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An inter-laboratory investigation of the Arctic sea ice biomarker proxy IP_{25} in marine sediments: key outcomes and recommendations

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Abstract. We describe the results of an inter-laboratory investigation into the identification and quantification of the Arctic sea ice biomarker proxy IP_{25} in marine sediments. Seven laboratories took part in the study, which consisted of the analysis of IP_{25} in a series of sediment samples from different regions of the Arctic, sub-Arctic and Antarctic, additional sediment extracts and purified standards. The results obtained allowed 4 key outcomes to be determined. First, IP_{25} was identified by all laboratories in sediments from the Canadian Arctic with inter-laboratory variation in IP_{25} concentration being substantially larger than within individual laboratories. This greater variation between laboratories was attributed to the difficulty in accurately determining instrumental response factors for IP_{25}, even though laboratories were supplied with appropriate standards. Second, the identification of IP_{25} by 3 laboratories in sediment from SW Iceland that was believed to represent a blank, was interpreted as representing a better limit of detection or quantification for such laboratories, contamination or mis-identification. These alternatives could not be distinguished conclusively with the data available, although it is noted that the precision of these data was significantly poorer compared with the other IP_{25} concentration measurements. Third, 3 laboratories reported the occurrence of IP_{25} in a sediment sample from the Antarctic Peninsula even though this biomarker is believed to be absent from the Southern Ocean. This anomaly is attributed to a combined chromatographic and mass spectrometric interference that results from the presence of a di-unsaturated highly branched isoprenoid (HBI) pseudo-homologue of IP_{25} that occurs in Antarctic sediments. Finally, data are presented that suggest that extraction of IP_{25} is consistent between Accelerated Solvent Extraction (ASE) and sonication methods and that IP_{25} concentrations based on 7-hexylnonadecane as an internal standard are comparable using these methods. Recoveries of some more unsaturated HBIs and the internal standard 9-octylheptadecene, however, were lower with the ASE procedure, possibly due to partial degradation of these more reactive chemicals as a result of higher temperatures employed with this method. For future measurements, we recommend the use of reference sediment material with known concentration(s) of IP_{25} for determining and routinely monitoring instrumental response factors. Given the significance placed on the presence (or otherwise) of IP_{25} in marine sediments, some further recommendations pertaining to quality control are made that should also enable the two main anomalies identified here to be addressed.

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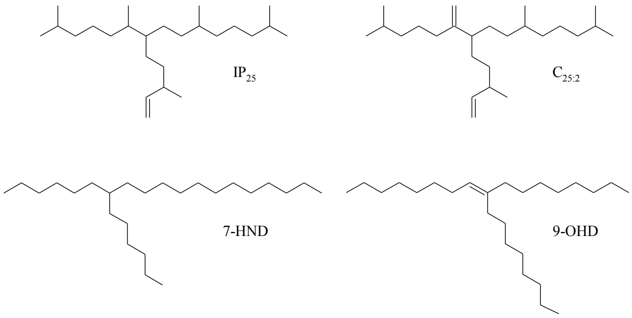

Fig. 1. Structures of IP_{25}, $C_{25:2}$ and internal standards (7-HND and 9-OHD).

1 Introduction

The reconstruction of past sea ice conditions in the Arctic and Antarctic is key for understanding past environmental changes on Earth and for informing climate prediction models. However, few detailed records of polar sea ice exist beyond the historical or observational records and, in any case, are highly variable in terms of spatial and temporal assessment. In recent years, a number of proxy-based approaches to sea ice reconstruction have been developed and employed to provide new insights into sea ice conditions (and changes to these) for both the Arctic and the Antarctic (e.g. Gersonde and Zielinski, 2000; Knies et al., 2001; Sarnthein et al., 2003; de Vernal et al., 2005; Belt et al., 2007; Andrews, 2009; Armand and Leventer, 2010; Polyak et al., 2010; Massé et al., 2011; Stein et al., 2012). Many sea ice proxy methods are based on the characteristic signatures provided by various biological species that are either closely associated with, or influenced by, sea ice cover (e.g. de Vernal et al., 2005; Armand and Leventer, 2010; Belt and Müller, 2013; Cronin et al., 2013; Seidenkrantz, 2013). One of the most recent sea ice proxy developments has been the analysis of a biomarker lipid, termed IP_{25} (Fig. 1), that is biosynthesised by Arctic sea ice diatoms during the spring bloom and, upon ice melt, is deposited into underlying sediments (Belt et al., 2007). IP_{25} has not been observed in sea ice or sediments from the Antarctic or from open water phytoplankton from both polar regions, so its occurrence in Arctic sediments appears to provide a selective signal of seasonal Arctic sea ice. A further feature of IP_{25} is its distinctive isotopic (^{13}C) signature, which is characteristic of a sea ice origin (Belt et al., 2008). Importantly, this isotopic signature is retained for sedimentary IP_{25} (Belt et al., 2008), which provides further evidence for an exclusive sea ice source.

The extent to which this qualitative proxy measure can be extended to provide more quantitative accounts of past Arctic sea ice, however, requires a greater understanding of the production (e.g. identification of the diatoms that produce IP_{25}) and fate (e.g. transfer through the water column) of IP_{25} as described by Belt and Müller (2013). Nevertheless, sedimentary abundances of IP_{25} in marine sediments from various Arctic regions covering a broad range of geological intervals are normally consistent with known sea ice conditions or those inferred from other environmental variables (Massé et al., 2008; Müller et al., 2009, 2012; Vare et al., 2010; Tolosa et al., 2013). In any case, it is clear that the reliable identification and quantification of IP_{25} is essential if palaeo sea ice reconstructions based on this biomarker are to be interpreted and used with confidence. A detailed experimental protocol for the measurement of IP_{25} in sediments has been reported recently (Belt et al., 2012b) and some key aspects relating to quality control are also provided as part of this method. However, as far as we are aware, the extent to which this or alternative protocols have been followed or evaluated by different laboratories is not known. The assessment of experimental approaches is further restricted by the general lack of detail that exists in the majority of methodological descriptions in the literature.

In the current study, we have carried out a multi-laboratory investigation into the identification and quantification of IP_{25} in a series of marine sediments, made comparisons between the outcomes from different laboratories and identified some further recommendations for performing such measurements in the future. This type of inter-laboratory investigation has been carried out previously for other organic geochemicals including those used for sea surface temperature reconstruction via the $U_{37}^{K'}$ and TEX_{86} indices (e.g. Rosell-Melé et al., 2001; Schouten et al., 2009).

2 Study design

A general recommendation was made at the 1st PAGES Sea Ice Proxy (SIP) meeting (Montreal, 2012) that an inter-laboratory investigation into the measurement of IP_{25} in marine sediments would add to the value of studies based on this biomarker in the future. Therefore, a number of laboratories were contacted who had either contributed to published IP_{25} data or were known to be planning to do so. The invitation consisted of a description of the basic aims of the study and a timescale within which to carry out the analyses and report back findings. Agreement was obtained from 9 laboratories. Since one laboratory offered to provide data from 2 different researchers, 10 potential datasets were available. In practice, 2 laboratories were not able to provide data by the deadline, so the outcomes presented here represent the output from 7 laboratories and one pseudo-duplicate (2 researchers from the same laboratory (A1 and A2)).

At an early stage, it was decided to focus the study on a small number of specific objectives and to limit these to the type of data that has (so far) been reported in the literature. Thus, each laboratory was asked to carry out the analysis of IP_{25} in a number of marine sediment samples and report concentration values in mass (IP_{25})/mass (dry sediment). As a result, the main outcomes represent comparisons between concentration data derived from the overall analytical procedure conducted in each laboratory rather than on individual steps such as the extraction method, any purification steps or instrumental set-up (GC-MS). That said, the documenting of some procedural elements by each laboratory and a small amount of follow-up analysis has also enabled the significance of some of the different experimental aspects (e.g. sediment extraction method) to be examined in more detail. Samples were sent to laboratories in January 2013 and all analyses were completed by June 2013. Data were recorded in a standardised spreadsheet.

3 Experimental methods

3.1 Selection of samples

Marine sediment samples representing 5 different locations were taken from core material kept within the Plymouth laboratory. Three of the core locations were within the Canadian Arctic (CA) and sediments from these cores (S1, S2, S3) were known to contain variable amounts of IP_{25} (e.g. Belt et al., 2007, 2010; Vare et al., 2009). In order to provide a control sediment (S4), or one in which it was expected that IP_{25} would be absent, a 4th core location was chosen that corresponded to a region (SW Iceland; ca. 64° N, 24.5° W) where sea ice has not been observed in recent decades/centuries. Sediment was also taken from a further (5th) control study site (S5) from the Antarctic Peninsula (ca. 67.7° S, 68° W), since it is believed that IP_{25} is not present in sediments (or sea ice) from the Southern Ocean (e.g. Massé et al., 2011). For each CA core, sediment material was homogenised (pestle and mortar) and divided into 3 sub-samples. The same treatment was carried out for the 4th (2 samples) and 5th (1 sample) sediment samples. As such, each laboratory received 12 sediment samples and these were labelled randomly (A–L), including the triplicates, before distribution. None of the laboratories received any of the above information regarding the sediments and so were not influenced either by a knowledge of the origin of the material (and, therefore, of any presumed content) or by the notion of replicates which may also have influenced aspects of reproducibility. An additional comparison of the influence of extraction procedures was carried out on sediment obtained from the Fram Strait (ca. 81° N, 12° E; S6). A summary of the sediment samples is shown in Table 1.

In addition to the sediment samples, laboratories received 2 aliquots of partially purified sediment extracts (E1 and E2) that were obtained from S1 and S2. The aim of providing these additional samples was to attempt to identify any influences of instrumentation on final outcomes, thus removing potential differences introduced by other factors such as extraction procedures. Finally, each laboratory was sent a sample containing known relative concentrations of IP_{25} and two internal standards (7-hexylnonadecane (7-HND) and 9-octylheptadecene (9-OHD); Fig. 1) (Belt et al., 2012b) from which instrumental response factors could be determined.

Table 1. Description of sediments analysed in the current study.

Interlab ID	Description in text	Location	Lat/Long (Approx.)
A	S3	CAA 3	70° N, 123° W
B	S1	CAA 1	74° N, 91° W
C	S5	Antarctic Peninsula	67.7° S, 68° W
D	S2	CAA 2	69° N, 106.5° W
E	S2	CAA 2	69° N, 106.5° W
F	S3	CAA 3	70° N, 123° W
G	S4	SW Iceland	64° N, 24.5° W
H	S3	CAA 3	70° N, 123° W
I	S1	CAA 1	74° N, 91° W
J	S4	SW Iceland	64° N, 24.5° W
K	S1	CAA 1	74° N, 91° W
L	S2	CAA 2	69° N, 106.5° W
ASE/SON	S6	Fram Strait	81° N, 13° E

3.2 Treatment of data

All laboratories provided summaries of experimental procedures together with their raw data, descriptions of calculations and IP_{25} concentrations. The inclusion of all of these allowed any errors or variability between methods of calculation to be identified and resolved. For example, Belt et al. (2012b) have stated that concentrations of IP_{25} may be influenced by some interference from the GC-MS signal from a related di-unsaturated biomarker ($C_{25:2}$; Fig. 1) and have suggested an adjustment to accommodate this. For the current study, it was evident that some laboratories, but not all, had adopted this adjustment. Therefore, for the purposes of uniformity, some submitted concentration data were re-calculated in order that comparisons between laboratories could be made on an equivalent basis. For each laboratory, concentration data were analysed according to sediment number and type. Thus, mean, standard deviations and relative standard deviations (%RSD) were calculated for triplicate samples; the latter being used as an indication of variability between measurements. All extractions were carried out using the same mass of sediment (ca. 0.5 g).

4 Results and interpretation

4.1 Sediments from the Canadian Arctic

4.1.1 Intra- versus Inter-laboratory consistency

All 8 laboratories identified IP_{25} in each of the 9 sediments that were known to contain IP_{25} (S1, S2, S3; 3 samples of each). In the majority of cases, concentration data were submitted (or could be calculated from raw data) such that comparisons between outcomes obtained by using two different

Table 2. Summary of IP_{25} concentrations (ng g^{-1}) for all sediments and laboratories. Values correspond to mean ± sd (%RSD) and have been obtained using 9-OHD as an internal standard. Values are either rounded to the nearest integer (> 1) or shown to 1 significant figure (< 1). Data for S5, E1 and E2 from individual laboratories are single measurements. * Relative concentrations.

	S1	S2	S3	S4	S5	E1*	E2*
A1	1093 ± 132 (12)	60 ± 12 (20)	13 ± 0.5 (4)	0 ± 0 (0)	0	28	3
A2	1050 ± 83 (8)	64 ± 1 (2)	14 ± 2 (14)	0 ± 0 (0)	0	17	2
B	2775 ± 421 (15)	1342 ± 1394 (104)	275 ± 224 (81)	0 ± 0 (0)	0	16	2
C	1121 ± 65 (6)	108 ± 8 (7)	25 ± 2 (7)	9.4 ± 13 (141)	8.8	20	3
E	1071 ± 7 (0.6)	113 ± 2 (2)	27 ± 3 (11)	0 ± 0 (0)	0	17	2
F	3510 ± 694 (20)	184 ± 22 (12)	43 ± 0.9 (2)	0 ± 0 (0)	0	42	4
H	709 ± 25 (4)	87 ± 10 (11)	21 ± 0.3 (2)	1 ± 2 (104)	3.4	15	2
I	–	–	–	–	–	–	–
All	1619 ± 1050 (65)	280 ± 627 (224)	60 ± 115 (192)	2 ± 5 (325)	2 ± 3 (192)	22 ± 10 (43)	3 ± 0.8 (30)
All (-B)	1426 ± 1000 (70)	103 ± 44 (43)	24 ± 10 (43)	–	–	–	–

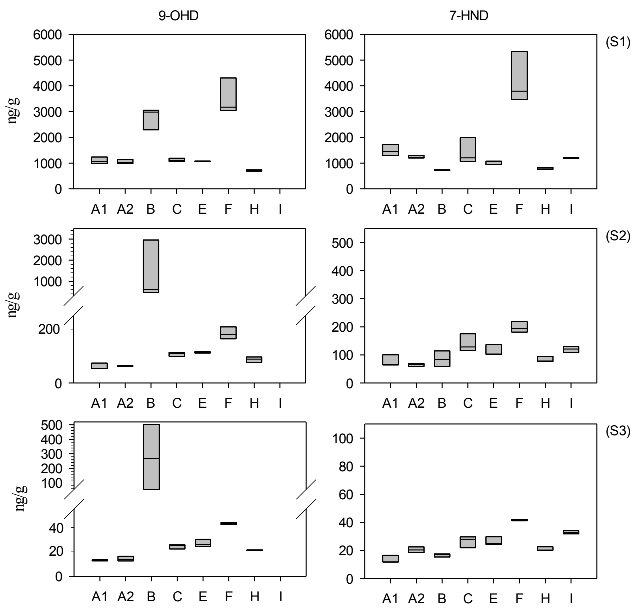

Fig. 2. IP_{25} concentration data for S1–S3 measured using two internal standards (9-OHD and 7-HND). In each case, the horizontal lines within each box correspond to the individual measurements within triplicates.

internal standards (7-HND and 9-OHD) could also be made. The IP_{25} (9-OHD) concentration data for S1–S3 are shown in Fig. 2 and Tables 2, 3. S1 had the highest IP_{25} content of the 3 IP_{25}-containing sediments and concentrations for most labs were ca. 1000 ng g^{-1}, although the values obtained from Labs B & F were ca. 3 times higher. However, Lab B also stated that they had previously experienced problems with consistency in the recovery of 9-OHD (attributed to an extraction method not employed by any of the other laboratories), which probably explains the higher mean and %RSD (15 %) values from this laboratory. Further, %RSDs for IP_{25} (9-OHD) concentration data from Lab B for S2 (104 %) and S3 (81 %) were even higher, so these concentration data were not included in the subsequent comparisons. Interestingly, the average (mean) of the individual %RSDs for each laboratory (8 %) was substantially lower than that for the overall %RSD for all (no Lab B) laboratories (70 %), suggesting greater intra-laboratory consistency than between laboratories for S1, at least.

When the analyses were carried out using 7-HND as the internal standard, the higher (and more variable) IP_{25} concentrations for Lab B were no longer observed, but the mean value from Lab F was still higher than for all other laboratories. In addition, the mean individual %RSD (12 %) was again notably lower than the corresponding value for all laboratories (74 %), and both of these were slightly higher than for 9-OHD.

The 2nd sediment (S2) contained IP_{25} at a concentration that was ca. 15 times lower compared to S1 (Fig. 2; Tables 2, 3). Similar to observations made for S1, the mean IP_{25} concentration obtained from Lab F was higher than for all other laboratories (using both internal standards). Similarly, individual %RSDs (9 % (9-OHD); 17 % (7-HND)) were noticeably lower than for all laboratories (43 % (9-OHD); 40 % (7-HND)). Finally, the IP_{25} concentration in S3 was ca. 60 times lower compared to S1 (Fig. 2; Tables 2, 3). Consistent with outcomes from S1 and S2, the mean IP_{25} concentration obtained from Lab F was higher than for all other laboratories (using both internal standards). Similarly, individual %RSDs (7 % (9-OHD); 10 % (7-HND)) were clearly lower than for all laboratories (43 % (9-OHD); 36 % (7-HND)). Finally, Labs H & I carried out triplicate analyses of each sediment extract (S1–S3) and, for these, %RSDs were ca. 2–4 % (i.e. lower than for triplicates of the same sediment sub-samples).

4.1.2 Analysis of standard sediment extracts

A number of factors may potentially contribute to the larger inter-laboratory variation compared to that observed within

Table 3. Summary of IP_{25} concentrations (ng g^{-1}) for all sediments and laboratories. Values correspond to mean ± sd (%RSD) and have been obtained using 7-HND as an internal standard. Values are either rounded to the nearest integer (> 1) or shown to 1 significant figure (< 1). Data for S5, E1 and E2 from individual laboratories are single measurements. * Relative concentrations.

	S1	S2	S3	S4	S5	E1*	E2*
A1	1491 ± 223 (15)	77 ± 20 (27)	13 ± 2 (21)	0 ± 0 (0)	0	41	3
A2	1239 ± 47 (4)	65 ± 5 (7)	20 ± 2 (10)	0 ± 0 (0)	0	34	3
B	730 ± 10 (1)	86 ± 28 (32)	17 ± 1 (7)	0 ± 0 (0)	0	21	3
C	1421 ± 494 (35)	140 ± 31 (23)	27 ± 4 (15)	9 ± 13 (141)	12	12	2
E	1023 ± 74 (7)	114 ± 19 (17)	26 ± 3 (12)	0 ± 0 (0)	0	18	2
F	4199 ± 996 (24)	197 ± 19 (10)	41 ± 0.5 (1)	0 ± 0 (0)	0	54	4
H	802 ± 38 (5)	84 ± 10 (12)	21 ± 1 (7)	2 ± 2 (105)	4	18	2
I	1190 ± 26 (2)	120 ± 12 (10)	33 ± 1 (4)	3 ± 3 (104)	9	34	4
All	1512 ± 1121 (74)	110 ± 44 (40)	25 ± 9 (36)	2 ± 5 (280)	3 ± 5 (156)	29 ± 14 (49)	3 ± 0.7 (25)

Table 4. Instrumental (GC-MS) response factors (RF) for IP_{25} versus different internal standards (IS) and monitoring ions (m/z) from various laboratories. Each RF has been obtained from the peak area ratio IS/IP_{25} using a standard solution containing equal concentrations of each analyte. *calculated from a reference sediment of known IP_{25} concentration.

	A1	A2	B	C	E	F	H	I
9-OHD (350)	6.2	6.2	3.9	9.1	3.6	7.7	6.9	–
7-HND (99)	27.6	27.6	–	23.8	7.1	37.9	21.2	6.4
7-HND (266)	–	–	29.6 (30.3*)	26.3	–	8.8	–	22.8

individual laboratories. Such factors relate to the sample treatment steps (e.g. extraction), while others pertain to the instrumental analysis (GC-MS). For the latter, a key parameter used during the conversion of raw GC-MS peak integration data into analyte (e.g. IP_{25}) concentration is the instrumental response factor (RF). The RF reflects the relative GC-MS responses of (in this case) IP_{25} and an internal standard, so that peak area ratios of these can be further normalised to obtain true concentrations. As such, any differences in peak ratios that are likely obtained from a sample containing the same concentration but analysed on different GC-MS instruments can be accommodated once the corresponding RFs have been applied. Instrument-specific RFs can be determined by analysis of solutions of IP_{25} and internal standards with known concentrations. In the current study, such a solution was prepared in the Plymouth laboratory using a standard of IP_{25} obtained from a large-scale sediment extraction (Belt et al., 2012a) and internal standards synthesised previously (Belt et al., 2012b). Aliquots of this mixture were then analysed by each laboratory to obtain individual RFs (Belt et al., 2012b) and these were found to be different, as expected (Table 4). Individual RFs were used, however, in the calculation of IP_{25} concentrations for S1–S3, so outcomes are directly comparable.

If the determination of individual RFs using this approach is robust, then the larger observed inter-laboratory variation in IP_{25} concentration should, presumably, reflect differences in extraction and/or purification efficiency prior to analysis by GC-MS. However, the evaluation of individual extraction and purification steps is challenging to achieve, in practice. Instead, for the current study, we evaluated the reliability of the measurement of individual RFs by examination of 2 further sediment extracts (provided by the Plymouth laboratory) obtained using a common extraction and partial purification process. Thus, analysis of aliquots of these extracts (E1 and E2) by each laboratory should have yielded closely matched IP_{25} concentrations if respective RFs had been determined accurately.

Each laboratory identified IP_{25} in E1 and E2, consistent with the outcomes from the sediment extraction component of the study. In each case, GC-MS responses for IP_{25} were normalised to those of the two internal standards and the instrumental response factors determined from the mix of standards described previously. This calculation therefore yielded relative IP_{25} concentrations that could be compared between laboratories. The data summarised in Tables 2, 3 show a clear variation in relative concentrations between laboratories and these differences are further highlighted from %RSD data. Thus, %RSDs for E1 (43 % (9-OHD) and 49 % (7-HND)) and E2 (30 % (9-OHD) and 25 % (7-HND)) were similar to those found for sediment samples S1-S3 for all laboratories (Tables 2, 3) and higher than %RSDs within each

Table 5. Summary of DIP_{25} ratios for all sediments and laboratories. Values correspond to mean ± sd (%RSD) and are either expressed to 1 decimal place (> 0.1) or 1 significant figure (< 0.1). Data without error estimates correspond to single measurements.

	S1	S2	S3	S4	S5	E1	E2
A1	1.0 ± 0.01 (0.6)	1.1 ± 0.06 (5.2)	0.5 ± 0.04 (8.2)	–	–	0.9	1.2
A2	1.1 ± 0.04 (3.8)	1.2 ± 0.07 (5.8)	0.9 ± 0.1 (12.8)	–	–	1.0	1.2
B	1.0 ± 0.1 (11.2)	0.7 ± 0.4 (57.5)	0.6 ± 0.3 (58.0)	–	–	1.0	1.0
C	0.02 ± 0.003 (18.1)	0.04 ± 0.01 (32.7)	0.1 ± 0.03 (41.5)	0.1	0.1	1.1	1.2
E	0.9 ± 0.01 (1.0)	1.1 ± 0.01 (1.1)	0.9 ± 0.12 (13.6)	–	–	0.9	1.0
F	1.0 ± 0.05 (4.8)	1.2 ± 0.2 (12.6)	0.9 ± 0.03 (3.4)	–	26.0	1.0	1.2
H	1.2 ± 0.02 (1.3)	1.4 ± 0.04 (3.0)	1.2 ± 0.05 (4.3)	1.4 ± 0.1 (4.9)	25.3	1.3	1.4
I	1.0 ± 0.02 (1.8)	1.0 ± 0.002 (0.2)	0.9 ± 0.03 (3.2)	0.9 ± 0.1 (9.5)	15.3	1.3	1.4
All	0.9 ± 0.4 (39.8)	1.0 ± 0.4 (44.0)	0.7 ± 0.4 (47.3)	0.9 ± 0.5 (44)	16.7 ± 12.1 (73)	1.0 ± 0.1 (12)	1.2 ± 0.1 (13)
All (-C)	1.0 ± 0.4 (34.9)	0.8 ± 0.3 (30.0)	1.1 ± 0.4 (38.7)	–	–	–	–
All (-B&C)	1.0 ± 0.1 (11.7)	1.2 ± 0.2 (12.9)	0.9 ± 0.2 (24.9)	–	–	–	–

laboratory (often < 10 %; Tables 2, 3). Since these differences cannot be explained by variations in extraction efficiency or subsequent work-up, it may be assumed that the primary (or only) reason for variation across these measurements is due to inaccuracy in the determination of individual instrumental RFs for IP_{25} using the approach taken (mix of standards). In order to investigate a potential reason for this, one of the aliquots containing standards of IP_{25}/7-HND/9-OHD was returned to the Plymouth laboratory and re-analysed using GC-MS. Significantly, the response factor was ca. twice the original value (pre-distribution), presumably reflecting a change in composition of the mix of standards at some point. Further, this change was associated with the mix of standards used by Lab F, whose reported IP_{25} concentrations from S1–S3 were consistently higher than those from other laboratories (Fig. 2). As such, not only do these data demonstrate clearly the importance of instrumental response factors when calculating absolute IP_{25} concentrations, but also that determining these accurately is not a trivial exercise, even when the relevant standards are available.

4.1.3 Analysis of the DIP_{25} ratio

Although the main focus of the current study was on the measurement of IP_{25}, each laboratory also collected GC-MS data for a closely related di-unsaturated HBI ($C_{25:2}$; Fig. 1). $C_{25:2}$ is also known to be produced by Arctic sea ice diatoms (Belt et al., 2007; Brown et al., 2011) and its concentration in underlying sediments is normally strongly correlated with that of IP_{25} (e.g. Vare et al., 2009; Cabedo-Sanz et al., 2013). In some previous studies, it has been suggested that the $C_{25:2}$ / IP_{25} ratio (the so-called DIP_{25} index; Cabedo-Sanz et al., 2013) may provide further insights into Arctic sea ice conditions (e.g. Fahl and Stein, 2012; Stein et al., 2012; Cabedo-Sanz et al., 2013; Xiao et al., 2013) although this is in need of further investigation. In terms of the current study, the occurrence of both biomarkers within the sediments, compared with the addition of internal standards prior to extraction, provided the opportunity to examine a different aspect of reproducibility.

DIP_{25} ratios were calculated from the peak areas of $C_{25:2}$ (m/z 348) and IP_{25} (m/z 350) as per the recommendation of Cabedo-Sanz et al. (2013). Consistent with previous observations, DIP_{25} ratios were generally ca. 1, although there was some small variation between sediments (S1–S3) and the majority of laboratories (Table 5). Exceptionally, DIP_{25} values from Lab C were particularly low, and this was subsequently shown to be attributable to the partial purification step of sediment extracts (use of alumina rather than silica in the chromatography step reduces the recovery of $C_{25:2}$) prior to analysis by GC-MS. Further, DIP_{25} ratios from Lab B were much more variable within triplicates than for other laboratories, with %RSDs for S2 and S3 being particularly high (> 50 %), probably due to greater variability in the extraction efficiency for $C_{25:2}$ with the extraction method (ASE) used by this laboratory (see Sect. 4.4). Consequently, DIP_{25} data from Labs B & C were not included in further comparisons. For the remaining laboratories, mean %RSDs were lower for individual laboratories than %RSDs for the collective datasets, consistent with the observations made previously for IP_{25} alone; however, both of these measures of variability were lower than for the corresponding values for IP_{25}. This probably reflects the difference between the extraction of 2 near identical analytes already contained within the sediment (IP_{25} and $C_{25:2}$) versus an analyte (e.g. IP_{25}) and a somewhat different internal standard (e.g. 7-HND) that has been added to the sediment matrix and may not behave in the same way as the analyte during extraction. Significantly, the mean %RSDs for DIP_{25} values for all laboratories (no Labs B & C) for the sediments S1 (11.7 %) and S2 (12.9 %) were virtually identical to those for extracts E1 (11.9 %) and E2 (12.6 %) that were obtained from additional samples of the same sediments (Table 5). These data show that, while intra-laboratory consistency in deriving DIP_{25} ratios is very good, agreement between laboratories is less so, but largely independent of extraction method (Labs B & C excluded).

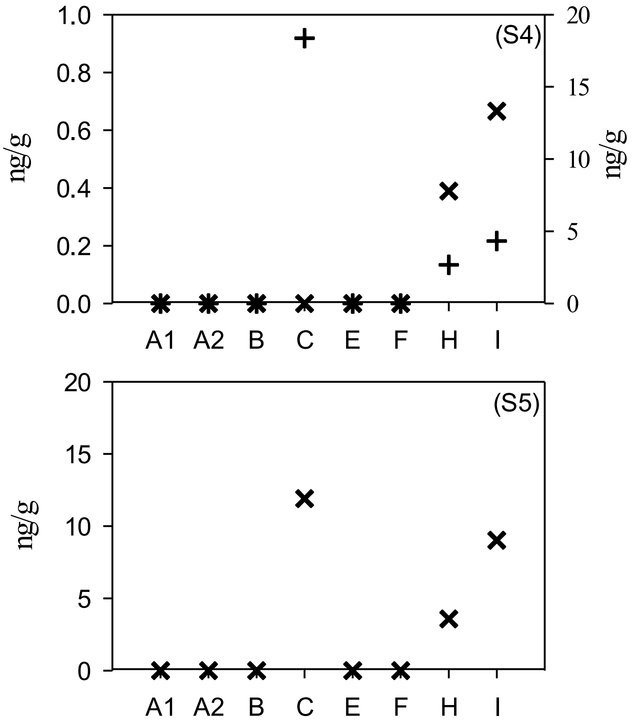

Fig. 3. Top: IP_{25} concentrations in north Atlantic sediments (S4). Individual values within duplicates are represented by: left axis (X) and right axis (+). Bottom: Concentrations of IP_{25} in sediment from the Antarctic Peninsula (S5).

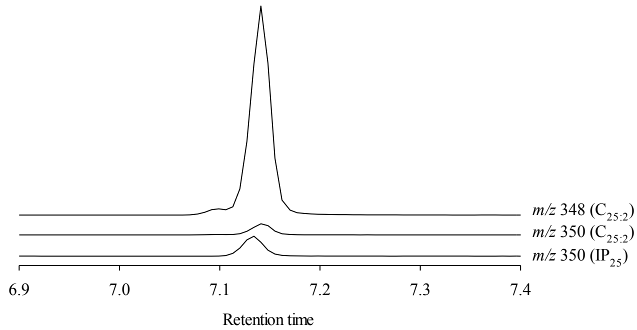

Fig. 4. Partial SIM chromatograms obtained from purified standards of $C_{25:2}$ and IP_{25}. The m/z 348 peak is due to the molecular ion of $C_{25:2}$ while the smaller contribution from m/z 350 (M+2 ion) for the same biomarker is shown in the middle chromatogram. The bottom chromatogram (m/z 350; IP_{25}) illustrates the (partial) chromatographic overlap between IP_{25} and $C_{25:2}$.

Thus, inter-laboratory variation in DIP_{25}, like with IP_{25} concentrations, likely arises from differences in RFs between analytes ($C_{25:2}$ and IP_{25}). Previously, Cabedo-Sanz et al. (2013) suggested that determining DIP_{25} ratios using relative peak areas of m/z 348 ($C_{25:2}$) and m/z 350 (IP_{25}) was probably a more reliable method than using concentrations of the two biomarkers, especially when comparing DIP_{25} ratios from different laboratories; however, the data here suggest that RFs for $C_{25:2}$ and IP_{25} can vary substantially between different GC-MS instruments, despite the structural similarity between the two biomarkers and their monitoring MS ions (m/z 348 and 350, respectively).

4.2 Sediments from the North Atlantic

Two of the 12 sediment samples represented homogenised material from a core obtained from SW Iceland. Samples of this sediment had previously been analysed by Lab A2 and no IP_{25} had been detected. As such, it was considered to be a suitable reference sediment or blank. The individual S4 sediment samples were labelled G and J during the study (Table 1). IP_{25} was not identified by 5 out of the 8 laboratories consistent with the previous finding of Lab A2. However, Lab C identified and quantified IP_{25} in sediment J but not G, while Labs H & I identified IP_{25} in both (Fig. 3; Tables 2, 3). Further, for Labs H & I, there was a large difference in the relative concentrations of IP_{25} between sediments G and J. Thus, the reported IP_{25} concentration was 6-7 times larger in J than for G (for both Labs H & I) (Fig. 3; Tables 2, 3), despite these sediments being duplicates.

At this stage, we do not have a definite explanation for these anomalies, but it is feasible that Labs C/H/I have increased limits of detection/quantification compared to the other laboratories; however, this explanation is not consistent with the failure for Lab C to detect IP_{25} in sediment G. Further, the large difference in IP_{25} concentration between sediments G and J reported by Labs H and I is not consistent with the reproducibility data obtained from S1–S3 previously. It is worth noting, however, that the sediment sample that immediately preceded sediment J was one of the S1 sub-samples (I; Table 1) with a particularly high IP_{25} content (mean ca. 1500 ng g^{-1}). Therefore, an alternative explanation for these anomalies may be the occurrence of some "carryover" during the laboratory work (e.g. extraction and partial purification) or within the analysis phase (GC-MS). This suggestion, however, could not be tested further given the information available.

4.3 Sediments from the Antarctic Peninsula

The final sediment within the full inter-laboratory study (S5) was taken from the Antarctic Peninsula, which, like sediment S4, was considered to represent a blank for IP_{25} since this biomarker has not been detected in sediments from the Southern Ocean (e.g. Massé et al., 2011). However, unlike S4, sediment S5 was taken from a region of known seasonal sea ice cover and the related di-unsaturated HBI biomarker ($C_{25:2}$) has been reported in sediments from such regions in the Antarctic. Indeed, the measurement of $C_{25:2}$ has been proposed as a proxy measure of sea ice when detected in Antarctic sediments (Massé et al., 2011).

IP_{25} was not identified in S5 by Labs A1/A2/B/E/F, but data attributable to IP_{25} were reported by Labs C/H/I (Fig. 3; Tables 2, 3). To explain this difference, we first note that all laboratories identified $C_{25:2}$ in S5 extracts (measured from m/z 348 data from the GC-MS analysis), although quantification of this biomarker was not carried out by all laboratories due to the absence of a GC-MS response factor. Previously, Belt et al. (2012b) described how the presence of one particular $C_{25:2}$ isomer (the one in the study here; Fig. 1) can potentially result in interferences in IP_{25} analysis. This occurs, firstly, due to the co-elution of IP_{25} and $C_{25:2}$ on relatively non-polar GC phases and secondly, since $C_{25:2}$ has an M+2 ion (m/z 350) that coincides with the monitoring ion for IP_{25}. A combination of these two factors means that sediments containing $C_{25:2}$ only, may also appear to contain IP_{25} if m/z 350 data are collected along with those for $C_{25:2}$ (m/z 348) (Fig. 4). The contribution from $C_{25:2}$ to the intensity of m/z 350 is relatively small (ca. 4 %) compared to that of m/z 348, so for sediments containing similar concentrations of IP_{25} and $C_{25:2}$, this interference is likely to be very small, especially when all other experimental factors are considered. In any case, this influence can be removed by appropriate subtraction of part of the $C_{25:2}$ signal (Belt et al., 2012b). In contrast, for sediments with no IP_{25} but abundant $C_{25:2}$, this interference needs more careful consideration. In the current study, the most conspicuous evidence that the apparent presence of IP_{25} in S5 can probably be attributed to this mass spectral interference is the magnitude of the $C_{25:2}/IP_{25}$ ratio or so-called DIP_{25} index (e.g. Cabedo-Sanz et al., 2013). For sediments containing both IP_{25} and $C_{25:2}$ (i.e. those from the Arctic), this ratio is normally in the range 1–3 (e.g. Cabedo-Sanz et al., 2013). In contrast, if the mass spectrometric interference from $C_{25:2}$ is assumed to be ca. 4 % (Belt et al., 2012b), then the DIP_{25} value is likely to be > 20 for sediments that contain $C_{25:2}$ only. Significantly, the S5 DIP_{25} values for Labs H/I were both > 15, suggesting that the apparent presence of IP_{25} in these extracts can probably be explained by mass spectrometric interference from $C_{25:2}$.

This chromatographic/mass spectrometric interference does not explain the apparent identification of IP_{25} in S5 by Lab C, since the DIP_{25} value for this extract was 0.1. However, at the time of carrying out the study, this laboratory was having difficulties in the purification and analysis of $C_{25:2}$, so this value cannot be considered with confidence. It is also noted that, like sediment J (see Sect. 4.2), the sediment from the Antarctic Peninsula (S5 here; sediment C in the original sequence; Table 1) followed a sediment with an especially high IP_{25} content (S1; sediment B), so some carryover may also have occurred with this sample.

It is also worth noting that this type of potential interference cannot be used to explain the anomalies in the S4 data (Labs C/H/I) since the DIP_{25} ratios for these extracts were all low (< 1.5; Table 5).

Table 6. Relative concentrations of biomarkers measured against 2 internal standards (7-HND & 9-OHD) and IP_{25} using different extraction methods – Accelerated Solvent Extraction (ASE) and sonication (SON). Values correspond to the ratios of mean values (from triplicates) of each Analyte/Reference derived from each method expressed as a percentage – i.e. [mean (ASE)/mean (SON)] × 100.

Reference	Analyte	S1	S2	S3	Mean
7-HND	IP_{25}	104	106	99	103
	$C_{25:2}$	98	96	97	96
	$C_{25:3}$ (Z)	78	75	82	79
	$C_{25:3}$ (E)	82	78	79	80
	9-OHD				90
9-OHD	IP_{25}	112	117	110	113
	$C_{25:2}$	105	105	109	106
	$C_{25:3}$ (Z)	84	82	92	86
	$C_{25:3}$ (E)	88	86	89	88
IP_{25}	$C_{25:2}$	94	90	98	94
	$C_{25:3}$ (Z)	75	71	83	77
	$C_{25:3}$ (E)	78	74	80	78

4.4 Influence of extraction method

Within the current study, we have not carried out a comprehensive assessment of the influence of the extraction procedure on the determination of IP_{25} concentration; largely, due to the difficulties in examining this parameter in a systematic and isolated manner, but also because most laboratories adopted the same basic method of extraction (sonication (SON)) and purification as described by Belt et al. (2012b). The exception to this was Lab B, who used an Accelerated Solvent Extraction (ASE) method for extracting sediments (e.g. Müller et al., 2011; Fahl and Stein, 2012; Stein et al., 2012; Stein and Fahl, 2013). Since sonication and ASE represent the two extraction methods used in published work, we decided to carry out a preliminary comparison of them and this was achieved in two ways. Firstly, Lab A2 (sonication) and Lab B (ASE) each obtained 9 further extracts from 3 sets of triplicate samples from S1-S3 (randomly sequenced as before). These were then analysed (following partial purification), back-to-back, by Lab A2, using the same GC-MS instrumentation, so the only difference between the two sets of samples was the extraction step. Mean IP_{25} (and other HBI) concentrations were calculated from each set of triplicates and the ASE/SON ratios (expressed as a %) of respective values were compared. For IP_{25} measured against 7-HND, the mean ASE/SON ratios were 104, 106 and 99 % for S1, S2 and S3, respectively, with an overall mean of 103 % demonstrating excellent agreement between the two extraction methods. The corresponding values for IP_{25} against 9-OHD were slightly higher (mean 113 %; Table 6), however, indicating a small loss of 9-OHD during the extraction step. This was further verified by calculation of the ratio

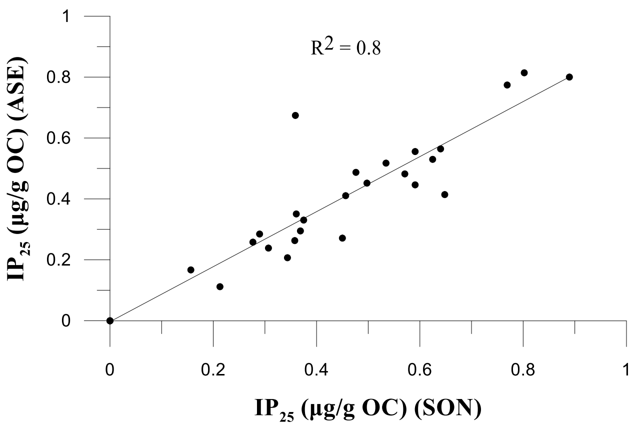

Fig. 5. Comparison of IP_{25} concentration data obtained following extraction of sediment material using Accelerated Solvent Extraction (ASE) and sonication (SON) methods. Concentrations have been normalised to total organic carbon (TOC) in each case.

(ASE/SON) of mean 9-OHD/7-HND values for all samples (90 %; Table 6).

Similar ASE/SON ratios were found for $C_{25:2}$ (7-HND) (Table 6) with an overall mean of 97 %, although overall mean DIP_{25} ratios between the two methods indicated a small (ca. 5 %) depletion of this biomarker relative to IP_{25} (Table 6). This depletion was more noticeable, however, for two tri-unsaturated HBIs (*Z* / *E* $C_{25:3}$; Belt et al., 2000), with ASE / sonication ratios (7-HND) of ca. 80 % (Table 6). For both $C_{25:2}$ and $C_{25:3}$, ASE/sonication ratios were again higher for 9-OHD compared to 7-HND normalised data, likely for the same reasons identified previously for IP_{25} concentrations.

Second, IP_{25} concentration data were obtained on additional sediment material using sonication and ASE extraction methods (S6; Table 1) by the same laboratory (Lab B). On this occasion, IP_{25} concentration was observed to vary downcore, but there was a good correlation between values obtained by each extraction method (Fig. 5).

These data suggest that recoveries using the ASE extraction method may depend on the unsaturation for both HBIs and internal standards, with those containing a larger number of double bonds and/or tri-substituted double bonds (e.g. 9-OHD and $C_{25:3}$) exhibiting lowest recoveries, likely as a result of the higher temperatures associated with the ASE method leading to some degradation of these more reactive chemicals. Further, re-analysis of the original Lab B extracts by Lab A2 (data not shown) suggests that the slightly lower recoveries for ASE for $C_{25:2}$, $C_{25:3}$ (and 9-OHD) are not consistent and may require further investigation before interpretations based on the concentrations of these HBIs (and internal standard) using this extraction method are to be carried out with confidence. In contrast, on the basis of the data obtained in the current study, IP_{25} concentrations derived following extraction using the ASE method (and 7-HND as an internal standard) appear to be extremely similar to those obtained using sonication.

5 Key outcomes and recommendations

The structure of this investigation, together with the outcomes presented here, enable 4 key outcomes to be identified.

First, there is the significance of the GC-MS RF. The identification of IP_{25} in all S1-S3 sediments is encouraging from a basic analytical point-of-view and the generally good agreement (< 10 % %RSD) for triplicates within laboratories provides a useful outcome when it comes to how relative changes of IP_{25} (e.g. downcore) are interpreted. %RSDs for individual laboratories were slightly lower overall when IP_{25} concentrations were determined using 9-OHD compared to 7-HND (see Sect. 4.1.1), but this trend was not systematic for each laboratory so we find no compelling reason to recommend the use of either internal standard over the other (note: the exception to this concerns the use of 9-OHD using the ASE extraction method (see later)). In contrast, the greater variation in IP_{25} concentration determinations observed between laboratories for the same sediment requires further attention. Here, we attribute these enhanced variations to inaccuracy in the determination of instrumental RFs. With the exception of Lab B, such RFs were calculated using a mixture of standards of known concentration, but this method appears not to have been robust for the current study. The reason for this is not clear, but may, in part, be due to the difficulties with working with ultra-low quantities of IP_{25} and internal standards, especially as it is known that significant losses of IP_{25} can occur during blow-down of extracts (Belt et al., 2012b). In any case, given the lack of availability of large quantities of authentic and pure IP_{25} that would otherwise enable standard solutions to be prepared with greater analytical reliability, it is important to identify an alternative means by which individual RFs can be determined and monitored on a routine basis. The approach taken previously by Lab B (and used in the current study) has been to calculate RFs on the basis on GC-MS responses of IP_{25} in sediment material with known concentration (e.g. Müller et al., 2011; Fahl and Stein, 2012; Stein et al., 2012; Stein and Fahl, 2013). The success of this approach depends clearly on the certainty of the IP_{25} concentration; however, it is worth noting that, for the current study, there was only a 2 % difference between the RF for IP_{25} (7-HND) calculated by this reference sediment approach and one determined from the mix of standards. In addition, determination of RFs using the reference sediment approach also integrates aspects of extraction and purification differences that may exist between laboratories, in addition to those associated with the GC-MS instrumentation. As such, we strongly recommend the use of a reference sediment with known IP_{25} concentration for the determination of procedural (including instrumental) RFs. We also believe that determination of RFs should be carried out as part of routine quality control procedures (see below) since the magnitude likely varies with instrumental operating conditions, and the same checks should also be made when calculating other ratio-based measurements such as the DIP_{25} ratio.

The second key outcome relates to the data obtained from S4. On the basis of prior analysis, this sediment was thought to contain no IP_{25}, consistent with the location from which the sediment was obtained (SW Iceland). However, although 5 laboratories did not identify IP_{25}, as expected, this biomarker was detected and quantified by 3 (Labs C/H/I; Fig. 2). We are unable to provide a definitive explanation for this anomaly on the basis of information available, but we suggest that it either reflects differences in limits of detection between laboratories or is due to contamination or misidentification of IP_{25}. We believe that all of these demand serious attention, especially as sea ice reconstruction studies carried out thus far have depended critically, not only on the variable abundance of IP_{25} (see Belt and Müller, 2013 for a review) but also on its presence/absence (e.g. Axford et al., 2011; Belt and Müller, 2013; Cabedo-Sanz et al., 2013; Méheust et al., 2013; Navarro-Rodriguez et al., 2013; Stoynova et al., 2013). As a further recommendation from this study, therefore, we propose that laboratories not only measure, but report, certain aspects pertaining to figures of merit for their analytical procedure, including assessments of precision (e.g. through %RSDs determined from replicate analyses of reference sediments or those under study), limits of detection (e.g. from signal/noise ratios) and descriptions of methods used to ensure unambiguous biomarker identification. For the latter, Belt et al. (2012b) have previously described the potential pitfalls associated with using GC-MS SIM methods for definitive identification of IP_{25} along with recommendations for addressing these. For example, in instances where IP_{25} cannot be identified unambiguously via its mass spectrum due to interference from co-eluting analytes, identification of IP_{25} via GC-MS SIM methods should not rely on the basis of the m/z 350 ion alone. We also encourage analysts to determine the stable isotopic composition ($\delta^{13}C$) of IP_{25}, where possible, to confirm its sea ice origin (Belt et al., 2008). In terms of contamination, such an influence is likely to be random rather than systematic, so adequate control of procedures (*Quality Control*) should be introduced, maintained and reported, in order that a consistently high standard of data can be claimed (*Quality Assurance*) and independently evaluated. In addition, since contamination (if relevant) cannot be assumed to be consistent and low for all analyses, it needs to be taken seriously; not least because concentrations of IP_{25} reported for S4 in the current study are comparable to (or greater than) those reported for IP_{25} in previously published work.

A third key outcome from this study pertains to the data derived from S5, which was sediment obtained from the Antarctic Peninsula, where IP_{25} is absent, but the related biomarker $C_{25:2}$ is often present (e.g. Massé et al., 2011). Previously, Belt et al. (2012b) explained the origin of the potential interference of $C_{25:2}$ on IP_{25} measurements which, in brief, relates to the overlapping chromatographic (GC) and mass spectrometric (MS) properties of the two biomarkers. The current study, however, represents a tangible and realistic example of this interference and, as already discussed (Sect. 4.3), the apparent detection of IP_{25} by Labs H/I is likely explained by this phenomenon. Interestingly, in the original dataset submitted by Lab F, the absence of IP_{25} only became evident once the influence of the mass spectral interference from $C_{25:2}$ had been subtracted from the observed m/z 350 intensity (note that the DIP_{25} ratio (26.0; Table 5) also verifies the occurrence of $C_{25:2}$ only; Sect. 4.3). Since it became clear, therefore, that the apparent presence/absence of IP_{25} might depend on whether this correction had been applied, we believed it important to determine to what extent other laboratories had made these corrections or assumptions during data work-up and submission. Therefore, Labs A1/A2/E were asked to clarify the absence of IP_{25} in their S5 extracts. In response, each laboratory stated that a GC-MS response had been detected at m/z 350 but, since its intensity was significantly lower than that of m/z 348 ($C_{25:2}$), it had been assumed to be due to the mass spectrometric interference from $C_{25:2}$ (as described above) and not IP_{25}. As such, the m/z 350 signal was ‘ignored’ or submitted as 0 by these laboratories, although (unlike Lab F) this was not evident from the originally submitted data. Labs H & I did not make the same assumption or correction and this may have been partly due to the blind nature of the samples (i.e. the laboratories were not aware that S5 came from the Antarctic Peninsula). Arguably, the interference of $C_{25:2}$ might have been clearer if the identity of S5 had been known; however, $C_{25:2}$ is common in the geosphere (e.g. Rowland and Robson, 1990; Johns, 1999; Johns et al., 1999) and its potential impact on the apparent occurrence of IP_{25} in a range of environmental settings, especially those which are free of sea ice, cannot be underestimated. Therefore, we also recommend that studies based on IP_{25} should be considered with caution unless they are accompanied by parallel determinations of $C_{25:2}$ and an evaluation of relative responses of these biomarkers (e.g. via the DIP_{25} index).

Finally, we have demonstrated that for the common methods of extraction reported previously (i.e. sonication and ASE), IP_{25} concentration determinations are comparable when using 7-HND as an internal standard, but that (inconsistent) losses can arise when using 9-OHD with the ASE method. Similarly, extraction efficiencies of more unsaturated HBI lipids (e.g. $C_{25:2}$ and $C_{25:3}$) appear to be lower and more variable with the ASE method, possibly as a result of a combination of the higher temperatures associated with the extraction procedure (typically 100 °C; Xiao et al., 2013) and the higher reactivity of lipids containing di- and tri-substituted double bonds.

6 Conclusions

In recent years, a growing number of laboratories have carried out the analysis of the Arctic sea ice biomarker IP_{25} (and related HBI lipids) in marine sediments and we anticipate that this will increase in the future. The outcomes of the current study demonstrate the importance of carrying out, and reporting in detail, accurate and quality controlled analytical measurements if interpretations based on this biomarker are to be made with confidence. Although beyond the scope of the current investigation, there remain other factors that still need addressing before the palaeoclimatic interpretations of IP_{25} presence and abundance can be fully understood (Belt and Müller, 2013). Continuing the analytical theme, one such factor includes appropriate calibration of IP_{25} concentrations with known sea ice conditions using the approaches of Müller et al. (2011), Navarro-Rodriguez et al. (2013) and Stoynova et al. (2013). Of particular importance, in this respect, will be the establishment of threshold levels of sedimentary IP_{25}, below which, sea ice reconstruction is considered unreliable. Such a threshold maybe be regional, in practice, especially given the broad range of IP_{25} concentrations found for different Arctic regions, including those with similar ice cover (Belt and Müller, 2013; Stoynova et al., 2013). Given the rapid and on-going advances in sensitivity enhancement associated with modern GC-MS instrumentation, establishing or proposing such thresholds is likely to become increasingly important for IP_{25}-based studies.

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