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The determination of volatile amines in aquatic marine systems: A review

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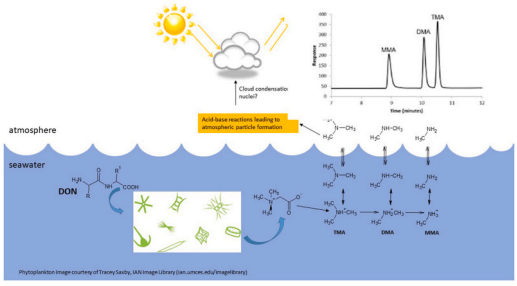
HIGHLIGHTS

- Methylamines (MAs) are ubiquitous in seawater and sediments.
- They could be involved in reactions affecting cloud formation.
- They are challenging to analyse due to their polarity and low molecular weight.
- Analytical methods usually involve pre-concentration due to low concentrations.
- A range of reported methods is examined to highlight strengths and limitations.

GRAPHICAL ABSTRACT



ABSTRACT

This review provides a critical assessment of knowledge regarding the determination of volatile, low molecular weight amines, and particularly methylamines, in marine aquatic; systems. It provides context for the motivation to determine methylamines in the marine aquatic environment and the analytical challenges associated with their measurement.While sensitive analytical methods have been reported in recent decades, they have not been adopted by the oceanographic community to investigate methylamines' biogeochemistry and advance understanding of these analytes to the degree achieved for other marine volatiles. Gas chromatography, high performance liquid chromatography, ion chromatography and infusion-mass spectrometry techniques are discussed and critically determined, alongside offline and online preconcentration steps. Interest in the marine occurrence and cycling of methylamines has increased within the last 10–15 years, due to their potential role in climate regulation. As such, the need for robust, reproducible methods to elucidate biogeochemical cycles for nitrogen and populate marine models is apparent. Recommendations are made as to what equipment would be most suitable for future research in this area.

1. Introduction

1.1. Analytical context

Certain trace gases play critical roles in marine biogeochemical cycles, atmospheric chemistry and climate [1]. Marine phytoplankton synthesise organic compounds as osmolytes/cryoprotectants, including dimethylsulfoniopropionate and quaternary amines (QAs). The former has received attention, as a precursor of the cloud-promoting gas dimethylsulfide (DMS); however, amines may be equally important [2, 3]. Examples where amines are important in marine biogeochemical cycles include their use as compatible solutes in nature [4], and as a source of base to the atmosphere [2]. Nitrogen-containing osmolytes (N-osmolytes) such as glycine betaine, trimethylamine-N-oxide and choline are produced by phytoplankton to maintain osmotic pressure [5, 6]. These N-osmolytes can degrade to produce methylamines [7–11]. Recently, marine bacteria have been shown to use methylamines as a source of energy, remineralising the nitrogen to ammonium [12]. Further, methylamines (MAs) are required by bacteria for conversion of DMS to dimethylsulfoxide [13]. In dissolved gaseous form, MAs can

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diffuse across the sea-air interface to participate in climate-regulation processes. Indeed, atmospheric MA concentrations above 65 nmol m^{-3} could account for observed atmospheric particle-formation rates [2].

As the MAs are low molecular weight (below 100 Da), polar, basic compounds, their aqueous determination is challenging. This is particularly so at the concentrations reported for surface waters [14–18]. Difficulties include achieving adequate sample volumes [19], reliance on derivatisation [20,21], and the separation of chemically-similar analytes within the sample [22,23].

An understanding of the biogeochemical amine cycle requires methodology for measuring concentrations in both the aquatic and atmospheric environments. Analytical methods for the determination of amines in the atmosphere have been more widely reported [24,25] and reviews of atmospheric occurrence and behaviour are available [26,27], along with recent studies identifying atmospheric amines and their sources [28–30]. Analytical methods for the aquatic measurement of MAs have also been developed [31], and data reported for a number of marine environments. However, the paucity of available methods, and challenges in their application for non-specialists, appears to have held back understanding of MA occurrence and cycling in these environments. As such, the systematic measurement of MAs has not been achieved, nor has standardisation of methodology. Given the potential global importance of MA cycling, a key driver for this review is to document and evaluate the methodologies reported for the determination of low molecular-weight amines in aquatic systems, focussing on the methylamines, and better understand the merits and feasibility of analytical approaches. Through this process, a standardised approach to the measurement of these analytes might be achieved and their environmental significance robustly evaluated. Although this review focuses on methylated amines, the sampling, pre-concentration and detection techniques discussed should be applicable to other amines with similar physico-chemical characteristics (e.g. molecular weight and aqueous solubility), some of which have been detected in marine atmospheric and aerosol samples [16,32–35].

1.2. Methylamines

Amines have the general formula $R_nNH_{(3-n)}$; they are alkylated analogues of ammonia and N is in the −3 oxidation state. In seawater, the most commonly reported low molecular weight amines are the methylamines (MAs), which exist as primary (monomethylamine; MMA), secondary (dimethylamine; DMA) and tertiary (trimethylamine; TMA) molecules [14,16,19,32,33,36,37]. The MAs are highly soluble in water. At the pH of seawater they are predominantly cations, through protonation, but in equilibrium with their dissolved, gaseous forms. Table 1 shows physico-chemical data for the MAs.

As mentioned, the MA gaseous fraction can pass from water to the atmosphere, adding a source of base to the latter in the form of molecules that can interact with acidic species to produce cloud condensation nuclei [2,3]. In protonated form, the non-volatile MA faction can sorb to particles. They have been detected at micromolar levels in estuarine environments, fractionating between sediment porewaters and particles [15,38–41]. The sorptive interactions between the MA and a particle surface are similar to NH_3 and are shown in Fig. 1. An ionic bond can form between the protonated MA and a negatively-charged surface group on the particle. In the gaseous form, a primary or secondary MA can react with a carbonyl functional group (known as carbonyl addition) to form a covalent bond (this is not possible for TMA or QAs as the molecule must contain at least one N–H bond). Data from a study on amino acid interactions with particulates [44] indicates that ionic bonding should be the dominant sorption process for MAs in marine sediments due to the predominance of the protonated form at seawater pH. However, carbonyl addition may also occur, analogous to melaniodin-type reactions [44].

2. Sample collection, extraction and pre-concentration

2.1. Sample collection

The key challenges associated with the measurement of MAs in aquatic systems are: 1) low environmental concentrations of the analytes; 2) separation of the analytes from their environmental matrix to produce a 'clean' sample for determination; 3) preservation of analytes. Aqueous sample matrices can include, *inter-alia*, particulate matter, sediments and saline water, where marine or estuarine samples are of interest.

Reported concentrations of the MAs in porewaters and sediments vary from micromolar to nanomolar levels in estuarine and oceanic environments, respectively [14–17,37,39,40,45]. Pre-cleaning of all sampling apparatus is essential. Soaking all sampling and processing vessels in 10% HCl is recommended to minimise adsorption of the analytes following collection and prior to extraction and determination. The anticipated MA levels and pre-concentration steps included will dictate the sample mass and volumes needed to quantitatively detect the analytes. Sediment sample masses reported are typically 1–10 g, from which porewater may be separated and determined discreetly [15,38,39,45,46]. For seawater samples, volumes of 0.5–1.0 L have been reported [14,45], with each technique employing a pre-concentration step. Potential bacterial degradation of MAs must be taken into account if samples are stored. Cree et al. [14] found that MA concentrations reduced to below limits of detection in filtered seawater samples collected from the English Channel and determined, untreated, after 24 h. However, acidification of replicate samples with hydrochloric acid (1:1000 v/v) preserved the analytes; acidification was also employed by Yang et al. [45]. Acidification will also increase the protonated: gaseous ratios for the MAs, reducing the chances of analyte loss by diffusion if a headspace is present. Wang and Lee [40] used mercuric chloride ($HgCl_2$; 0.5 g L^{-1}) as a biocide and preservative; however, the reported toxicity of this compound [47] makes it less attractive as a reagent.

2.2. Extraction of methylamines

Sediment samples (inter- and sub-tidal) have been collected as intact cores or grab samples [15,38,48,49]. Where separation of pore-waters was reported as a discreet measurement, it was achieved by centrifugation of the whole sample [49] or by extrusion under pressure [38]. Once separated, the analytes were removed from the aquatic matrix through a clean-up step which also served to pre-concentrate them (this approach is discussed in Section 2.3).

While pore-waters can be mechanically separated from the sediment

Table 1

Physico-chemical constants for the methylamines (MAs). The pH-dependent ratios of protonated to gaseous MAs in seawater were calculated as $Kb = \frac{[MAH+][OH-]}{[MA]}$

Compound	CAS number	Abbreviation	Formula	Average mass (Da)	BP (°C) [42]	K_b [43]	pK_b [43]	[MAH^+]: [MA] (pH 8.2)	[MAH^+]: [MA] (pH 8.1)
Monomethylamine	74-89-5	MMA	CH_3NH_2	31.06	−6.3	45 x 10^{-5}	10.6	285	357
Dimethylamine	124-40-3	DMA	$(CH_3)_2NH$	45.08	7.0	54 x 10^{-5}	10.7	342	429
Trimethylamine	75-50-3	TMA	$(CH_3)_3N$	59.11	3–4	6.5 x 10^{-5}	9.8	41	52

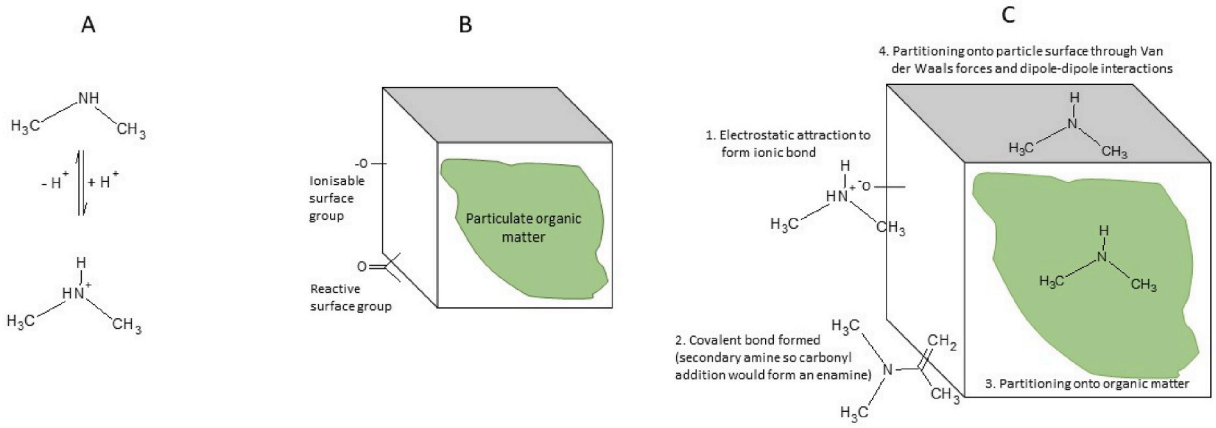

Fig. 1. An example of the possible sorptive interactions between the secondary amine DMA in the dissolved and particulate phases. These are: A) pH-dependent fractionation of DMA between the gaseous and cationic forms; B) Surface of a heterogeneous aquatic particle where sorption is likely to occur; C) The sorption processes that can take place: 1. The protonated DMA molecule forms an ionic bond with a negatively-charged surface group on the particle. 2. A gaseous (i.e., unprotonated) molecule reacts with a functional group on the particle to form a covalent bond. 3. The alkyl components of DMA undergo interactions with particulate organic matter (POM), or the cation can bond with negatively-charged functional groups within the POM. 4. Sorption through van der Waals forces and dipole–dipole interactions.

matrix, particle-associated amine fractions are released through a chemical treatment, such as volatilisation [19] or extraction with a concentrated salt solution [15,46]. Abdul-Rashid et al. extracted particle-associated MAs through immersion of sediment aliquots in a fixed volume of high pH water, converting the analytes to their gaseous forms, which desorbed from the particle-exchange sites [19]. This treatment was combined with a pre-concentration step to trap the gaseous amines in a small volume of acid, where they were converted back to protonated form. A more commonly-used approach has been the extraction of sediment samples with a concentrated salt solution, such as LiCl or KCl (1–2 M). This step is based on reported methods for the extraction of particle-associated ammonium, an analogue of the MAs, in soils [50]. The efficacy of a one-step extraction for ammonium was evaluated by Laima [51], who found that cumulative extractions of a sample were a better indication of the particle-associated fraction. This was due to equilibration of the ammonium cation between fractions of differing sorption strength, with bonds disrupted and the analyte released through repeat extractions. Applying this technique to sediments from the Thames estuary, UK, increased the amounts of the MAs desorbed [15].

The existence of a non-extractable, or fixed, fraction of MAs has been reported [40,49]. In these studies, the fraction was isolated through digestion with a mixture of hydrofluoric (5 M) and hydrochloric (1 M) acids, after removal of the salt-extracted MA fraction. However, since a single extraction step likely underestimates the exchangeable MA-concentration [15,51,52], the existence of a non-extractable MA fraction is uncertain, and further evaluation to delineate fractions that could be identified as bioavailable and non-bioavailable fractions is desirable.

2.3. Pre-concentration of methylamines

Pre-concentration techniques have been developed to achieve detection of MAs at environmental levels. An additional desire for such a step is to remove the analytes from a complex matrix in preparation for determination. Techniques deployed to achieve analyte pre-concentration have included diffusion, purge and trap, solid phase extraction (SPE) and solid phase microextraction (SPME).

Diffusion of the analytes is preceded by pH adjustment of the sample to convert the amines to their gaseous forms. These gaseous analytes can then diffuse into an acidic medium where they are reprotonated and pre-concentrated. Abdul-Rashid et al. measured nanomolar concentrations of each MA in seawater and particulate samples in a sealed, secured Cavett Flask [19]. The diffusion step comprised conversion of the MAs to gaseous form in a 50 mL volume of high pH seawater during a 24 h incubation at 60 °C. Analytes in the flask headspace were then trapped in 0.2 mL of hydrochloric acid (0.5 M), which was directly determined after pH adjustment. They reported limits of detection of 2–12 nM.

Gibb et al. [53] employed a pre-concentration method comprising MA conversion to gaseous forms then diffusion across a membrane into an acidic acceptor solution (Fig. 2). The circulation diffusion system was split into two distinct subsections: a diffusion side (basic) and a trap side (acidic). Seawater samples were pumped through the diffusion system after adjustment to pH > 12, to convert the MAs to their gaseous forms. The gaseous amines selectively diffused across the membrane and into a recirculating, aqueous-acidic, trapping solution, where they were re-protonated. Chelation of Mg^{2+} and Ca^{2+} with ethylene diamine tetraacetic acid (EDTA) prevented their precipitation at the high pH employed. Diffusion times were 15–30 min, with detection by ion chromatography, and limits of detection of 3–5 nM were reported. This 'trapping solution' mechanism was also employed by Yang et al. [45] with both static and circulation diffusion possible depending on the anticipated analyte concentrations (low μM and low nM, respectively). The sample volume was also a key variable, with 500 mL deemed suitable for amine concentrations of 5–10 nM and 1 L recommended for concentrations below 5 nM [45].

While the diffusion-trapping techniques reported were suitable for measuring MAs at environmental levels, each system requires custom-made apparatus. This may explain their lack of uptake by the oceanographic community, despite scientific drivers to understand the sources, sinks, and distribution of MAs in seawater.

Solid-phase extraction (**SPE**) has been applied to the measurement of volatile amines [54,55]. Through this process, compounds dissolved in a liquid mixture are separated from the sample matrix according to their physical and chemical properties. However, suitable sorbents must be paired with non-polar organic solvents for gaseous amines, or aqueous solvents of low ionic strength for protonated amines [56]. This reduces the efficacy of SPE for measurement of MAs in a strongly-ionic saline matrix as the analytes' size reduces opportunities for organic interactions with sorbents. Furthermore, the protonated MA fraction must compete with seawater cations for anionic exchange sites on the sorbent. SPE methods for measurement of MAs in water samples have been combined with derivatisation of the analytes *in situ* [57]. However, this is only applicable to primary and secondary amines [54,55] as TMA cannot form a bond with a derivative molecule without cleavage of a N–C bond to produce DMA [20]. Cháfer-Pericás et al. measured TMA

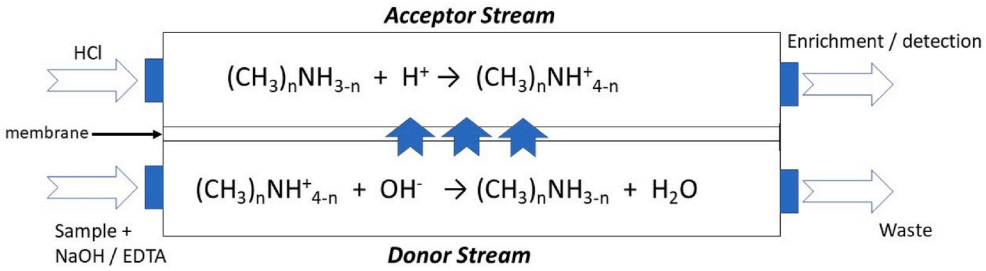

Fig. 2. The diffusion system employed for the preconcentration of methylamines in seawater samples by Gibb et al. [53]. The diffusion system contained two distinct subsections: a diffusion side (basic) and trap side (acidic). Seawater samples were adjusted to pH > 12, to convert amines to their gaseous forms. The analytes then diffused across a Goretex membrane and into an acidic acceptor solution, where they were re-protonated in an acidic medium for subsequent detection by ion chromatography.

using extraction with Bond Elut C18 cartridges followed by derivatisation with 9-fluorenylmethyl chloroformate (FMOC), as shown in Fig. 3 [57]. Determination using HPLC achieved a limit of detection of 84 nM, which is well above previously reported MA concentrations for seawater.

Liu and Zhang reported a method for the measurement of MAs in aerosol particulate matter using SPE pre-concentration and detection by ion chromatography [58]. Using this approach, the three MAs can be detected simultaneously as derivatisation is not required. As such, this approach could potentially be applied to the measurement of MA concentrations in marine particulate samples, after removal of seawater.

Solid phase microextraction (SPME) is a solvent-free extraction process that simultaneously extracts and pre-concentrates analytes from aqueous samples or a sample headspace [59]. The analytes partition between the sample and a suitable polymer-coated fibre stationary phase and are then solvent-extracted, or thermally-desorbed for determination. The choice of stationary phase depends on the compounds to be determined. SPME is influenced by a number of variables, including solution pH, ionic strength, and temperature [60]. Extraction time is also a factor and a sensitive and reproducible measurement of the extracted analytes is the goal of this technique rather than absolute recovery. For the MAs, quantification using SPME falls into two categories: methods that require a further derivatisation step, and methods that do not.

A method combining SPME and HPLC determination was used to measure the three MAs in aqueous samples [22,61]. Carbowax-templated resin SPME fibres were used to preconcentrate the samples and limits of detection of 161, 111 and 4200 nmol dm^{-3} were achieved for MMA, DMA and TMA, respectively. However, as the derivatisation process employed for the determination converts TMA to the DMA-derivative, their concurrent determination in natural samples could not be achieved. A similar approach with FMOC as the derivatising agent and polydimethylsiloxane divinylbenze (PDMS/DVB) polymer as the SPME coating achieved quantification of MMA in aqueous solutions [62] and DMA in vapour phase atmospheric samples [23]. A polyphenylmethylsiloxane (PPMS) polymer coating was successfully applied to the determination of MMA and DMA in aqueous samples, using derivatisation with N-succinimidyl benzoate (SIBA) followed by determination using gas chromatography (GC) equipped with a flame ionisation detector (FID). The reported limits of detection for this method were 0.13–7.2 nM.

SPME coupled with derivatisation clearly can achieve suitable limits of detection for some MAs in a range of matrices. However, this 2-step approach increases the potential for analyte losses, and cannot separate DMA and TMA concentrations in the same sample, limiting its applicability to environmental samples. Two methods for the quantification of all three MAs using conventional HS-SPME have been reported [14,63]. The first report was for sewage-polluted water, and measurement was achieved using SPME in conjunction with GC [63]. A polydimethylsiloxane (PDMS) fibre was chosen and exposed to the headspace of a 20 mL water sample for 30 min, achieving limits of detection of approximately 0.19–0.87 μmol dm^{-3}. Similarly, a PDMS/DVB polymer fibre was used to extract the three MAs from seawater samples, achieving limits of detection of 0.4–2.9 nM [14]. This method required a sample size of 1 L, a sample temperature of 60 °C and an extraction time of 2.5 h. The method was successfully applied to the measurement of MA concentrations in the English Channel, UK [14], and Southern Ocean [37].

SPME extraction provides flexibility, with a variety of polymer coatings available, and can achieve the degree of preconcentration needed to achieve environmentally realistic limits of detection [14]. In addition, the HS-SPME approach can significantly reduce matrix effects. The lifetime of the SPME fibre is dependent on the extraction matrix (i.e. liquid extraction leads to a shorter fibre lifetime than headspace extraction) and the number of samples determined. Cree et al. reported that approximately 200 headspace extractions for MA determination could be performed before replacement of the fibre was required [14]. Headspace moisture has been identified as impacting the chromatography of MAs where SPME was combined with GC-MS [64]. Here, a split peak for DMA was observed. The phenomenon of split peaks was also reported by Cree et al. [14] but only for MMA. Drying of the fibre post-sampling was found to improve both peak shape and sensitivity for DMA [64].

Advances in SPME developments may improve the sensitivity of determination. SPME Arrow uses a larger sorbent volume coated onto a steel rod with a sharp closed tip. The larger sorbent volume is claimed to increase analyte sorption by up to ten times, while a larger surface area achieves equilibrium more quickly, reducing the extraction time. SPME Arrow with a PDMS/Carboxen polymer fibre was used to extract DMA and TMA from ambient air and wastewater [65]. This study compared SPME Arrow with conventional SPME, concluding that the SPME Arrow was suitable for extraction of volatile amines from complex matrices,

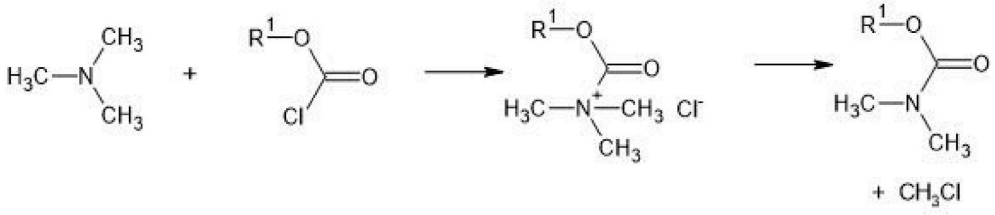

Fig. 3. Scheme of the reaction of a chloroformate with trimethylamine; R = alkyl substituent [57].

providing improved sensitivity and robust methodology.

2.4. Internal standards

A challenge with the incorporation of an internal standard to the analytical process of MAs, and other volatile amines, is the availability of suitable compounds. As alkylated, low molecular weight amines below 100 Da are ubiquitous in the environment, there is little choice of compounds meeting the physico-chemical characteristics of these analytes. Abdul-Rashid et al. used cycloproylamine and cyclobutylamine for marine samples as recovery and injection standards, respectively [16,19,53], while Gibb et al. spiked cyclopropylamine in seawater samples with 2-aminobutane added to the acceptor stream (Fig. 2) [16,53].

3. Separation and detection of methylamines

Almost all reported analytical methods for the determination of MAs have comprised a chromatography step, normally preceded by offline or online pre-concentration of the analytes (Section 2.3). Limits of detection at the low nM level have been achieved with each detection technique. Reported instrumental techniques are evaluated in this section.

3.1. Gas Chromatography (GC)

Has been most frequently reported as an analytical technique for determination of MAs in marine samples (Table 2). GC exploits the volatility of the analytes in their gaseous form and coupling this separation technique with a nitrogen-selective detector allows selective detection of the amines, even where other volatile organic molecules are present. The choice of GC columns has developed from a point where only packed columns were suitable [19] to now include capillary columns with specialist packing for separation of volatile amines [14]. Packed columns, while limited in terms of column length, contained column packings to facilitate direct aqueous injection of the analytes at high pH. The stationary phase has consisted of a non-polar polymer treated with a basic reagent, such as potassium hydroxide, to optimise analyte interactions with the stationary phase [19,49,66]. Capillary columns, while evidencing improved chromatography, can be sensitive to the presence of high pH aqueous solutions [67]. As such, thermal desorption has been employed as an injection technique to avoid interactions of aqueous solution with the stationary phase that could impair column performance [14]. Nitrogen selective detectors coupled with GC include nitrogen-phosphorus detectors (NPD) and chemiluminescent detectors. The NPD allows selective detection of nitrogen-containing organic molecules in samples containing other volatiles. It operates in a similar way to a flame ionisation detector (FID), where ions are collected on an electrode and combusted, creating a change in the ion current which can be quantified. In addition to selectivity for nitrogen, the NPD is approximately 50 times more sensitive than an FID [68]. A chemiluminescent nitrogen detector has also coupled with GC [49,66]. This detector is selective for nitrogen and measures light emitted during the degradation of metastable NO_2^* produced from combustion of organic nitrogen and subsequent reaction with ozone.

Table 2
Concentrations of methylamines (MAs) measured in aqueous marine samples, including sediments and porewaters. Other low molecular amines detected in field samples are also reported. MD-GC-NPD = microdiffusion-gas chromatography-nitrogen phosphorus detection SPME-GC-NPD = solid phase microextraction-gas chromatography-nitrogen phosphorus detection; FI-GC-IC = flow injection-gas chromatography-ion chromatography; UHPLC/ESI-Orbitrap-MS = ultra high performance liquid chromatography-electrospray ionisation-orbitrap mass spectrometry; FI-GC-GC-NSD = flow injection-gas diffusion-gas chromatography-nitrogen selective detection; DA-APPI-TOFMS - dopant-assisted atmospheric pressure photoionization time-of-flight mass spectrometry. GC-CLD = gas chromatography with chemiluminescence detection. HPLC-UV = high performance liquid chromatography with ultraviolet detection; CD-GC-NPD = circulation diffusion-gas chromatography-nitrogen phosphorus detection.

Location	Sample	$[MA_{(aq)}]$	Limits of detection	Most abundant MA	Other amines detected	Method	Authors
Liverpool Bay, UK	Seawater	200–500 nM	2–12 nM	TMA	no	MD-GC-NPD	[19]
Western English Channel	Seawater	4–22 nM	0.4–2.9 nM	TMA	no	SPME-GC-NPD	[14]
Mediterranean Sea	Seawater	3–38 nM	3–5 nM	MMA	no	FI-GD-IC	[53]
Indian Ocean (Arabian Sea)	Seawater	0.2–22 nM	0.2–2.3 nM	MMA	Ethylamine	FI-GD-IC	[16,33]
Atlantic Ocean (Cape Verde)	Sea surface microlayer,	20–50 nM (SSM)	Not reported	DMA (TMA not measured)	Diethylamine	UHPLC/ESI-Orbitrap-MS	[34]
Southern Ocean	Seawater	bd-6.9	0.4–2.9 nM	TMA	no	SPME-GC-NPD	[37]
Marguerite Bay, Antarctica	Seawater	bd-36 nM	1.65–5.65 nM	MMA	Ethylamine	FI-GD-IC	[32]
Dalian, China	Seawater	3–8 nM	0.5 nM	TMA (other MAs not measured)	Triethylamine	DA-APPI-TOFMS	[35]
Mersey estuary, UK	Sediment	1–10 μM	2–12 nM	TMA	no	MD-GC-NPD	[19]
North Sea, Norfolk, UK	Sediment	up to 4.60 μmol g^{-1}	8.7–21.6 nM	TMA	no	MD-GC-NPD	[39]
	Porewater	up to 4.68 μM					
Thames estuary, UK	Sediment	3.4–10.0 μmol g^{-1}	9–22 nM	TMA	no	MD-GC-NPD	[15]
	Porewater	60–370 nM		DMA			
Ria Formosa, Portugal	Sediment	0.51–72.96 μmol kg^{-1}	Not reported	TMA	no	MD-GC-NPD	[38]
	Porewater	0.05–8.26 μmol kg^{-1}		MMA			
Buzzards Bay, MA, USA	Sediment	22–260 nmol g^{-1}	15 ng	DMA	no	GC-CLD	[49]
	Porewater	0.4–48 μM					
Eastern Tropical North Pacific	Sediment	0.2–24 nmol g^{-1}	15 ng	DMA	no	GC-CLD	[49]
	Porewater	0.08–1.3 μM					
Flax Pond, NY, USA	Sediment	2–47 nmol g^{-1}	0.2 nmol g^{-1}	DMA (TMA not measured)	no	HPLC-UV (254 nm)	[46]
	Porewater	0.03–4.5 μM	0.2 nM				
Flax Pond, NY, USA	Seawater	3–80 nM	<10 nM (dependent on sample volume)	DMA (SW)	no	CD-GC-NPD	[45]
	Porewater	154–587 nM		TMA (PW)			

3.2. High Performance Liquid Chromatography (HPLC)

Has been deployed as an analytical technique for methylamine measurement. HPLC is particularly suited to non-volatile analytes and has been coupled with fluorescent and ultraviolet detectors. As MAs do not sensitively fluoresce or absorb UV light, pre-column derivatisation is needed to facilitate detection. Wang and Lee used HPLC-UV to measure MAs and derivatised the analytes pre-column with phenylisothiocyanate [46]. A major limitation of derivatisation is the exclusion of TMA which, as a tertiary MA, cannot be derivatised [34,46,69]. Since TMA is frequently reported as the most abundant MA in field studies, this approach risks overlooking a major analyte fraction.

3.3. Ion Chromatography (IC)

Has been used to achieve sensitive detection of all three MAs. Derivatisation was not necessary and a thermal conductivity detector was used, coupled with an online preconcentration. This ensured that the low sensitivity challenge associated with this universal detector could be overcome [16,32,53].

3.4. Other instrumental techniques

While chromatography is most commonly used for MA determination, other techniques for seawater have been reported. For example, Wu et al. developed a low volume, high sensitivity technique for the determination of TMA in seawater [35]. Samples were purged from a seawater sample adjusted to high pH and transferred to an interface for atmospheric pressure photo ionisation coupled with a mass spectrometer where analytes were separated by time of flight. Limits of detection were reported as 0.5 nM for TMA, which is the lowest LoD reported for any of the MAs (Table 2). However, as MMA and DMA were not measured it is not clear how effective this technique could be for these MAs.

4. Conclusions and way forward

It is clear from the methods and studies reported that analytical techniques have been developed that are sensitive enough to measure methylamine concentrations in seawater, where the lowest aqueous concentrations have been observed. However, the methodology and analytical techniques have not been replicated in further studies outside of the developing teams. Most of the analytical techniques employ equipment that is readily available (e.g. GC and HPLC) and it may be the pre-concentration steps and associated custom-built apparatus that present an obstacle to the wider adoption of these analytical methods. A number of previous studies quantified the contribution of the MAs and reported them to comprise a low fraction of the total nitrogen concentration, which may also have reduced interest and opportunities for further studies. The increased interest in the occurrence and fate of MAs in oceanic systems in the past decade relates to their sea-air flux and involvement in atmospheric processes. As such, analytical techniques are now in demand to respond to the need for measuring standing stocks of the analytes so that their role and importance can be quantified. As a number of techniques has been successfully developed for such measurements, there is an opportunity to optimise this approach and move towards integrated, comparable methodology for sensitive determination of MA concentrations. Gas chromatography with nitrogen-selective detection enables measurement of all three analytes so would be the most appropriate instrument on which to base further method developments. Solid phase microextraction is also a widely available preconcentration technique that can be coupled with GC determination. While inter-laboratory comparisons and calibration exercises would be dependent on the development of analytical protocols at a critical mass of institutes, this would be a valuable step forward for validating these techniques. It would also improve confidence in datasets for future studies of these analytes to evaluate their role and importance within marine systems and biogeochemical cycles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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