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海洋环境中有机胺的迁移转化研究进展*

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摘要 大气中的有机胺具有潜在的气候效应, 这是当今国际的研究热点之一。海洋是大气中有机胺的重要来源, 但由于海水中有机胺检测难度较大, 导致海洋环境中有机胺的产生机制尚不清楚。本文概述了海洋生物体内有机胺前体物的浓度特征及其对环境中有机胺的影响, 阐述了沉积物、海水及大气中有机胺的浓度特征, 分析了海洋大气气溶胶中有机胺的形成途径, 并指出海水中有机胺检测的难点及现阶段亟待解决的科学问题。为深入认识海洋环境中有机胺的迁移转化规律及其潜在气候效应提供科学依据。

关键词 有机胺; 海洋生物; 盐度; 形成途径; 检测方法
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大气中的有机胺可促进新粒子生成及颗粒物增长, 进而增加云凝结核数浓度, 通过改变辐射强迫对气候变化产生潜在重要的影响(Almeida *et al*, 2013; Chen *et al*, 2016; Sellegri *et al*, 2016; Yao *et al*, 2018)。大气中有150余种有机胺, 其中, 三甲胺(TMA)、二甲胺(DMA)和一甲胺(MMA)是最常见且含量最高的有机胺(Ge *et al*, 2011; Yu *et al*, 2014)。海洋是这3种有机胺的重要来源, 每年向大气中释放80 Gg N (Ge *et al*, 2011)。有机胺还是海洋生物很重要的氮源和能量源, 例如, TMA可被约占海洋水体中总细菌20%的玫瑰杆菌(*Roseobacter*)降解为NH_4^+, 同时释放三磷酸腺苷(ATP), ATP可为该细菌提供能量, NH_4^+则可被其他生物利用(Lidbury, 2015); 在海洋沉积物中, TMA是温室气体甲烷(CH_4)的重要前体物之一, 在含盐环境中, 35%~90%的CH_4是由TMA降解而来的(Oremland *et al*, 1982; King *et al*, 1983)。但当有机胺浓度过高时, 也会对生物造成危害, 如在海水养殖环境中, TMA和DMA是鱼类和藻类腐烂所释放气体(鱼腥味)的重要组成部分(Chung *et al*, 2009), 也是致癌物–亚硝基胺的前体物质。高浓度的TMA和DMA会抑制大分子物质(如DNA、RNA和蛋白质)的合成, 对动物晶胚有致畸作用(Guest *et al*, 1992)。因此, 认识海洋环境中有机胺的形成机制、浓度变化特征等对海洋生物的健康、海洋氮循环乃至全球气候变化具有重要的意义。

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1　海洋环境中有机胺的源与汇

有机胺主要来源于细菌或酶对甜菜碱(GBT)、氧化三甲胺(TMAO)、胆碱(CHO)等季铵化合物的降解(图1)(Welsh, 2000; Carpenter *et al*, 2012; Lidbury *et al*, 2014; Lidbury, 2015; Lidbury *et al*, 2015a、2015b; Cree, 2015)。在海洋环境中,为了应对高盐度(NaCl)的压力,海洋植物、动物和微生物需要合成或吸收GBT、TMAO来调节细胞渗透压(Carpenter *et al*, 2012; Oren, 2015; Cree, 2015; Sun *et al*, 2019)。所以,季铵化合物在海洋生物中的含量远远大于淡水生物。季铵化合物被玫瑰杆菌等细菌降解后会释放出有机胺(图1) (Carpenter *et al*, 2012; Lidbury, 2015; Lidbury *et al*, 2017)。以上大部分有机胺的形成过程主要发生在碎屑颗粒、浮游动物肠道及沉积物等厌氧环境中(Carpenter *et al*, 2012; Cree, 2015)。因此,有机胺在海洋沉积物和水体中广泛存在。海洋沉积物或水体中有机胺的汇主要有以下3种方式:一部分通过海气交换从海水释放到大气中;一部分被硅藻和鞭毛藻等浮游植物直接吸收(Cree, 2015);剩余部分被降解后最终转化为NH_4^+、CH_4和CO_2。因此,季铵化合物及有机胺是海洋环境中很重要的碳源、氮源、能量源(Chen, 2012; Lidbury, 2015; Lidbury *et al*, 2015a; Cree, 2015; Taubert *et al*, 2017; Mausz *et al*, 2019; Sun *et al*, 2019)。

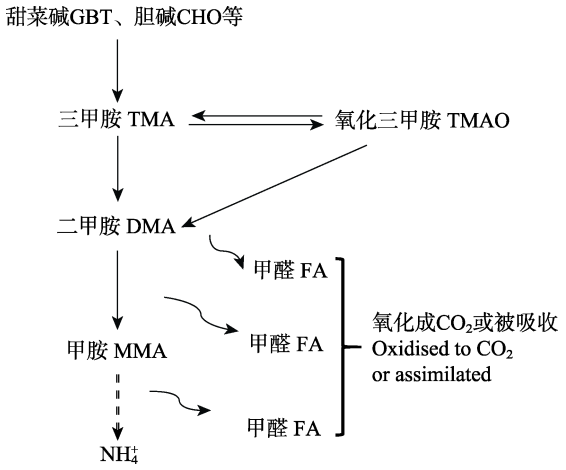

图 1　海洋环境中有机胺的产生与降解过程

Fig.1　Production and degradation processes of amines in marine environment (Carpenter *et al*, 2012; Mausz *et al*, 2019)

2　海洋生物体内有机胺前体物的浓度分布特征

国内外很多研究发现,海洋植物生物量的增加会显著促进水体或大气中有机胺浓度的增加(Gibb *et al*, 1999a; Facchini *et al*, 2008; Müller *et al*, 2009; Hu *et al*, 2015、2018; Yu *et al*, 2016; Dall'Osto *et al*, 2017),这主要是因为GBT和TMAO等季铵化合物广泛存在于海洋大型植物和浮游植物等体内,GBT 可占藻类干重的2% (Blunden *et al*, 1992)。这些GBT通过细胞破裂和摄食等方式释放到环境中,在含螺旋藻(*Spirulina* sp.)的沉积物中,GBT浓度可达100 μmol/gdw (King, 1988)。另外,de Vooys等(2002)研究发现,贝类体内也含有大量的GBT,在地中海贝类体内GBT的浓度高达30.0 g/kg。

20世纪30年代,Beatty(1938)在腐烂的鱼中第1次发现了TMA,因为在鱼类及软体动物中广泛存在有机胺的另一种重要前体物TMAO (Seibel *et al*, 2002; Summers *et al*, 2017)。TMAO占海洋生物(鱼类和甲壳类等)组织干重的7% (de Vooys, 2002)。在海洋鱼类体内,TMAO可应对盐度、温度和浮力的变化,还可增加蛋白质的稳定性(Summers *et al*, 2017)。例如,广盐性鲨鱼从淡水转入海水中,体内TMAO浓度显著增加(Pillans *et al*, 2005)。广盐性软骨鱼随着盐度的减小,TMAO的浓度显著降低(Sulikowski *et al*, 2003)。Chung等(2009)通过对香港89种(共266条)海水鱼、海水和淡水两栖鱼类、淡水鱼体内的TMAO分析发现,9种淡水鱼中只有3种可检测出TMAO,8种海水和淡水两栖鱼类中有6种可检测出TMAO,而72种海水鱼均可检测出TMAO,海水鱼体内TMAO的浓度范围为(0.12~3.5) g/kg,平均浓度为(1.4±0.75) g/kg。在山东青岛阿根廷鱿鱼(*Illex argentinus*)的TMAO含量为8.8 g/kg,硬骨鱼TMAO的含量范围为(0.35~2.3) g/kg,甲壳类TMAO的含量>1.7 g/kg,贝类的TMAO含量低于0.5 g/kg。因此,在不同种类动物体内TMAO的含量存在差异,例如,头足类>甲壳类>硬骨鱼类>贝类(姜城子等, 2014)。海洋动物会通过分泌、排泄或被降解向环境中释放TMAO (Sun *et al*, 2019)。通过宏基因组研究发现,海洋环境中含有TMAO还原酶(把TMAO降解为TMA),这说明TMAO降解产生的TMA也可能是海洋环境中TMA等有机胺的一个重要来源(Sun *et al*, 2019)。因此,海洋动物越多,海洋环境中有机胺的浓度就会越高(Sørensen *et al*, 1987)。虽然,海洋环境中有大量鱼类等动物(陆尧等, 2019; 戴芳群等, 2020),但现阶段关于海洋动物对海水中有机胺影响的报道较少,特别是关于海洋动物种类、数量与海水或大气中有机胺浓度的定性或定量关系鲜有报道。

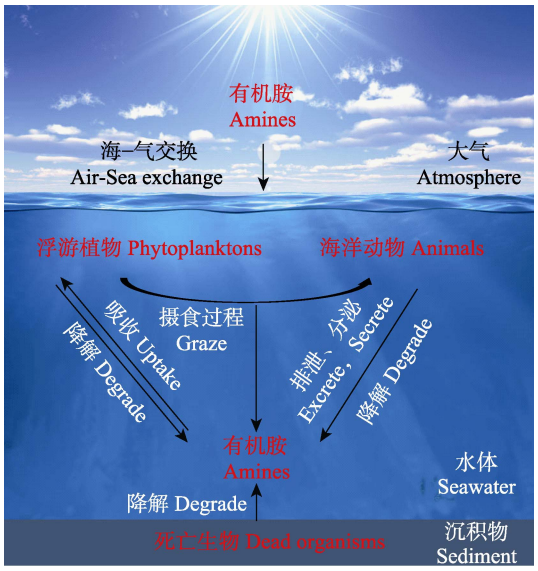

图 2 海洋植物和动物对环境中有机胺的影响示意图
Fig.2 Effects of marine plants and animals on amines in the environment

3 海洋环境中有机胺的浓度特征

海洋生物体内的 TMAO、GBT 和 CHO 等被降解后会影响环境中有机胺的浓度(图 2)。Mausz 等(2019)和 Sun 等(2019)对海水及沉积物空隙水中有机胺的浓度做了详细总结，一般情况下，1 L 海水中有机胺的浓度为纳摩尔级，其浓度较低，所以检测难度较大，1 L 沉积物的孔隙水中有机胺的浓度较 1 L 海水中高 1~3 个数量级(微摩尔级)。例如，在英国默尔塞河口沉积物的孔隙水中 MMA、DMA 和 TMA 的最高浓度分别是 319、9 和 50 μmol/L (Mausz *et al*, 2019)。由于沉积物中的有机质可吸附有机胺，所以，沉积物中有机胺的浓度也较高(Wang *et al*, 1990; Wang *et al*, 1994)。例如，在泰晤士河口沉积物中 3 种有机胺的浓度之和可达 26 μmol/g (Fitzsimons *et al*, 2006)。

一般情况下，海洋大气中颗粒态有机胺盐的浓度是皮克至纳克级(Cree, 2015; van Pinxteren *et al*, 2019)。例如，阿拉伯海大气$PM_{1.0}$(空气动力学直径≤1.0 μm 的颗粒物)中TMA^+和DMA^+的浓度范围为(0.02~0.9)和(1.0~17.1) ng/m^3 (Gibb *et al*, 1999b)；van Pinxteren等(2019) 2011~2013年在热带大西洋的佛得角岛进行观测，发现$PM_{1.0}$中MMA^+和DMA^+的浓度范围为(0~0.6)和(2.2~13.0) ng/m^3；地中海东部克里特岛大气$PM_{1.0}$中DMA^+的平均浓度为(9.0±36.1) ng/m^3，但是TMA^+浓度低于检测限(Violaki *et al*, 2010)；北大西洋(爱尔兰西海岸)大气$PM_{8.0}$中DMA^+的浓度<(1.0~24.0) ng/m^3 (Facchini *et al*, 2008)；我国近海大气PM_{10}(或$PM_{0.056\sim10}$)中DMA^+和TMA^+的平均浓度范围为(0~49.5)和(6.5~44.9) ng/m^3 (Yu *et al*, 2016; Xie *et al*, 2018; Hu *et al*, 2018; Zhou *et al*, 2019)，而$PM_{0.1}$中DMA^+和TMA^+的浓度范围分别是(0.0~5.4)和(2.7~19.5) ng/m^3 (Yu *et al*, 2016)。这说明我国近海大气中有机胺盐的浓度比世界上大部分其他海域高，特别是2012年5月PM_{11}中有机胺盐浓度甚至比世界其他海域高1~3个数量级(Hu *et al*, 2015)，如此高浓度有机胺可能具有很重要的气候效应，但其形成原因有待近一步确认。

4 海洋大气气溶胶中有机胺盐的形成途径

目前，国际上对海洋大气气溶胶中有机胺盐的形成途径存在争议。国际主流观点认为，海水中有机胺通过海气交换进入大气中，一部分以气态形式存在，另一部分气体再通过大气化学反应形成二次有机胺盐(即来自二次源)(Gibb *et al*, 1999b; Facchini *et al*, 2008; Müller *et al*, 2009; Myriokefalitakis *et al*, 2010; Köllner *et al*, 2017; Willis *et al*, 2017)。例如，Müller 等(2009)研究发现，海洋大气气溶胶中高浓度的有机胺盐主要分布在(0.14~0.42) μm 粒径段上，Facchini 等(2008)研究发现，海洋大气气溶胶中高浓度的有机胺盐主要分布在(0.25~0.50) μm 粒径段上，并且与二次生成的NH_4^+、SO_4^{2-}和甲基磺酸盐(MSA^-)的粒径分布相似，认为该大气气溶胶中有机胺盐是二次生成的。通过对 2012~2016 年从我国近海到西北太平洋 10 多个航次分析发现，大气气溶胶中的DMA^+和TMA^+主要分布在(0.20±0.10)、(0.40±0.10)和(0.80±0.20) μm 等的粒径段上，推测这些有机胺盐也是来自二次源(Hu *et al*, 2015; Yu *et al*, 2016; Xie *et al*, 2018)。

但是，Frossard 等(2014)在开阔大洋的一次源有机气溶胶中检测出了有机胺官能团；Gorzelska 等(1990)推测，在大风浪天气条件下，富含有机胺的海洋表层物质可能会随着海盐气溶胶被传输到大气中，从而导致大气气溶胶中有机胺盐浓度升高；Hu 等(2018)在 2014 年春季对西北太平洋大气气溶胶中有机胺盐进行分析发现，该区域有机胺盐的平均浓度比近海高 1 个数量级，TMA^+浓度最高(4.4 nmol/m^3)的样品是在风速最高时(14 m/s)被检测到，并且绝大部分样品中TMA^+的粒径分布与最高浓度样品的相似，即：大气气溶胶中TMA^+的浓度随粒径的减小逐渐升高(Hu *et al*, 2018)。Hu 等(2017)研究发现，当风速>5.4 m/s 时，西北太平洋水体中的有机质和细菌可能会通过海洋飞沫气溶胶被传输到大气中，并且海洋飞

沫气溶胶中有机质的丰度会随粒径的减少而增加(Gantt *et al*, 2013; Quinn *et al*, 2014、2015)。另外，国际上很多专家通过室内海洋飞沫气溶胶模拟实验，也发现海水中有机质主要富集在亚微米大气气溶胶上(Quinn *et al*, 2015; Hultin *et al*, 2010; Rastelli *et al*, 2017)。因此，Hu 等(2018)推测，在高风速条件下，海水中的 TMA^+随海洋飞沫被直接传输到大气中(即来自一次源)。Dall'Osto 等(2019)研究显示，大气气溶胶中一次源有机胺盐占总有机胺盐的 11%~25%。总体来说，现阶段关于一次源有机胺盐对总有机胺盐占比的报道仍然较少。

5　海水中有机胺的检测方法

现阶段，国际上关于海洋生物体内有机胺前体物浓度、大气中有机胺浓度的报道相对较多，但由于海水中有机胺浓度较低(nmol/L级)，且MMA、DMA和TMA具有易溶于水、极性强和易挥发等特点，一直以来海水中有机胺的检测具有较大的挑战(Carpenter *et al*, 2012; Cree, 2015; Sun *et al*, 2019)，从而也限制了对海洋环境中有机胺迁移转化规律的认识。目前，海水中有机胺的检测主要分为3个关键的阶段：预浓缩阶段、分离阶段和检测阶段。预浓缩所用的前处理装置主要有：固相微萃取(SPME)、顶空固相微萃取(HS-SPME)和吹扫捕集装置(P&T)等。分离和检测阶段主要是由离子色谱(IC)或气相色谱仪(GC)等组合不同检测器完成(Cree, 2015)。

采用 IC 可检测大气中有机胺的浓度(Hu *et al*, 2015、2018; Yu *et al*, 2016; Xie *et al*, 2018)，但由于有机胺分析柱承载不了海水中高浓度的 Na^+，导致海水中有机胺不能直接在IC上测试(Ferreira *et al*, 2017)。Ferreira 等(2017)通过向 P&T 装置中加入 NaOH，把含盐水体中有机胺挥发出来，再进行浓缩，最后进入IC测试。但P&T-IC方法对有机胺检测的灵敏度较低，且在吹扫捕集的捕集阱内会存在严重残留，且捕集阱内装填的吸附剂种类不同其吸附性能差异也较大(中华人民共和国国家标准 HJ 1042-2019)，也不适合对海水中低浓度有机胺的浓缩。Gibb 等(1995)采用流动注入气体扩散(FIGD)装置与 IC 结合可很好地测试海水中的有机胺。但由于 FIGD 比较复杂，近 20 年来该方法未得到广泛地应用(Cree, 2015)。

GC 对有机胺检测的灵敏度较高(Huang *et al*, 2014)。国内外很多专家采用 GC 结合不同检测器来测定大气、水体、孔隙水和沉积物中的有机胺，如气相色谱仪–质谱仪(GC-MS)、气相色谱仪–火焰检测器(GC-FID)和气相色谱仪–氮磷检测器(GC-NPD)(Cree, 2015)。采用该仪器检测大气中有机胺的方法与水体的大体相似。基本原理是把大气采样膜或沉积物中的有机胺萃取到水体中，然后，通过衍生或把有机胺挥发、再浓缩后进行测试。但 GC-MS 只能测 DMA^+或 TMA^+中的 1 种(Liu *et al*, 2017; Zhuang *et al*, 2017、2018)，很难实现 DMA^+和 TMA^+的同步检测(Cree *et al*, 2018)。GC-FID 和 GC-NPD 可同步检测以上 2 种有机胺。与 GC-FID 相比，GC-NPD 对海水中有机胺的灵敏度会更高(Cree, 2015)。Cree 等(2018)研究显示，可采用 SPME-GC-NPD 检测海水中的 TMA^+、DMA^+和 MMA^+，检测限可达(0.4~2.9) nmol/L。虽然，该方法也存在一些不足之处，如该前处理方法耗时较长、分析较低浓度样品时可能会存在实验误差等(Sun *et al*, 2019)，但相比较而言，目前，该方法是国际上检测海水中有机胺比较有效的方法之一。

6　存在问题及展望

综上所述，虽然目前国内外对海洋生物体内有机胺前体物的浓度、降解这些前体物的优势细菌及大气中有机胺的潜在气候效应等方面开展了一定的研究，但海洋环境中有机胺的迁移转化规律还不清楚，还有许多问题需要解决，具体体现在以下几点：

(1)海洋生物对环境中有机胺的贡献。系统分析不同种类浮游植物、动物体内有机胺前体物的浓度分布特征；阐明这些前体物在食物链上的传递规律；鉴定天然海域中把这些前体物降解为有机胺的优势细菌；通过计算海洋生物量与环境中有机胺浓度的比值，估算海洋生物对环境中有机胺的贡献。

(2)海水中有机胺向大气中传输的影响机制。通过利用在线离子色谱获取高时空分辨率的气态和颗粒态有机胺数据，解析温度、相对湿度和风速等气象因子对它们从海水向大气中传输的影响。

(3)我国近海高浓度有机胺的来源解析。我国近海不仅藻华和绿潮等灾害频发，同时，还进行着大规模的海水养殖。通过现场观测，进一步解析我国近海大量的浮游植物和养殖动物对我国近海大气中高浓度有机胺的贡献。

(4)海水中有机胺检测方法的建立。目前，GC-NPD 是一种有效分离 3 种有机胺的检测方法，但采用 SPME 浓缩海水中有机胺的方法还存在一定的不足，未来通过研发更好的海水中有机胺的提取方法，再结合 GC-NPD 实现海水中有机胺的检测。从而进一步阐明有机胺在海洋生物、水体和大气中的迁

移转化规律, 以提升对海洋大气中有机胺潜在气候效应的认识。

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Advancements in the Transport and Transformation of Amines in the Marine Environment

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Abstract In the atmosphere, amines play potentially important roles in climate change, which is a hot spot of the current international research. The ocean is an important source of amines in the atmosphere; however, the mechanism of the formation of amines in the environment has not been elucidated due to the difficulty of detecting amines in seawater. This article outlines the concentration characteristics of amine precursors in marine organisms and their impact on amines in the marine environment; summarizes the concentration characteristics of amines in sediments, seawater, and the atmosphere; analyzes the formation pathway of amines in marine atmospheric particles; and identifies the difficulties in the detection of amines in seawater and the related problems that need urgent attention. This study provides insights into the transport and transformation of amines in the marine environment and the resulting climatic effects on the marine atmosphere.

Key words Amines; Marine organisms; Salinity; Formation pathways; Detection methods

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