



OPEN ACCESS

EDITED BY

Zhaohui Zhang,
Zhejiang University, China

REVIEWED BY

Mark Francis Fitzsimons,
University of Plymouth, United Kingdom
Qingjing Hu,
Chinese Academy of Fishery Sciences (CAFS),
China

*CORRESPONDENCE

Guang-Chao Zhuang
✉ zgc@ouc.edu.cn

†These authors have contributed
equally to this work and share
first authorship

RECEIVED 16 December 2023

ACCEPTED 12 March 2024

PUBLISHED 27 March 2024

CITATION

Jiang F, Zhou Z, Wang J-Y, Guan W-J,
Han L-G, Lin X-B and Zhuang G-C (2024)
Simultaneous determination of seawater
trimethylamine and methanol by purge and
trap gas chromatography using dual
nitrogen-phosphorus detector and
flame-ionization detector.
Front. Mar. Sci. 11:1356801.
doi: 10.3389/fmars.2024.1356801

COPYRIGHT

© 2024 Jiang, Zhou, Wang, Guan, Han, Lin and
Zhuang. This is an open-access article
distributed under the terms of the [Creative
Commons Attribution License \(CC BY\)](https://creativecommons.org/licenses/by/4.0/). The
use, distribution or reproduction in other
forums is permitted, provided the original
author(s) and the copyright owner(s) are
credited and that the original publication in
this journal is cited, in accordance with
accepted academic practice. No use,
distribution or reproduction is permitted
which does not comply with these terms.

Simultaneous determination of seawater trimethylamine and methanol by purge and trap gas chromatography using dual nitrogen-phosphorus detector and flame-ionization detector

Fei Jiang^{1,2,3†}, Zhen Zhou^{1,2,3†}, Jin-Yan Wang^{1,2,3},
Wen-Jia Guan^{1,2,3}, Lei-Gang Han⁴, Xian-Biao Lin^{1,2,3}
and Guang-Chao Zhuang^{1,2,3*}

¹Frontiers Science Center for Deep Ocean Multispheres and Earth System/Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao, China,

²Laboratory for Marine Ecology and Environmental Science, Qingdao Marine Science and Technology Center, Qingdao, China, ³College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, China, ⁴Beijing Juxin Zhuifeng Technology, Ltd., Beijing, China

Compounds containing one carbon atom or no carbon-carbon bond (C1 compounds), such as trimethylamine and methanol, are important climate relevant gases in the atmosphere and play key roles in global warming. The ocean is a significant source or sink of such compounds, while the concentrations of trimethylamine and methanol in seawater remain largely unconstrained due to the analytical challenges involved. Therefore, it is necessary to establish a continuous, rapid and sensitive method for the determination of these compounds with high polarity, volatility or solubility at low seawater concentrations. Here we developed a purge and trap system, coupled to a gas chromatography equipped with dual nitrogen phosphorus detector (NPD) and flame ionization detector (FID) for the simultaneous online analysis of trimethylamine and methanol at nanomolar range using a small sample volume (~ 10 mL). The dual detection of trimethylamine and methanol with NPD or FID was achieved by installing a capillary flow splitter between the capillary column and detectors. After modification and optimization of the setup and conditions, excellent linearity ($R^2 > 0.99$) and repeatability (< 6%) were obtained for both compounds; the detection limits for trimethylamine and methanol were 0.3 nM and 17.6 nM, respectively. Using this method, water samples collected from coastal and open ocean were analyzed; trimethylamine and methanol concentrations ranged from 0.6 to 18.8 nM and 26.0 to 256.2 nM, respectively. Collectively, this method allowed for online, rapid, sensitive and simultaneous quantification of trace trimethylamine and methanol concentrations with low-cost instrumentation and small sample volume, which makes it promising for further application in volatile compounds analysis in marine environments.

KEYWORDS

trimethylamine, methanol, purge and trap, gas chromatography, dual detectors

1 Introduction

One carbon (C1) compounds, defined as molecules with no carbon-carbon bond, such as methane, methanol, methyl sulfides and methyl amines, are widespread on earth and play key roles in atmospheric chemistry and global warming (Yang et al., 2013; Masson-Delmotte et al., 2018; Sun et al., 2019; Mao et al., 2022; Hopkins et al., 2023; Bange et al., 2024). While methane and dimethyl sulfide have been intensively studied due to their impact on climate change (Charlson et al., 1987; Dean et al., 2018; Zhuang et al., 2018a; Forster et al., 2021; Mao et al., 2021), little is known about the biogeochemical cycling of other C1 compounds, such as trimethylamine and methanol (Van Neste et al., 1987; King, 1988; Singh et al., 2001; Zhuang et al., 2019; Fitzsimons et al., 2023). Gaseous amines in the atmosphere, including trimethylamine, can enhance particle nucleation as well as growth and affect secondary organic aerosol formation (Yao et al., 2018). Methanol is one of the most abundant oxygenated volatile organic compounds that can contribute to the formation of atmospheric ozone (Heikes et al., 2002).

Seawater represents an important sink and source of C1 compounds with respect to the atmosphere. Trimethylamine can be released by phytoplankton from the degradation of quaternary amines (e.g., glycine betaine) and derived from the excretion or decay of marine animals and microorganisms (Carpenter et al., 2012; Mausz and Chen, 2019). Containing both carbon and nitrogen, trimethylamine can be used as carbon, nitrogen and energy sources for marine microbes (Taubert et al., 2017; Zhuang et al., 2018b). Similar to trimethylamine, methanol is ubiquitous in marine systems and largely produced by phytoplankton (Yang et al., 2013; Mincer and Aicher, 2016). Methanol is predominately used as a microbial energy source for CO₂ production (Zhou et al., 2023), and was also observed as an important carbon source channeled into biomass in highly productive areas (Dixon et al., 2013b; Zhuang et al., 2018b). Therefore, the metabolism of trimethylamine and methanol constitute an important part of the marine carbon and nitrogen cycles.

Despite the significance of trimethylamine and methanol in the ocean, large uncertainty remains for global sea-air exchange fluxes due to limited measurements of their concentrations. A few studies reported that trimethylamine and methanol concentrations were within the nanomolar range in seawater (Beale et al., 2011, 2013; Cree et al., 2018; Wu et al., 2020). Determination of trimethylamine and methanol at such low concentrations is challenging and an efficient enrichment for preconcentration is usually required before chromatographic (GC) or mass spectrometric (MS) analysis. The basic nature and high polarity lead to the strong adsorption of trimethylamine to the surface of glassware and instruments, while the high solubility of methanol makes it difficult to be extracted from seawater. Several approaches have been developed to determine the low concentrations of trimethylamine or methanol in seawater, for example, solid-phase microextraction with gas chromatography method and dopant-assisted atmospheric pressure photoionization time-of-flight mass spectrometry method for trimethylamine and inlet-proton transfer reaction/mass spectrometer method for methanol (Beale et al., 2011;

Cree et al., 2018; Wu et al., 2020). However, the time-consuming pretreatment with manipulative steps and requirement of a large sample volume, or the employment of high-cost instruments, has limited the routine application of these methods in marine research. Furthermore, the purge and trap (P&T) pretreatment with gas chromatography has been widely used for the trace analysis of marine volatile compounds (Zhang et al., 2004, Zhang et al., 2015; Yang et al., 2010, Yang et al., 2011; Zhong et al., 2012) due to its versatility with easy operation, high extraction efficiency, and the requirement of low-cost instrumentation. Recently, we have successfully developed P&T-GC-MS or P&T-GC methods to analyze concentrations of trimethylamine or methanol in sedimentary pore waters with 5 – 6 mL samples (Zhuang et al., 2014, 2017).

In this study, we sought to establish a P&T-GC method for the simultaneous determination of seawater trimethylamine and methanol. To achieve this, the two compounds were separated by a single column but detected using dual nitrogen-phosphorus detector (NPD) and flame-ionization detector (FID). We further optimized the P&T conditions (e.g., purge flow rate, purge temperature and trap temperature) to improve the sensitivity of the method. After optimization, we assessed the performance and applied this method to determine natural seawater samples collected from the coastal waters of Jiaozhou Bay and the open ocean of the western Pacific.

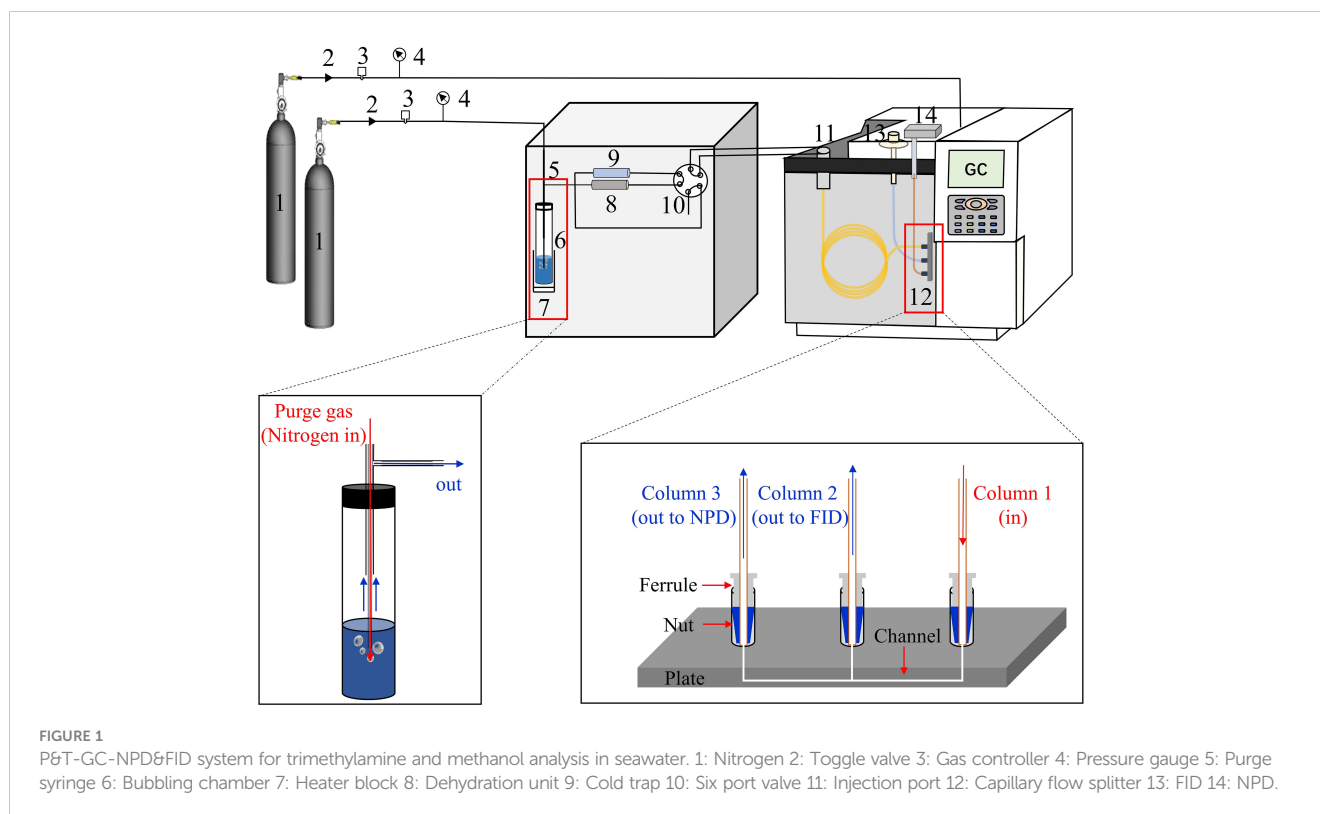
2 Materials and methods

2.1 Chemicals and solutions

Trimethylamine hydrochloride (98%) and methanol (analytical reagent) were purchased from Merck (KGaA, Germany) and Sinopharm Chemical Reagent, Ltd (Shanghai, China), respectively. The primary stocks of trimethylamine (1.2 mM) and methanol (12.3 mM) were prepared separately in double-distilled water and both stock solutions were stored < 1 week in a 50 mL serum vial without headspace at 4°C in the dark. Standard solutions for calibration (trimethylamine: 0.5 – 7.2 nM; methanol: 24.0 – 360.0 nM) were made by mixing and diluting the trimethylamine and methanol primary stocks to desired concentrations. Ammonium chloride (> 99.5%) and sodium hydroxide (> 96%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 P&T system coupled to GC-NPD&FID

A modified P&T system (Acrichi PTC, Beijing Juxin Zhufeng Technology, Ltd, China) was used for the preconcentration of trimethylamine and methanol before GC analysis. The P&T system includes a purge unit to extract the volatiles from the seawater, a dehydration unit to remove the moisture, and a trap unit to concentrate the volatile gases (Figure 1). Briefly, 10 mL seawater was introduced into a 40 mL glass vial and capped with a silicone/PTFE septum. After injecting 400 µL of 5 M NaOH and 200



μL of 20 mM NH_4Cl through the septum, the 40 mL glass vial, used as the bubbling chamber, was placed on a heating bracket at 85°C . The addition of NaOH helps to release trimethylamine from the non-volatile hydrochloride form at seawater pH ~ 8.2 and NH_4Cl would reduce the adsorption of trimethylamine on the surface of labware and column (Dalene et al., 1981). A sparging needle pierced through the septum, and then the sample was purged with nitrogen gas. The evolved gas passed through an inert hollow condenser pipe electronically set at -5°C to condense the water, and then entered a cryogenic trap packed with Tenax TA, which was electronically controlled at -25°C . After 10 min of purging and trapping, the cold trap was heated to 220°C for 2 min and the vaporized analytes were channeled to the GC with high-purity nitrogen. After the introduction of gas into GC, the P&T system was purged with high-purity nitrogen (99.999%) for 3 min to eliminate moisture and the cryogenic trap was heated to 300°C to avoid carryover between samples. All tubes, components, and connectors of the P&T system were deactivated and maintained at 180°C to minimize adsorption.

The quantification of trimethylamine and methanol was performed using an Agilent 8890 GC equipped with NPD and FID. This is achieved through a splitter based on the capillary flow technology of Agilent, which was installed between the capillary column and detectors and connected the NPD and FID in parallel (Figure 1). Volatile compounds were separated with a HP-PLOT Q column ($30\text{ m} \times 0.32\text{ mm}$, Agilent Technologies Inc., USA). The optimized GC conditions included: split ratio, 0.5:1; injection temperature, 70°C ; oven temperature started at 40°C for 2 min, ramped to 240°C at $35^\circ\text{C min}^{-1}$ and held at 240°C for 3 min. Carrier gas flow rates were optimized to increase the analytes response (5.5 mL min^{-1} , see section 3.1). The NPD temperature was set at

320°C and the flow rates of hydrogen and air were 10 mL min^{-1} and 60 mL min^{-1} . The temperature of the FID was 300°C , with a hydrogen and air flow of 30 mL min^{-1} and 400 mL min^{-1} , respectively. Parameters for the P&T system were detailed in Supplementary Table S1.

2.3 Procedural blank and contamination tests

To test for potential contamination from the laboratory, a procedural blank of non-spiked water was measured using the same procedure as the standards. While trimethylamine was not detected in non-spiked double-distilled water, there was a consistent background presence of methanol in the water. Additional tests confirmed that the P&T system did not introduce trimethylamine and methanol blank by purging an empty vial without adding water. Therefore, the calibration for methanol was conducted by subtracting the blank from the water. To prevent methanol contamination, the septa used to seal the bubbling chamber were baked at 75°C for 72 h. Furthermore, all measurements were conducted in a laboratory free of trimethylamine and methanol, as confirmed by exposing blank water in the lab for two weeks (Zhuang et al., 2014).

2.4 Sample collection

Surface seawaters were collected from shallow waters of Jiaozhou Bay and open ocean of the western Pacific (Supplementary Figure S1)

during May 2022 and August 2022, respectively. Seawater samples from Jiaozhou Bay and the western Pacific Ocean were collected using a 5 L plexiglass water sampler and using 12 L Niskin bottles deployed on a Seabird 911 conductivity-temperature-depth rosette system, respectively. After collection, seawater was immediately transferred into 60 mL serum vials and sealed with thick butyl rubber stoppers to minimize gas loss and air contamination. All samples were stored at -80°C immediately after sampling (< 10 min) on board to prevent biological loss and potential degradation before analysis (Zhuang et al., 2018b), as methylamines can be consumed quickly without preservation (Cree et al., 2018). Samples were not filtered before analysis as the filtering process could lead to the release of organic volatiles or introduce contaminations (Beale et al., 2011). Therefore, our measurements represented the total concentrations of TMA and methanol in the environments, including dissolved and particulate fractions. However, it should be noted that separating dissolved and particulate phases of TMA through filtration is necessary for quantifying the fluxes of TMA to the atmosphere, which is an important measurement to assess the residence time in seawater once produced. All glass bottles for sampling were soaked in hydrochloric acid (3% v/v) for > 24 h and rinsed with double-distilled water three times before use.

2.5 Data analysis

One-way analysis of variance (One-way ANOVA) was performed on Origin 2023 (OriginLab Corporation, Northampton, MA, USA) and the significance of differences during optimization was tested with a significance level of 0.05. Sampling sites and the distribution of trimethylamine and methanol were mapped using

Ocean Data View 5.3.0 (Schlitzer, Reiner, Ocean Data View, odv.awi.de, 2022).

3 Results and discussion

3.1 Dual detection of trimethylamine and methanol with NPD and FID

Given the different responses of volatile compounds to specific detectors, trimethylamine and methanol were analyzed with the NPD and FID, respectively. As such, a splitter based on capillary flow technology was installed between the capillary column and detectors to split carrier gas from the same column to the NPD and FID. Accordingly, continuous online quantification of trimethylamine and methanol could be achieved with single injection after P&T preconcentration using a small sample volume (~ 10 mL). This not only significantly reduced running time but was particularly important for volume-limited samples (e.g., pore water and microlayer samples).

The split of carrier gas into two streams would result in an over 50% reduction in the response of trimethylamine and methanol. The decrease could be attributed to the disparity in textures between the capillary and inertia tee-junction. This can be improved by increasing the carrier gas flow, but high flow would also lead to the elution of the column's stationary phase. Therefore, optimal flow rates were examined between 3.0 to 6.0 mL min^{-1} , and a final flow of 5.5 mL min^{-1} was used to yield a satisfactory response without compromising the column performance. After optimization, trimethylamine and methanol were separated with good peak shapes and detected simultaneously with NPD and FID (Figure 2).

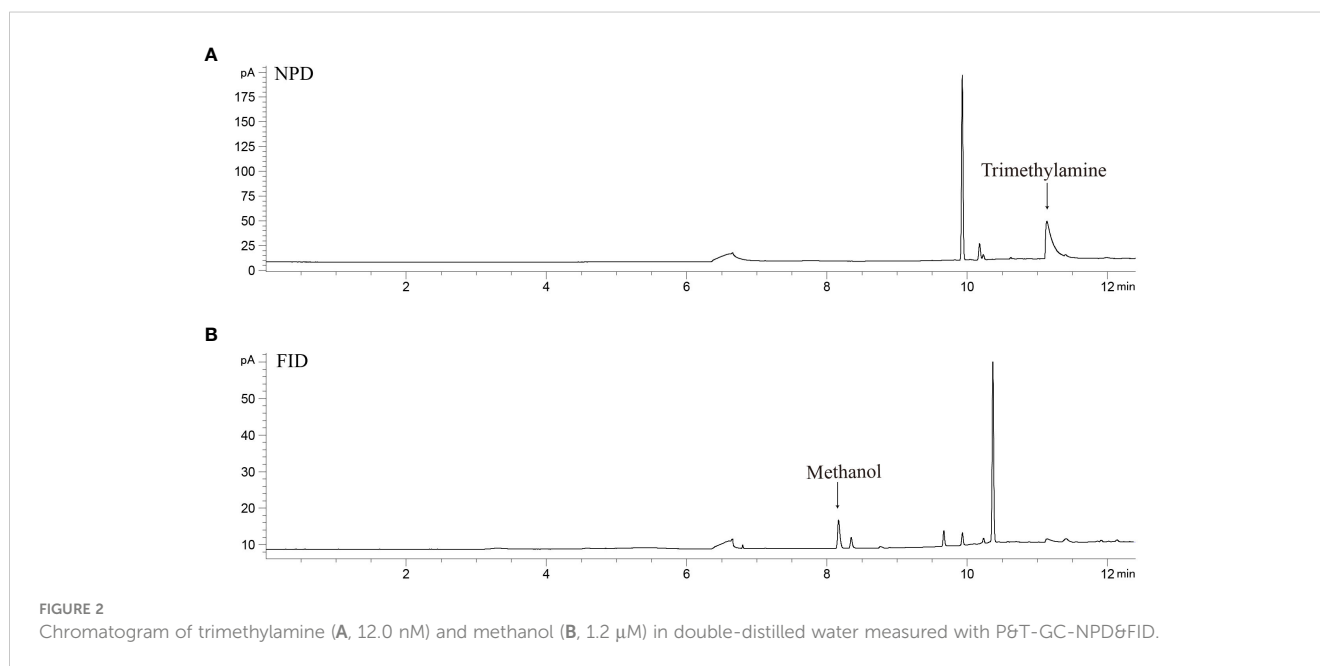


FIGURE 2
Chromatogram of trimethylamine (A, 12.0 nM) and methanol (B, 1.2 μM) in double-distilled water measured with P&T-GC-NPD&FID.

3.2 Optimization of purge and trap system

To preconcentrate the target compounds more efficiently, a series of P&T conditions were optimized. We assessed the effect of purge parameters, such as purge flow, purge time and purge temperature on the extraction efficiency (Zhuang et al., 2014, 2017).

Purge time and flow reflect the total gas volume used for degassing, which help the volatiles escape to the headspace. For methanol, the responses generally increased with purge flow from 50 to 90 mL min⁻¹ (Figure 3A). Similarly, higher flow (> 70 mL min⁻¹) also resulted in elevated response for trimethylamine (Figure 3A). Considering that higher flow would cause the loss of adsorbent in the trap and large purging gas volume would elute the analyte compounds from the adsorbents, we selected a flow rate of 90 mL min⁻¹ for 10 min.

Temperature is also important for extraction and both trimethylamine and methanol signals increased significantly from ambient to 85°C (Figure 3B). Heating at high temperature introduced more moisture to the cold adsorbent trap. To avoid clogging, a hollow condenser pipe at -5°C was used for dehydration before trapping, which removed moisture from the gas stream without significant loss of methanol. For the temperature of the adsorbent trap, while methanol was not affected, the recovery of trimethylamine decreased at -15°C compared to other lower temperature (Figure 3C). Based on these facts, our samples were heated at 85°C during purging, dried at -5°C, and finally trapped with Tenax TA at -25°C.

We tested the effect of NaOH and NH₄Cl on the recovery of trimethylamine and methanol. As expected, the signal of trimethylamine without NaOH was only 8.1% of those purged with 400 μL 5 M NaOH (Figure 3D). This is because

trimethylamine, with a pK_b value of 4.19, exists mostly in non-volatile hydrochloride form under neutral or seawater condition (pH ~ 8.2). The addition of NH₄Cl significantly improves the response of trimethylamine, since NH₃ reduces the adsorption of trimethylamine by competing for sites on the surface of the P&T system (Figure 3E). Moreover, methanol response was also improved with the addition of NaOH, which could be attributed to the “salting-out effect” (Peng and Wan, 1998). Ultimately, 200 μL 20 mM NH₄Cl and 400 μL 5 M NaOH were added to the sample to release trimethylamine and reduce adsorption.

3.3 Analytical performances

Under the optimum conditions, we assessed the performance of the method. A six-point calibration curve was conducted for trimethylamine (0.5 – 7.2 nM) and methanol (24.0 – 360.0 nM), and excellent linearity was observed with R² > 0.99 (Figure 4). The repeatability, calculated from the relative standard deviation (RSD) of repeated measurements of the standard solution (n = 7) was better than 6%, suggesting the good stability of the method (Table 1). Good reproducibility was also observed for the seawater sample (RSD < 8%), which was measured repeatedly seven times.

The method detection limit (MDL) was calculated according to Equation 1.

$$\text{MDL} = 3.143\delta \quad (1)$$

where δ is the standard deviation of replicate measurements (n = 7) of standards spiked with low concentrations of analytes according to EPA. Using this method, the calculated MDL for trimethylamine and

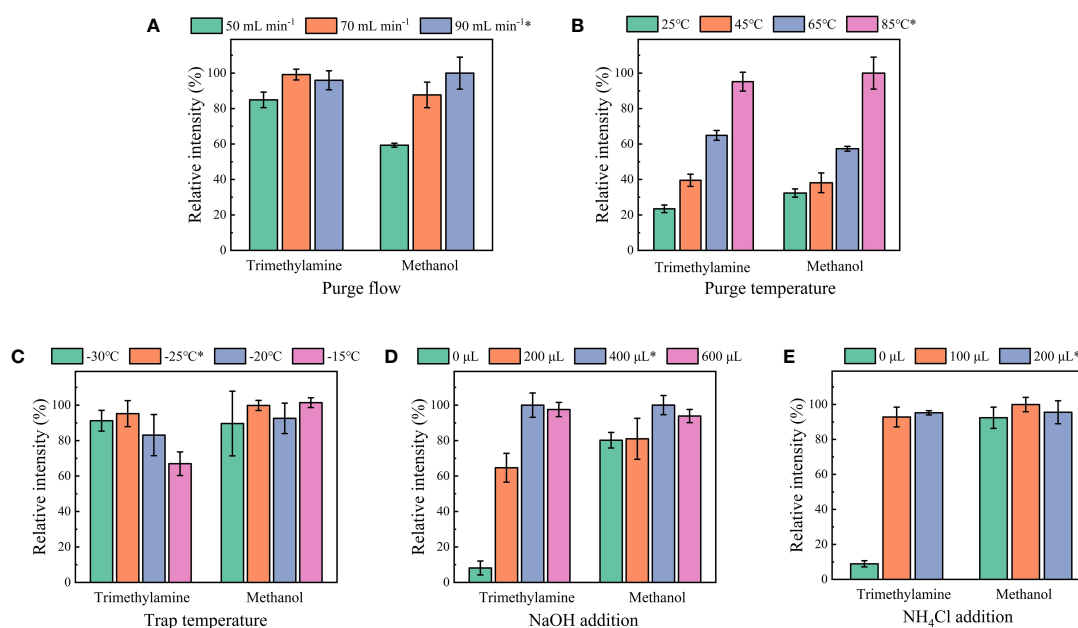


FIGURE 3

The effects of (A) purge flow, (B) purge temperature, (C) trap temperature, (D) NaOH addition and (E) NH₄Cl addition on the response of trimethylamine and methanol measured with P&T-GC-NPD&FID. In each panel, 100% relative intensity corresponds to the highest signal observed. Error bars represent the standard deviation of triplicate measurements, and ultimate conditions are denoted with * in each panel.

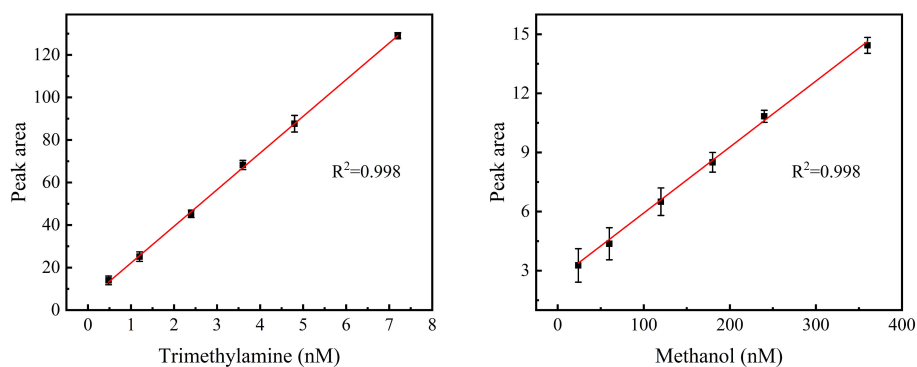


FIGURE 4

Six-point calibration curves for trimethylamine (0.5 – 7.2 nM) and methanol (24.0 – 360.0 nM). Error bars represent the standard deviation of triplicate measurements.

TABLE 1 Linearity, repeatability, and detection limits for trimethylamine and methanol analysis by P&T-GC-NPD&FID.

Compounds	Detection limit ^a	Repeatability ^b		Linearity	
	nM			Concentration range	R ²
Trimethylamine	0.3	5.4% (2.4 nM)	4.7% (24.0 nM)	0.5 – 7.2 nM	0.998
Methanol	17.6	4.7% (36.0 nM)	5.1% (1.2 μM)	24.0 – 360.0 nM	0.998

^aMethod detection limits (MDLs) were determined as 3.143 times the standard deviation of replicate measurements (n = 7) of low concentration standards according to EPA.

^bRepeatability was calculated from the relative standard deviation of repeated measurements of the standards (n = 7).

methanol was 0.3 nM and 17.6 nM, respectively (Table 1). Compared to previous methods, this is a significant improvement on the detection of trimethylamine and methanol with a 10 mL sample volume. Taking the preconcentration and GC running time into account, the total process time for each sample is 20 min (Table 2). The short processing time, the high sensitivity of detection, the relatively low requirement of sample volume, and the capability to analyze two Cl compounds simultaneously, make our method a suitable assay for rapid and sensitive analysis of trimethylamine and methanol in marine environments.

3.4 Application to natural samples

The application of the developed method for trimethylamine and methanol analysis was evaluated using seawater samples retrieved from Jiaozhou Bay and the western Pacific Ocean. Both trimethylamine and methanol were detected in the seawater at all sampling sites (Supplementary Table S2). In Jiaozhou Bay, the concentrations of trimethylamine varied from 1.3 to 18.8 nM (5.2 ± 4.4 nM). Methanol concentrations ranged from 26.0 to 256.2 nM, with an average of 93.2 ± 62.1 nM. These values were comparable to the measured concentrations in coastal waters (Table 3). The highest concentrations of trimethylamine and methanol were observed at site D4 of the east bay mouth, which was close to Qingdao Cruise Port (Figure 5). The elevated concentration at this site suggested that anthropogenic activity might influence marine productivity and also the production of trimethylamine and methanol. In the Pacific Ocean, the

concentrations of trimethylamine were much lower, ranging from 0.6 to 2.3 nM (1.1 ± 0.7 nM). In seawater, trimethylamine is mainly derived from the degradation of its precursors (trimethylamine N-oxide, glycine betaine, carnitine) that serve as osmolytes in marine organisms (Jameson et al., 2016). Given the dominance of biological source for trimethylamine, it is not surprising that the abundance of trimethylamine was higher in coastal water than in the open ocean due to the high primary production.

By comparison, methanol concentrations in oceanic waters (122.8 ± 48.0 nM) were comparable to those measured in Jiaozhou Bay and were also generally within the wide range reported in the Atlantic, and Pacific oceans (Table 3). In contrast to trimethylamine, the sources of methanol can be more complex, such as phytoplankton production, photochemical decomposition of organic matter, and atmosphere deposition (Schink and Zeikus, 1980; Yang et al., 2013; Dixon et al., 2013a; Mincer and Aicher, 2016). In the Atlantic Ocean, methanol is mostly derived from biological production, while photoproduction seemed to be negligible for gross *in situ* production (Dixon et al., 2013a). Although production rates can be higher in coastal waters, rapid consumption of methanol in near-shore waters would maintain methanol concentration at a low level. In the Northwest Pacific Ocean, atmospheric deposition is also a source of methanol and it accounted for 22.7% of microbial methanol consumption in the mixed layer (Zhou et al., 2023). Collectively, the *in situ* concentrations of trimethylamine and methanol reflected the relative importance of production and consumption processes involved in their cycling in marine environments.

TABLE 2 Comparison of different methods used for the analysis of trimethylamine and methanol in marine system.

Compounds	Sample volume	Analysis time	LODs nM	Methods	Reference
Trimethylamine	50 mL	> 48 h	11	MD-GC-NPD ^a	(Abdul-Rashid et al., 1991)
	< 500 mL	> 4 h	10	CD-GC-NPD ^b	(Yang et al., 1993)
	< 50 mL	15 – 30 min	3 – 5	FIGD-IC ^c	(Gibb et al., 1995)
	5 mL	25 min	20	P&T-GC-MS ^d	(Zhuang et al., 2017)
	1 L	> 2.5 h	0.38 – 0.89	SPME-GC-NPD ^e	(Cree et al., 2018)
	2 mL	2 min	0.53	DA-APPI-TOFMS ^f	(Wu et al., 2020)
	10 mL	20 min	0.3	P&T-GC-NPD&FID ^g	This work
Methanol	2 L	2 min	12	EI-PTR-MS ^h	(Kameyama et al., 2010)
	6 mL	50 min	60	P&T-GC-FID ⁱ	(Zhuang et al., 2014)
	116 mL	29 min	27	MI-PTR/MS ^j	(Beale et al., 2011)
	10 mL	20 min	17.6	P&T-GC-NPD&FID ^g	This work

^aMicrodiffusion-gas chromatography-nitrogen phosphorus detection.

^bCirculation diffusion-gas chromatography-nitrogen phosphorus detection.

^cFlow injection gas diffusion-ion chromatography.

^dPurge and trap in combination with gas chromatography coupled to mass spectrometry.

^eSolid phase microextraction-gas chromatography-nitrogen phosphorus detector.

^fDopant-assisted atmospheric pressure photoionization time-of-flight mass spectrometry.

^gPurge and trap in combination with gas chromatography coupled to nitrogen phosphorus detector and flame ionization detector.

^hEquilibrator inlet-proton transfer reaction-mass spectrometry.

ⁱPurge and trap in combination with gas chromatography coupled to flame ionization detector.

^jMembrane inlet-proton transfer reaction/mass spectrometer.

TABLE 3 Concentrations of trimethylamine and methanol measured in marine waters.

Compounds	Concentration nM	Sampling sites	References
Trimethylamine	< 7	Offshore, Mediterranean Sea	(Gibb et al., 1995)
	4 – 22	Coast, Mediterranean Sea	
	0 – 13	Tamar and Plym Estuaries, UK	
	12 ± 3	Pacific-Hawaii coast	(Van Neste et al., 1987)
	5 – 60	Flax Pond, USA	(Yang et al., 1994)
	< 4	Arabian Sea	(Gibb et al., 1999)
	1.6 ± 1.8	Coast, Antarctica	(Gibb and Hatton, 2004)
	1.4 – 6.9	Southern Ocean	(Cree et al., 2018)
	1.7 – 8.3	Dalian coast, China	(Wu et al., 2020)
Methanol	118.4 ± 48.2	Tropical Atlantic	(Williams et al., 2004)
	77.9 – 325.0	Western Pacific Ocean	(Kameyama et al., 2010)
	48 – 361	Atlantic Ocean	(Beale et al., 2013)
	15 – 62	Atlantic Ocean	(Yang et al., 2013)
	7 – 28	Atlantic Ocean	(Yang et al., 2014)
	16 – 78	Plymouth coast, UK	(Beale et al., 2015)
	67 ± 35	Southern Ocean	(Wohl et al., 2020)
	< 12 – 391	Northwest Pacific Ocean	(Zhou et al., 2023)

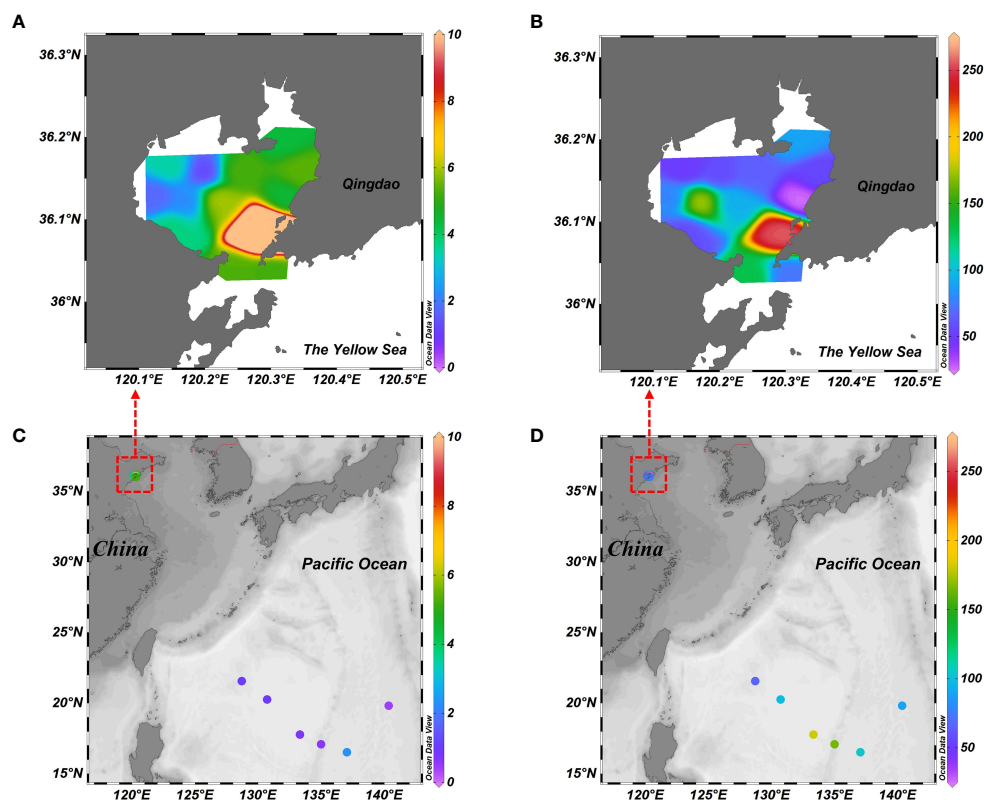


FIGURE 5

Distributions of trimethylamine (A, C; nM) and methanol (B, D; nM) in the surface seawater of Jiaozhou Bay and the western Pacific Ocean.

4 Conclusion

Investigating the concentrations and distributions of trimethylamine and methanol is a prerequisite to understand their biogeochemical cycling in the ocean. In this study, we established a rapid and sensitive GC approach for online and simultaneous analysis of trimethylamine and methanol in seawater. After preconcentration with a P&T setup, trimethylamine and methanol were analyzed with GC equipped with dual NPD and FID. We optimized GC and P&T conditions and obtained good performance of linearity, repeatability and detection limit. The application of this approach was validated using the seawater samples collected from Jiaozhou Bay and the western Pacific Ocean, and trimethylamine and methanol were detected at all sites with spatial variability. Overall, this method is simple, relatively fast with high sensitivity and small sample volume for simultaneous analysis of trimethylamine and methanol using a GC. Furthermore, this method could be extended for the analysis of other methylamines or alcohols with optimizations, not only in the seawater, but possibly in air samples, which would be

helpful for future investigation of C1 or other volatile organics in marine environments.

Data availability statement

The original contributions presented in the study are included in the article/[Supplementary Material](#). Further inquiries can be directed to the corresponding author.

Author contributions

FJ: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. ZZ: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. J-YW: Supervision, Visualization, Writing – original draft, Writing – review & editing. W-JG:

Methodology, Software, Writing – review & editing. L-GH: Resources, Writing – review & editing. X-BL: Writing – review & editing. G-CZ: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Software, Supervision, Validation, Writing – original draft, Writing – review & editing.

Funding

The author(s) declare financial support was received for the research, authorship, and/or publication of this article. This work was supported by the National Key Research and Development Program of China (Grant 2022YFE0136300), the National Natural Science Foundation of China (Grant 42076031), the Taishan Scholars Program of Shandong Province (Grant tsqn201909057).

Acknowledgments

We thank Agilent for providing technical support during the method development. We acknowledge the captain, crew, and scientists of the R/V “*Dongfanghong 3*” for their kind assistance and cooperation during sampling. We sincerely thank the editor and reviewers for their constructive suggestions for improving the overall quality of our manuscript.

References

- Abdul-Rashid, M. K., Riley, J. P., Fitzsimons, M. F., and Wolff, G. A. (1991). Determination of volatile amines in sediment and water samples. *Anal. Chim. Acta* 252, 223–226. doi: 10.1016/0003-2670(91)87219-W
- Bange, H. W., Mongwe, P., Shutler, J. D., Arévalo-Martínez, D. L., Bianchi, D., Lausset, S. K., et al. (2024). Advances in understanding of air–sea exchange and cycling of greenhouse gases in the upper ocean. *Elem. Sci. Anthd* 12, 44. doi: 10.1525/elementa.2023.00044
- Beale, R., Dixon, J. L., Arnold, S. R., Liss, P. S., and Nightingale, P. D. (2013). Methanol, acetaldehyde, and acetone in the surface waters of the Atlantic Ocean. *J. Geophys. Res. Oceans* 118, 5412–5425. doi: 10.1002/jgrc.20322
- Beale, R., Dixon, J. L., Smyth, T. J., and Nightingale, P. D. (2015). Annual study of oxygenated volatile organic compounds in UK shelf waters. *Mar. Chem.* 171, 96–106. doi: 10.1016/j.marchem.2015.02.013
- Beale, R., Liss, P. S., Dixon, J. L., and Nightingale, P. D. (2011). Quantification of oxygenated volatile organic compounds in seawater by membrane inlet-proton transfer reaction/mass spectrometry. *Anal. Chim. Acta* 706, 128–134. doi: 10.1016/j.aca.2011.08.023
- Carpenter, L. J., Archer, S. D., and Beale, R. (2012). Ocean-atmosphere trace gas exchange. *Chem. Soc. Rev.* 41, 6473–6506. doi: 10.1039/c2cs35121h
- Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G. (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326, 655–661. doi: 10.1038/326655a0
- Cree, C. H. L., Airs, R., Archer, S. D., and Fitzsimons, M. F. (2018). Measurement of methylamines in seawater using solid phase microextraction and gas chromatography. *Limnol. Oceanogr. Methods* 16, 411–420. doi: 10.1002/lom3.10255
- Dalene, M., Mathiasson, L., and Jönsson, J.Å. (1981). Trace analysis of free amines by gas-liquid chromatography. *J. Chromatogr. A* 207, 37–46. doi: 10.1016/S0021-9673(00)82690-4
- Dean, J. F., Middelburg, J. J., Röckmann, T., Aerts, R., Blauw, L. G., Egger, M., et al. (2018). Methane feedbacks to the global climate system in a warmer world. *Rev. Geophys.* 56, 207–250. doi: 10.1002/2017RG000559
- Dixon, J. L., Beale, R., and Nightingale, P. D. (2013a). Production of methanol, acetaldehyde, and acetone in the Atlantic Ocean. *Geophys. Res. Lett.* 40, 4700–4705. doi: 10.1002/grl.50922
- Dixon, J. L., Sargeant, S., Nightingale, P. D., and Colin Murrell, J. (2013b). Gradients in microbial methanol uptake: productive coastal upwelling waters to oligotrophic gyres in the Atlantic Ocean. *ISME J.* 7, 568–580. doi: 10.1038/ismej.2012.130
- Fitzsimons, M. F., Tilley, M., and Cree, C. H. L. (2023). The determination of volatile amines in aquatic marine systems: A review. *Anal. Chim. Acta* 1241, 340707. doi: 10.1016/j.aca.2022.340707
- Forster, P., Storelymo, T., Armour, K., Collins, W., Dufresne, J.-L., Frame, D., et al. (2021). “The earth’s energy budget, climate feedbacks, and climate sensitivity,” in *Climate change 2021: the physical science basis. Contribution of working group I to the sixth assessment report of the intergovernmental panel on climate change* (Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA), 923–1054. doi: 10.1017/9781009157896.009
- Gibb, S. W., and Hatton, A. D. (2004). The occurrence and distribution of trimethylamine-n-oxide in antarctic coastal waters. *Mar. Chem.* 91, 65–75. doi: 10.1016/j.marchem.2004.04.005
- Gibb, S. W., Mantoura, R. F. C., and Liss, P. S. (1995). Analysis of ammonia and methylamines in natural waters by flow injection gas diffusion coupled to ion chromatography. *Analytica Chimica Acta* 316, 291–304. doi: 10.1016/0003-2670(95)00372-7
- Gibb, S. W., Mantoura, R. F. C., Liss, P. S., and Barlow, R. G. (1999). Distributions and biogeochemistries of methylamines and ammonium in the arabian sea. *Deep-Sea Res. II: Top. Stud. Oceanogr.* 46, 593–615. doi: 10.1016/S0967-0645(98)00119-2
- Gibb, S. W., Wood, J. W., Fauzi, R., and Mantoura, C. (1995). Automation of flow injection gas diffusion-ion chromatography for the nanomolar determination of methylamines and ammonia in seawater and atmospheric samples. *J. Automatic Chem.* 17, 205–212. doi: 10.1155/S1463924695000320
- Heikes, B. G., Chang, W., Pilson, M. E. Q., Swift, E., Singh, H. B., Guenther, A., et al. (2002). Atmospheric methanol budget and ocean implication. *Glob. Biogeochem. Cycles* 16, 80-1-80-13. doi: 10.1029/2002GB001895
- Hopkins, F. E., Archer, S. D., Bell, T. G., Suntharalingam, P., and Todd, J. D. (2023). The biogeochemistry of marine dimethylsulfide. *Nat. Rev. Earth Environ.* 4, 361–376. doi: 10.1038/s43017-023-00428-7
- Jameson, E., Doxey, A. C., Airs, R., Purdy, K. J., Murrell, J. C., and Chen, Y. (2016). Metagenomic data-mining reveals contrasting microbial populations responsible for

Conflict of interest

Author L-GH was employed by the company Beijing Juxin Zhufeng Technology, Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher’s note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmars.2024.1356801/full#supplementary-material>

- trimethylamine formation in human gut and marine ecosystems. *Microb. Genomics* 2, e000080. doi: 10.1099/mgen.0.000080
- Kameyama, S., Tanimoto, H., Inomata, S., Tsunogai, U., Ooki, A., Takeda, S., et al. (2010). High-resolution measurement of multiple volatile organic compounds dissolved in seawater using equilibrator inlet-proton transfer reaction-mass spectrometry (E1-PTR-MS). *Mar. Chem.* 122, 59–73. doi: 10.1016/j.marchem.2010.08.003
- King, G. M. (1988). Methanogenesis from methylated amines in a hypersaline algal mat. *Appl. Environ. Microbiol.* 54, 130–136. doi: 10.1128/aem.54.1.130-136.1988
- Mao, S.-H., Zhang, H.-H., Zhuang, G.-C., Li, X.-J., Liu, Q., Zhou, Z., et al. (2022). Aerobic oxidation of methane significantly reduces global diffusive methane emissions from shallow marine waters. *Nat. Commun.* 137309. doi: 10.1038/s41467-022-35082-y
- Mao, S.-H., Zhuang, G.-C., Liu, X.-W., Jin, N., Zhang, H.-H., Montgomery, A., et al. (2021). Seasonality of methylated sulfur compounds cycling in north China marginal seas. *Mar. Pollut. Bull.* 170, 112635. doi: 10.1016/j.marpolbul.2021.112635
- Masson-Delmotte, V., Zhai, P., Pörtner, H.-O., Roberts, D., Skea, J., Shukla, P. R., et al. (2018). “An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. Summary for Policymakers,” in *Global warming of 1.5°C* (Cambridge University Press, Cambridge, UK and New York, NY, USA), 3–24. doi: 10.1017/9781009157940.001
- Mausz, M. A., and Chen, Y. (2019). Microbiology and ecology of methylated amine metabolism in marine ecosystems. *Curr. Issues Mol. Biol.* 33, 133–148. doi: 10.21775/cimb.033.133
- Mincer, T. J., and Aicher, A. C. (2016). Methanol production by a broad phylogenetic array of marine phytoplankton. *PLoS One* 11, e0150820. doi: 10.1371/journal.pone.0150820
- Peng, J., and Wan, A. (1998). Effect of ionic strength on Henry’s constants of volatile organic compound. *Chemosphere* 36, 2731–2740. doi: 10.1016/S0045-6535(97)10232-6
- Schink, B., and Zeikus, J. G. (1980). Microbial methanol formation: a major end product of pectin metabolism. *Curr. Microbiol.* 4, 387–389. doi: 10.1007/BF02605383
- Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., et al. (2001). Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds. *Nature* 410, 1078–1081. doi: 10.1038/35074067
- Sun, J., Mausz, M. A., Chen, Y., and Giovannoni, S. J. (2019). Microbial trimethylamine metabolism in marine environments. *Environ. Microbiol.* 21, 513–520. doi: 10.1111/1462-2920.14461
- Taubert, M., Grob, C., Howat, A. M., Burns, O. J., Pratscher, J., Jehmlich, N., et al. (2017). Methylamine as a nitrogen source for microorganisms from a coastal marine environment. *Environ. Microbiol.* 19, 2246–2257. doi: 10.1111/1462-2920.13709
- Van Neste, A., Duce, R. A., and Lee, C. (1987). Methylamines in the marine atmosphere. *Geophys. Res. Lett.* 14, 711–714. doi: 10.1029/GL014i007p00711
- Williams, J., Holzinger, R., Gros, V., Xu, X., Atlas, E., and Wallace, D. W. R. (2004). Measurements of organic species in air and seawater from the tropical Atlantic. *Geophys. Res. Lett.* 31. doi: 10.1029/2004GL020012
- Wohl, C., Brown, I., Kitidis, V., Jones, A. E., Sturges, W. T., Nightingale, P. D., et al. (2020). Underway seawater and atmospheric measurements of volatile organic compounds in the southern ocean. *Biogeosciences* 17, 2593–2619. doi: 10.5194/bg-17-2593-2020
- Wu, C., Wen, Y., Hua, L., Jiang, J., Xie, Y., Cao, Y., et al. (2020). Rapid and highly sensitive measurement of trimethylamine in seawater using dynamic purge-release and dopant-assisted atmospheric pressure photoionization mass spectrometry. *Anal. Chim. Acta* 1137, 56–63. doi: 10.1016/j.aca.2020.08.060
- Yang, G.-P., Lu, X.-L., Song, G.-S., and Wang, X.-M. (2010). Purge-and-trap gas chromatography method for analysis of methyl chloride and methyl bromide in seawater. *Chin. J. Anal. Chem.* 38, 719–722. doi: 10.1016/S1872-2040(09)60046-3
- Yang, G.-P., Zhang, H.-H., Zhou, L.-M., and Yang, J. (2011). Temporal and spatial variations of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the East China Sea and the Yellow Sea. *Cont. Shelf Res.* 31, 1325–1335. doi: 10.1016/j.csr.2011.05.001
- Yang, M., Nightingale, P. D., Beale, R., Liss, P. S., Blomquist, B., and Fairall, C. (2013). Atmospheric deposition of methanol over the Atlantic Ocean. *Proc. Natl. Acad. Sci.* 110, 20034–20039. doi: 10.1073/pnas.1317840110
- Yang, M., Beale, R., Liss, P., Johnson, M., Blomquist, B., and Nightingale, P. (2014). Air-sea fluxes of oxygenated volatile organic compounds across the Atlantic Ocean. *Atmos. Chem. Phys.* 14, 7499–7517. doi: 10.5194/acp-14-7499-2014
- Yang, X.-H., Lee, C., and Scranton, M. I. (1993). Determination of nanomolar concentrations of individual dissolved low molecular weight amines and organic acids in seawater. *Anal. Chem.* 65, 572–576. doi: 10.1021/ac00053a014
- Yang, X.-H., Scranton, M., and Lee, C. (1994). Seasonal variations in concentration and microbial uptake of methylamines in estuarine waters. *Mar. Ecol. Prog. Ser.* 108, 303–312. doi: 10.3354/meps108303
- Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., et al. (2018). Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. *Science* 361, 278–281. doi: 10.1126/science.aao4839
- Zhang, H.-H., Li, J.-L., Yang, G.-P., Song, Y.-C., and Jin, N. (2015). Purge-trap gas chromatography and mass spectrometric method for analysis of isoprene in natural waters. *Chin. J. Anal. Chem.* 43, 333–337. doi: 10.1016/S1872-2040(15)60812-X
- Zhang, G. L., Zhang, J., Kang, Y. B., and Liu, S. M. (2004). Distributions and fluxes of methane in the East China Sea and the Yellow Sea in spring. *J. Geophys. Res. Oceans* 109, C07011. doi: 10.1029/2004JC002268
- Zhong, Z., Li, G., Luo, Z., and Zhu, B. (2012). Multi-channel purge and trap system coupled with ion chromatography for the determination of alkylamines in cosmetics. *Anal. Chim. Acta* 715, 49–56. doi: 10.1016/j.aca.2011.12.017
- Zhou, Z., Zhuang, G.-C., Mao, S.-H., Liu, J., Li, X.-J., Liu, Q., et al. (2023). Methanol concentrations and biological methanol consumption in the Northwest Pacific Ocean. *Geophys. Res. Lett.* 50, e2022GL101605. doi: 10.1029/2022GL101605
- Zhuang, G.-C., Heuer, V. B., Lazar, C. S., Goldhammer, T., Wendt, J., Samarkin, V. A., et al. (2018a). Relative importance of methylotrophic methanogenesis in sediments of the Western Mediterranean Sea. *Geochim. Cosmochim. Acta* 224, 171–186. doi: 10.1016/j.gca.2017.12.024
- Zhuang, G.-C., Lin, Y.-S., Bowles, M. W., Heuer, V. B., Lever, M. A., Elvert, M., et al. (2017). Distribution and isotopic composition of trimethylamine, dimethylsulfide and dimethylsulfoniopropionate in marine sediments. *Mar. Chem.* 196, 35–46. doi: 10.1016/j.marchem.2017.07.007
- Zhuang, G.-C., Lin, Y.-S., Elvert, M., Heuer, V. B., and Hinrichs, K.-U. (2014). Gas chromatographic analysis of methanol and ethanol in marine sediment pore waters: validation and implementation of three pretreatment techniques. *Mar. Chem.* 160, 82–90. doi: 10.1016/j.marchem.2014.01.011
- Zhuang, G.-C., Montgomery, A., and Joye, S. B. (2019). Heterotrophic metabolism of C1 and C2 low molecular weight compounds in northern Gulf of Mexico sediments: Controlling factors and implications for organic carbon degradation. *Geochim. Cosmochim. Acta* 247, 234–260. doi: 10.1016/j.gca.2018.10.019
- Zhuang, G.-C., Peña-Montenegro, T. D., Montgomery, A., Hunter, K. S., and Joye, S. B. (2018b). Microbial metabolism of methanol and methylamine in the Gulf of Mexico: insight into marine carbon and nitrogen cycling. *Environ. Microbiol.* 20, 4543–4554. doi: 10.1111/1462-2920.14406