74.1 µg g^{-1} ÷ 35.3 mg g^{-1} (Mn, Ca, Fe, Mg, Zn).

In addition, the accuracy of the method was determined using two sediments (IAEA 433 and JMS1) with certified concentrations of the measured elements (Table 3). In this case the samples of the reference materials were measured five times. The results show that for IAEA 433, the highest accuracy of measurements was achieved for zinc and manganese, with a recovery rate equal to 103.1% and 95.1%, respectively. Slightly lower accuracies were determined for other measured elements: 88.9% for Cd, 92.5% for Cu, 105.6% for Pb and 107.5% for Fe. In the case of the second reference material (JMS1), measurements were carried out only for three elements: Zn, Pb and Cu. The results indicate high accuracy, as recovery rates were equal to 85.2% for Zn, 102.7% for Pb and 101.2% for Cu. The precision values of the metal analyses, presented as relative standard deviations, were in the range 0.91 ÷ 4.66% for IAEA 433 and 0.7 ÷ 1.8% for JMS1. This may indicate that the JMS1 reference material matrix was better suited for the wet digestion procedure used. Thus the precision of the analysis of both the reference materials is slightly better than in the case of the Arctic sediment sample. This again may indicate that the sediment matrix composition influences the recovery of metals, more precisely, that some of the sediment components, as for example silica, can affect the efficiency of the wet digestion procedure. The overall results show how difficult it is to analyse environmental samples in a precise and accurate manner.

Table 3. Accuracy (given as recovery) and precision (given as standard deviation) of marine sediment analysis (IAEA 433 and JMS1)

Metal	Metal concentrations ± SD* [mg kg^{-1}]		Recovery [%]	Metal concentrations ± SD* [mg kg^{-1}]		Recovery [%]
	IAEA 433	Our values		JMS1	Our values	
Cd	0.153 ± 0.033	0.136 ± 0.005	88.9	–	–	–
Zn	101 ± 8	104.08 ± 2.2	103.1	264 ± 3	225 ± 1.5	85.2
Mn	316 ± 16	300.45 ± 14	95.1	–	–	–
Pb	26.0 ± 2.7	27.5 ± 0.91	105.6	49.0 ± 2	53.0 ± 0.98	102.7
Fe	40800 ± 1900	43870 ± 1110	107.5	–	–	–
Cu	30.8 ± 2.6	28.5 ± 0.26	92.5	88.0 ± 2	89.0 ± 0.92	101.2

* SD – standard deviation

For elements measured using ICPMS, the limits of detection (LOD) and the limits of quantification (LOQ) were also estimated. LOD has been determined as results of blank sample plus three times the standard deviation and LOQ as results of three times the limits of detection (Namieśnik et al., 2013; Uhrovcik, 2014) [7, 15]. The calculated limits of detection were 0.028 μg l^{-1} for Cu, 0.024 μg l^{-1} for Pb, and 0.012 μg l^{-1} for Cd, and results of the limits of quantification: 0.084 μg l^{-1} for Cu, 0.072 μg l^{-1} for Pb, and 0.036 μg l^{-1} for Cd. These results indicate that metals concentrations in the samples characterized by exceptionally low concentrations can be quantified and differentiated by means of ICPMS.

^{210}Pb activity concentration

The results obtained for the ^{210}Pb activity concentration were characterized by the lowest precision (RSD amounted to 9.5%) out of all of the conducted analyses. This could be caused by any or combination of following factors: (i) the multistep preparation of the sediment samples for measurements, (ii) inhomogeneity of the analysed material, despite that before each measurement, the sediment sample was carefully homogenized or (iii) influences of sediment matrix composition as it was mentioned in earlier chapter. In other studies devoted to radio-lead the precision of the measurements was significantly better (Pempkowiak, 1991; Zaborska et al., 2007) [8, 18].

The sensitivity of comparisons

Frequently, samples collected at different locations or/and at different times yield slightly differing results for measured properties (e.g. concentrations of chemical substances). Such a difference may or may not be statistically significant. Additionally, different methods used to determine the same property may produce different results, and thus should be checked for similarity.

In the following paragraph the threshold difference of concentrations securing statistically significant similarity, (at the significance level of 95%) between the average values of mois-ture, determined using two methods of analysis (drying and freeze-drying) is discussed. In Fig. 1 a dependence is presented between the hypothetical spread between two averages and the confidence level of similarity. Actual results of moisture analysis in the five subsamples were used. The graph allows for the determination of the threshold value. It shows that the value exceeds, by a factor of 1.23, the actual spread between the average results of the two methods used. Thus the difference is not statistically significant, and the methods used can be agreed to give similar results.

In addition, the threshold value of a spread between two hypothetical samples (collected at different locations or/and times) that is statistically significant and thus causing that the samples composition is different, was calculated. The actual precision and the number of the measurements presented in the preceeding chapters were retained. The results are presented in Table 4 and Table 5. Again a significance level of 95% was used. These estimates were made for all measured properties.

The data presented in Table 4 indicates that the differences between the averages of the two analysed samples, that cause statistically significant dissimilarity are relatively low. To compare these differences, the threshold difference has been recalculated into percentage values. It ranges from 1.6% of the average for total carbon stable isotopes composition ($\delta^{13}C_{tot}$) to 4.5% of the average for organic carbon stable isotopes composition ($\delta^{13}C_{org}$). This is because the measurements of these properties were executed with high accuracy and precision. Slightly higher values (except the zinc concentration), were determined for metal concentrations (Table 5), where the minimum percentage (of the average) change was: 1.0% for zinc, 3.4% for iron, 5.8% for manganese, 8.4% for calcium, 8.6 for cooper, 9.1% for magnesium, 9.5% for lead and 11.6% for cadmium. It has also been noted that the larger the relative standard deviation of the tested parameters, the larger the difference between the averages will have to be in order to interpret these differences as statistically insignificant. For example ^{210}Pb activity concentration, for which RSD was estimated at 9.5% and the minimum percentage difference between the two average values at 13.8%, or magnesium concentration with the values of 6.3% and 9.1%, respectively.
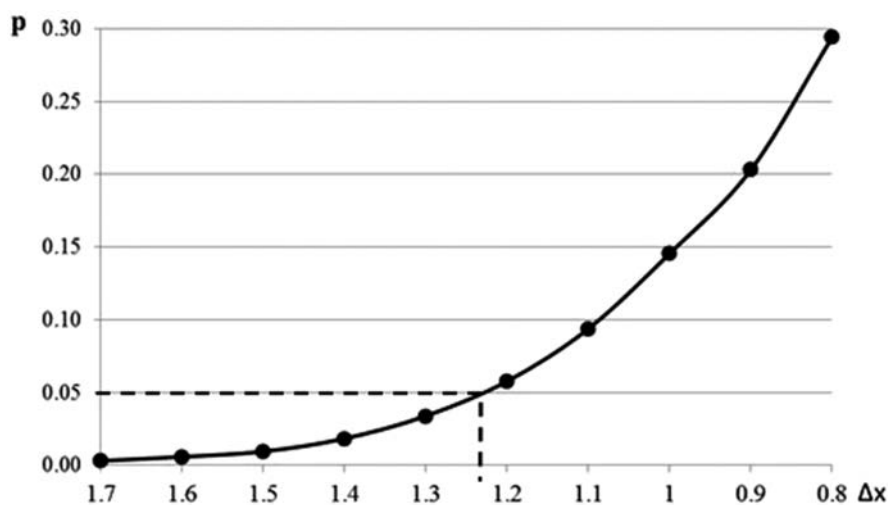

Fig 1. The sensitivity of the comparisons of the two methods
used to determine moisture (drying and freez-drying)
p – probability value; Δx – the spread between the average values of moisture, determined using the two methods

Table 4. The smallest difference, that is statistically significant, between the average results of the measured properties: loss on ignition (LOI), concentrations of: total nitrogen (N_{tot}), total carbon (C_{tot}) and organic carbon (C_{org}), and stable isotopes composition of: total nitrogen ($\delta^{15}N_{tot}$), total carbon ($\delta^{13}C_{tot}$) and organic carbon ($\delta^{13}C_{org}$)

Threshold value	Property measured						
	LOI [%]	N_{tot} [%]	C_{tot} [%]	C_{org} [%]	$\delta^{15}N_{tot}$ [‰]	$\delta^{13}C_{tot}$ [‰]	$\delta^{13}C_{org}$ [‰]
Δx*	0.094	0.004	0.038	0.032	0.312	0.285	1.022
Δx (%)**	1.7	2.6	2.3	2.0	5.8	1.6	4.5

* Δx – the threshold difference between the two average values

** Δx [%] – the threshold difference between the two average values given as percentage of the lower value

Table 5. The smallest difference, that is statistically significant, between the average results of the measured metal concentrations: copper (Cu), lead (Pb), cadmium (Cd), manganese (Mn), calcium (Ca), iron (Fe), magnesium (Mg), zinc (Zn) and ^{210}Pb activity concentration

Threshold value	Concentration measured								
	Mn	Zn	Fe	Mg	Ca	Cu	Pb	Cd	^{210}Pb
	μg g^{-1}		mg g^{-1}			μg g^{-1}			Bq kg^{-1}
Δx*	15.382	0.736	1.156	1.273	0.870	1.621	1.455	0.033	5.898
Δx (%)**	5.8	1.0	3.4	9.1	8.4	8.6	9.5	11.6	13.8

* Δx – the threshold difference between the two average values

** Δx [%] – the threshold difference between the two average values given as percentage of the lower value

Moreover, it was verified whether the analytical methods used in the study were characterized by comparable precision. For this purpose, all the results were normalized to the largest value (the results were divided by the highest value achieved when analysing the sub-samples by a particular method). Then an analysis of variance (ANOVA) was performed. The results show that the precision of the methods used does not differ in a statistically significant manner, except for the ^{210}Pb activity measurements.

CONCLUSIONS

The results of the study indicate that both the accuracy (recovery) and the precision (given as SD and RSD) of the selected analytical methods used in marine geochemical studies are high. This enables classifying the assessment of the differences between samples as statistically significant when the averages differ in the range of several percentage points.

REFERENCES

1. Frankowski M., Zioła-Frankowska A.: Analysis of labile form of aluminum and heavy metals in bottom sediments from Kongsfjord, Isfjord, Hornsund fjords. Environmental Earth Sciences, 71(3), 2014, 1147-1158.

2. Knies J., Brookes S., Schubert C. J.: Re-assessing the nitrogen signal in continental margin sediments: New insights from the high northern latitudes. Earth and Planetary Science Letters, 253(3-4), 2007, 471-484.

3. Koukina S. E., Vetrov A. A.: Metal forms in sediments from Arctic coastal environments in Kandalaksha Bay, White Sea, under separation processes. Estuarine Coastal and Shelf Science, 130, 2013, 21-29.

4. Koziorowska K., Kuliński K., Pempkowiak J.: Sedimentary organic matter in two Spitsbergen fjords: terrestrial and marine contribution based on carbon and nitrogen contents and stable isotopes composition. Continental Shelf Research, 113, 2016, 38-46.

5. Kuliński K., Kędra M., Legeżyńska J., Głuchowska M., Zaborska A.: Particulate organic matter sinks and sources in high Arctic fjord. Journal of Marine Systems, 139, 2014, 27-37.

6. Kędra M., Kuliński K., Walkusz W., Legeżyńska J.: The shallow benthic food web structure in the high Arctic does not follow seasonal changes in the surrounding environment. Estuarine Coastal and Shelf Science, 114, 2012, 183-191.

7. Namieśnik J., Konieczka P., Zygmunt B.: Ocena i kontrola jakości wyników pomiarów analitycznych. Wydawnictwo WNT, 2013.

8. Pempkowiak J.: Enrichment factors of heavy-metals in the Southern Baltic surface sediments dated with Pb210 and Cs137. Environment International, 17(5), 1991, 421-428.

9. Potts P. J.: Glossary of Analytical and Metrological Terms from the International Vocabulary of Metrology (2008). Geostandards and Geoanalytical Research, 36(3), 2012, 231-246.

10. Schoene B., Condon D. J., Morgan L., McLean N.: Precision and Accurancy in Geochronology, Elements, 2013, 19-14.

11. Schubert C. J., Calvert S. E.: Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. Deep-Sea Research Part I-Oceanographic Research Papers, 48(3), 2001, 789-810.

12. Smith R. W., Bianchi T. S., Allison M., Savage C., Galy V.: High rates of organic carbon burial in fjord sediments globally. Nature Geoscience, 8(6), 2015, 450-U46.

13. Stein R., Macdonald R. W.: The organic carbon cycle in Arctic Ocean. Springer, 2004.

14. Szczuciński, W., Zajączkowski, M., Scholten, J.: Sediment accumulation rates in subpolar fjords – Impact of post-Little Ice Age glaciers retreat, Billefjorden, Svalbard. Estuarine Coastal and Shelf Science, 85(3), 2009, 345-356.

15. Uhrovcik J.: Strategy for determination of LOD and LOQ values – Some basic aspects. Talanta, 119, 2014, 178-180.

16. Walkusz J., Roman S., J., P.: Contamination of the Southern Baltic surface sediments with heavy metals. Bull. Sea Fis. Inst., 1 (125), 1992, 33-37.

17. Winkelmann D., Knies J.: Recent distribution and accumulation of organic carbon on the continental margin west off Spitsbergen. Geochemistry Geophysics Geosystems, 2005, 6.

18. Zaborska A., Carroll J., Papucci C., Pempkowiak J.: Intercomparison of alpha and gamma spectrometry techniques used in Pb-210 geochronology. Journal of Environmental Radioactivity, 93(1), 2007, 38-50.

19. Zaborska A. et al.: Recent sediment accumulation rates for the Western margin of the Barents Sea. Deep-Sea Research Part Ii-Topical Studies in Oceanography, 55(20-21), 2008, 2352-2360.