

环境氨气被动采样法的适用性研究及在城市观测中的应用

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摘要:以环境 NH_3 为观测对象, 对 ALPHA 被动采样法的采样吸附膜制备、样品保存和采样时间开展适用性研究, 并与主动采样方法进行了对比验证, 在此基础上进一步在上海市不同功能区开展了实地观测应用研究。结果显示: 酸浸渍法制备的吸附膜 NH_4^+ 含量均值为 $(0.27 \pm 0.13) \mu\text{g}$, 比未处理吸附膜的 NH_4^+ 含量高约 8%, 且可在膜液比(张/mL)为 1:4~8:4 范围内增加膜的单次浸渍数量以降低制备过程中的溶剂使用量, 酸浸渍法的制备流程及不同膜液比处理方式对空白吸附膜的 NH_4^+ 含量影响不大。当采样温度为 20°C , 采样时长为 168 h 时, 该被动法测定环境 NH_3 的方法检出限为 $0.08 \mu\text{g}/\text{m}^3$ 。密实袋双层密封、 4°C 冷藏、保存时间小于 30 d 的保存方式未显著增加空白膜的 NH_4^+ 含量, 适用于空白吸附膜和样品膜的保存。采样时间适用性验证结果表明: 城市地区使用 ALPHA 被动采样法测定环境 NH_3 时, 采样时间不少于 6 d 且至少在 30 d 内进行连续采样。使用 ALPHA 被动采样法与主动采样方法观测 NH_3 浓度时, 观测结果变化趋势较一致, 测量结果吻合良好(相关系数为 0.87, 斜率为 1.16), 进一步证明了该研究采用的被动 NH_3 采样方法对环境 NH_3 浓度的测量具有较好的可靠性。实际观测结果显示, 2022 年上海市夏季环境 NH_3 平均浓度为 $(10.01 \pm 5.22) \mu\text{g}/\text{m}^3$, 受 2022 年夏季极端高温气候影响, NH_3 浓度水平明显高于已有研究结果。不同功能区的 NH_3 浓度排序为农业区 $[(13.36 \pm 5.24) \mu\text{g}/\text{m}^3] >$ 工业区 $[(11.22 \pm 5.24) \mu\text{g}/\text{m}^3] >$ 城区 $[(10.35 \pm 4.39) \mu\text{g}/\text{m}^3] >$ 生态区 $[(4.28 \pm 2.4) \mu\text{g}/\text{m}^3]$, 说明虽然与农业活动相关的监测站点 NH_3 浓度高值显著, 但城区和工业区的非农业源排放对 NH_3 浓度的影响同样不可忽视。ALPHA 被动采样方法能较好地捕捉城市不同功能区的 NH_3 浓度特征, 可满足城市环境 NH_3 浓度观测应用, 适用性验证及实际应用结果可为区域和城市 NH_3 的精准测量提供参考。

关键词: NH_3 ; 被动采样法; 适用性; 城市观测

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Study on the Applicability of Passive Sampling Method for Ambient Ammonia and Its Application in Urban Observation

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Abstract: In this study, the applicability of the ALPHA passive sampling method in terms of sampling adsorption filter preparation, sample preservation, and sampling period was carried out for ambient ammonia observation and compared with the active sampling method for validation, and further field observation application studies were conducted in different functional areas of Shanghai based on the results of the study. The results showed that the NH_4^+ content of the adsorption filters obtained by the acid immersion method was $(0.27 \pm 0.13) \mu\text{g}$, which was about 8% higher than that of the untreated adsorption filters, and the number

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of single immersions could be increased in the range of 1 : 4-8 : 4 (slice/mL) to reduce the amount of solvent used in the preparation process. The preparation process of the acid immersion method and the different filter-to-liquid ratio treatments had few effects on the NH_4^+ content of the blank adsorption filter. The method detection limit for this passive method of ambient ammonia determination was $0.08 \mu\text{g}/\text{m}^3$ when the sampling temperature was 20°C and the sampling period was 168 h. The preservation method using the double-sealed bag, 4°C frozen, and preserving for less than 30 days had not significantly increased the NH_4^+ content of the blank filter, which is suitable for the preservation of blank and sample filters. The applicability verification results of the sampling period showed that the number of the sampling period is recommended to be at least 6 days and at least 30 days for continuous sampling when using ALPHA passive sampling in urban areas to measure ambient ammonia. The observed NH_3 concentration trends of the ALPHA passive sampling method and active sampling method were more consistent, and the measurement results were correlated well (correlation coefficient of 0.87, slope of 1.16), which further proved that the passive NH_3 sampling method used in this study has good reliability for the measurement of ambient ammonia concentration. The actual observation results showed that the average ambient atmospheric NH_3 concentration during the summer of 2022 in Shanghai was $10.01 \pm 5.22 \mu\text{g}/\text{m}^3$, and the NH_3 concentration level affected by the extremely high-temperature climate in summer of 2022 was significantly higher than the results of past studies. The NH_3 concentrations in different functional areas were ranked as follows: agricultural area ($13.36 \pm 5.24 \mu\text{g}/\text{m}^3$) > industrial area ($11.22 \pm 5.24 \mu\text{g}/\text{m}^3$) > urban area ($10.35 \pm 4.39 \mu\text{g}/\text{m}^3$) > ecological area ($4.28 \pm 2.4 \mu\text{g}/\text{m}^3$), which showed that although the high concentrations of NH_3 at the monitoring stations related to agricultural activities were significant, the influence of non-agricultural source emissions on NH_3 concentrations in the urban and industrial areas could not be ignored as well. The ALPHA passive sampling method can better capture the characteristics of ammonia concentration in different functional areas of the city, which can meet the application of ammonia concentration observation in urban environment, and the applicability verification and application provide a reference for accurate measurement of NH_3 in the regional and urban atmosphere.

Keywords: NH_3 ; passive sampling method; applicability; urban observation

氨气 (NH_3) 是大气中最重要的碱性气体,对大气环境和生态系统起着至关重要的作用^[1-2]。一方面, NH_3 与大气中的酸性气体反应生成硫酸铵、硝酸铵等气溶胶,是导致细颗粒物 ($\text{PM}_{2.5}$) 和灰霾污染的重要原因;另一方面, NH_3 可以中和大气酸性物质,降低酸雨对生态环境的影响^[2]。此外, NH_3 作为生态系统的主要营养物质之一,也是全球氮循环的重要组成部分^[3]。中国中东部地区是全球 NH_3 排放最密集的地区之一^[4-7],尽管农业仍然占 NH_3 排放量的 80% 以上,是公认的 NH_3 主要排放源^[8],但近期基于排放^[9]和卫星的^[10]研究指出,非农业来源(特别是工业排放源)的贡献日益增加。城市作为一种开放而复杂的巨系统^[10],其规模与发展水平越大,功能区混合程度越高,城市污染来源越复杂。因此,从城市不同功能区的 NH_3 浓度分布入手,厘清其来源及转化,对于特大及超大城市的空气污染防治具有重大意义。

环境大气中 NH_3 的测量方法多样^[11-21],依据采样时是否需要额外能源动力供给,将观测方法分为主动法和被动法 2 类。目前,中国尚未对大气 NH_3 开展业务化观测,现行国家标准对环境空

气中 NH_3 的测量多采用主动法,应用于环境空气、固定污染源无组织排放监控点和制药、化工、炼焦等工业行业废气中 NH_3 的测定^[22]。与主动法采样相比,被动法不需要提供额外的能源动力,具有价格低廉、设备占地少和操作运维方便等优势^[23-29],适用于远程、高海拔或难以到达的野外环境,因此在长时间和大尺度的区域 NH_3 监测网中被广泛应用^[30-36]。目前普遍使用的被动采样器有 Ogawa、ALPHA、Analysts 和 Radiello 等^[30]。被动法的前期准备步骤较繁琐且人为干扰因素较多,存在一定的不确定性^[35,37-38],虽然 ALPHA 采样器已成功用于观测不同地区 NH_3 的垂直浓度^[39]和水平浓度^[40],但其适用性尚未得到很好的证实,特别是在功能区混合程度高的城市地区。

该研究采用英国生态水文中心 (CEH) 开发的 ALPHA (Adapted Low-Cost High Absorption Passive Samplers) 被动采样器^[41],在上海开展基于被动法的环境 NH_3 观测适用性研究及应用。适用性研究过程主要针对被动法观测中吸附膜制备、样品保存和采样时间等开展评估验证,并进一步与主动采样法的结果进行对比;在被动法适用性验证结果的基础上,在上海市 4 类不同功能区

的6个观测点开展此观测方法的实地应用研究,以期为区域及国家大气NH₃的精准测量提供参考。

1 研究方法

1.1 采样地点和时间

被动法采样的适用性评估观测点为徐汇站点(XH),该站点位于上海市环境科学研究院城市大气复合污染观测基地(32°10' N, 121°25' E)。

基于被动法的应用研究过程,选取上海市城区、工业区、生态区和农业区4类功能区共计6个观测站点,开展NH₃浓度的被动监测。其中,黄浦(HP)、静安(JA)和徐汇(XH)3个站点位于上海市中心城区,人口密度大,可代表典型城区;化工区(HGQ)站点位于上海化工区,可代表典型工业区;崇明(CM)站点位于崇明东滩自然保护区,作为生态区代表;农业园(NYY)站点位于青浦现代农业园试验田,作为农业区代表(图1)。观测时段为2022年6月20日—8月29日。

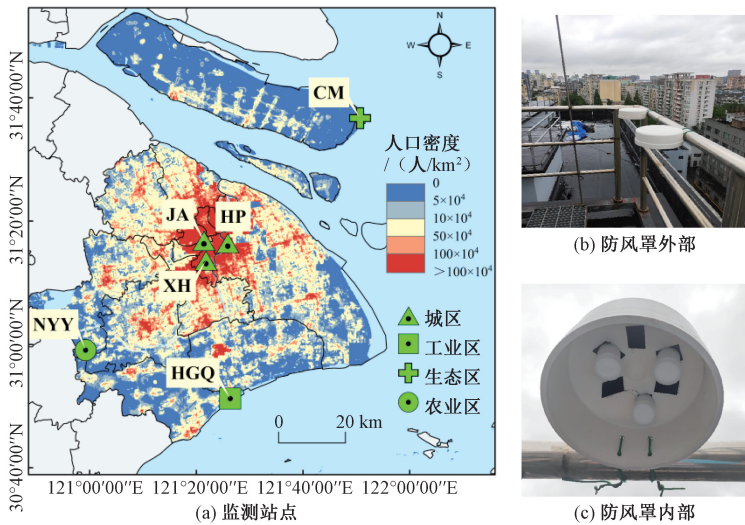


图1 大气NH₃被动监测站点位置及现场布设情况

Fig. 1 Locations of passive monitoring stations in Shanghai and site layout

1.2 被动采样吸附膜的制作及离子色谱分析

监测过程选用的ALPHA被动采样器以一端开口的聚乙烯管(长为26 mm,外径为27 mm)为主体^[30],从内到外依次装载浸渍了酸溶液的吸附膜、吸附膜固定圈、PTFE(Poly tetra fluoroethylene)材质的颗粒物阻隔膜和阻隔膜固定圈。采样过程中,NH₃基于扩散原理,被酸浸的吸附膜吸附,而颗粒物则被PTFE膜阻隔在采样器外面。

吸附膜选用纤维素膜定量滤纸(Low Ash 604, 3.463 cm²,德国Hahnemuehle公司)^[42],吸附剂为13%柠檬酸甲醇溶液。考虑吸附膜的使用量和方法普遍性,采用酸浸渍法,即将膜放入吸附剂中酸浸来制备NH₃采样吸附膜。酸浸渍法吸附膜制备的基本流程见图2^[43-45],具体操作步骤包括:①将50张空白未处理膜放置在200 mL吸附剂(13%柠檬酸甲醇溶液)中浸泡15 min,实

验过程中吸附剂使用后倒掉;②将膜放入200 mL超纯水浸泡5 min,再放入甲醇浸泡5 min,该步骤重复一次,实验过程中超纯水和甲醇使用后倒掉;③将膜再次放入200 mL吸附剂重新浸泡15 min,实验过程中吸附剂使用后倒掉;④将浸泡后的吸附膜单张斜靠在培养皿侧边,置于真空干燥器干燥后,双层密封冷藏备用。

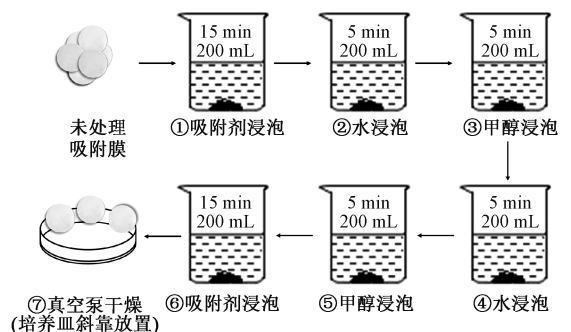


图2 吸附膜制备流程

Fig. 2 Flow chart of adsorption filters preparation

采样时将采样器按照上述装载顺序组装,然后将底部与防风罩内部的魔术贴粘连,见图1(c)。采样后的样品经超纯水提取后,使用离子色谱(940 Professional IC Vario,瑞士万通)进行定量分析^[46]。超纯水提取方法为将吸附膜从采样器中取出,置于15 mL离心管内,加入10 mL超纯水超声浸提10 min后,用注射器抽取5 mL提取液,再经0.22 μm聚醚砜(PES)微孔滤膜过滤,将得到的滤液进行离子色谱分析。分析过程中,利用离子色谱仪的Metrosep C4-100/4.0阳离子柱测定NH₄⁺含量,其中阳离子淋洗液为2.5 mmol/L HNO₃溶液。平行样品测定结果差控制在5%以内。将结果去除空白后,根据仪器厂家提供的转化公式计算参比状态下(101.3 kPa和25℃)的NH₃质量浓度。

1.3 NH₃浓度计算方法

根据Fick定律计算被动采样器采样膜表面的扩散速率^[30],气体在膜上扩散,采样器有效采样体积(V)计算公式如下。

$$V = DA/L = 0.1987 [(273.15 + T)/273.15]^{1.81} At/L \quad (1)$$

式中: D 为气体扩散系数,与温度有关^[47],单位为cm²/s; T 为环境温度,单位为℃; A 为采样器有效横截面积(3.463×10^{-4} m²); t 为采样时间,单位为h; L 为气体扩散距离(0.006 m)。

样品NH₃浓度计算公式如下。

$$C_{\text{NH}_3} = \frac{0.9442 \times (m_a - m_b)}{\beta_{\text{NH}_3} \times V} \quad (2)$$

式中: C_{NH_3} 为样品NH₃浓度,单位为μg/m³; m_a 为离子色谱仪测得的样品浸提液中NH₄⁺含量,单位为μg; m_b 为空白样品浸提液的NH₄⁺含量,单位为μg; β_{NH_3} 为传质校正系数;ALPHA被动采样器的质量转换校正系数为0.6699; V 为采样器有效采样体积,单位为m³。

1.4 与主动法同步比对实验

该研究于2022年2月7日—8月1日同步开展了ALPHA被动采样方法与主动采样方法的比对实验。ALPHA被动采样时间设置为7 d(每周一09:00开始采样),每组3个平行样,有效样本量为13组。主动采样方法采用在线气溶胶和气体监测仪(MARGA ADI 2080,瑞士万通)进行监测,设备基于气体扩散原理测量NH₃的浓度^[40,48],时间分辨率为小时^[49]。仪器在采样和分

析过程中,以浓度为10 mg/L的H₂O₂溶液为吸收液,以浓度为0.007 mol/L的Na₂CO₃和0.007 mol/L的NaHCO₃混合液为阴离子淋洗液,以浓度为0.003 2 mol/L的HNO₃溶液为阳离子淋洗液,以浓度为0.3 mol/L的H₃PO₄为抑制液。气体组分NH₃的最低检测限为0.05 μg/m³。使MARGA方法的采样时段与ALPHA方法的采样时段同步,然后进行同期对比分析。

1.5 质量保证和质量控制

将每月样品归为1个批次,每批次样品增加实验室空白,单站点每批次样品增加全程序空白,其测定结果应低于方法测定下限。使用离子色谱进行定量分析时,标准曲线的相关系数应≥0.995。

2 结果与讨论

2.1 被动吸附膜制备过程验证

根据酸浸渍法的制备程序(图2)制备吸附膜,并测定吸附膜NH₄⁺含量,可以评估不同操作步骤是否会引入NH₄⁺污染。图3给出了经过不同操作步骤获得的吸附膜NH₄⁺含量的测定结果。未处理吸附膜的NH₄⁺含量均值为(0.25 ± 0.02) μg,经操作步骤①~⑥获得的吸附膜NH₄⁺含量均值为(0.21 ± 0.06) μg,经最终干燥(步骤⑦)制备获得的吸附膜NH₄⁺含量均值为(0.27 ± 0.13) μg。可以看到,最终制备获得的吸附膜较未处理吸附膜的NH₄⁺含量高约8%,基于酸浸渍法制备吸附膜的不同操作步骤对吸附膜的NH₄⁺本底含量影响不大,表明该制备流程可应用于被动吸附膜的制备。根据上述酸浸渍法制备获得的空白膜NH₄⁺测量结果,计算得到不同温度和采样时间下的NH₃浓度数据。以3σ作为方法检出限,4倍检出限为测定下限。因此,当采样温度为20℃,采样时长为168 h时,被动法测定环境NH₃的方法检出限为0.08 μg/m³,测定下限为0.32 μg/m³。

为提高酸浸渍法制备溶剂(甲醇和柠檬酸)的使用率,同时减少实验室资源消耗和后期处理压力,通过跟踪空白膜的制备数量与溶剂使用量的不同比例(以下简称膜液比)下的NH₄⁺含量变化,可以获得膜液比对空白膜制备的影响,以探求更合适且高效的制备方案。该研究将膜液比由酸

浸渍法设定的 1 : 4 递增至 8 : 4, 图 4 为不同膜液比条件下获得的吸附膜 NH_4^+ 含量变化情况。由图 4 可知, 不同膜液比条件下制备的吸附膜 NH_4^+ 含量为 $(0.21 \pm 0.09) \sim (0.29 \pm 0.06) \mu\text{g}$, 平均为 $(0.24 \pm 0.03) \mu\text{g}$, 整体处于制备的吸附膜 NH_4^+ 含量变化范围内 $[(0.27 \pm 0.13) \mu\text{g}]$ 。改变膜液比后, 膜液比为 2 : 4 ~ 8 : 4 时, 制备的吸附膜的 NH_4^+ 含量为膜液比为 1 : 4 条件下的 78% ~ 107%, 表明提高膜液比并未显著增加吸附膜的 NH_4^+ 含量本底值。因此, 可在膜液比为 1 : 4 ~ 8 : 4 范围内增加膜的单次浸渍数量, 从而降低酸浸渍法吸附膜制备的溶剂使用量。

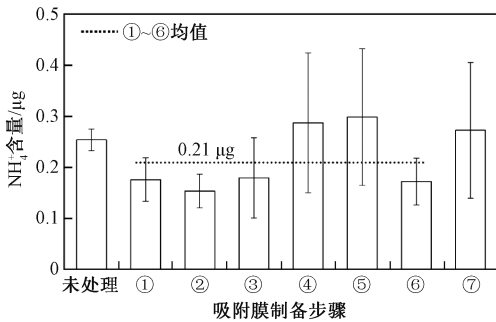


图 3 吸附膜制备过程中 NH_4^+ 含量的变化

Fig. 3 Variations of NH_4^+ contents during the preparation of adsorption filters

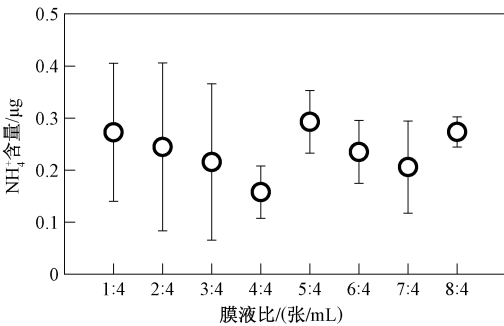


图 4 不同膜液比下吸附膜 NH_4^+ 含量

Fig. 4 NH_4^+ contents of adsorbed filters under different filters to liquid ratios

2.2 被动吸附膜保存过程验证

被动吸附膜通常在批量处理后继续放在低温中保存, 以满足长时间野外采样的需要^[50]。为评估长时间保存可能对吸附膜 NH_4^+ 含量造成的影响, 该研究将制备好的吸附膜用密实袋 (聚乙烯材质, 双面 16 丝) 双层密封后放入 4 °C 冰箱冷藏, 分别评估了保存 0、4、7、10、14、21、30 d 条件下吸附膜的 NH_4^+ 含量变化情况。图 5 显示了不同保

存时间下的吸附膜 NH_4^+ 含量变化情况。由图 5 可知, 4~30 d 保存时间下, 吸附膜的 NH_4^+ 含量为 $(0.22 \pm 0.02) \sim (0.34 \pm 0.06) \mu\text{g}$, 约为新制备膜 (保存时间为 0 d) NH_4^+ 含量的 81% ~ 126%, 说明采用密实袋双层密封、4 °C 冷藏、保存时间不超过 30 d 的保存方式, 并未显著增加吸附膜的 NH_4^+ 含量本底值, 可适用于空白吸附膜和样品膜的保存。

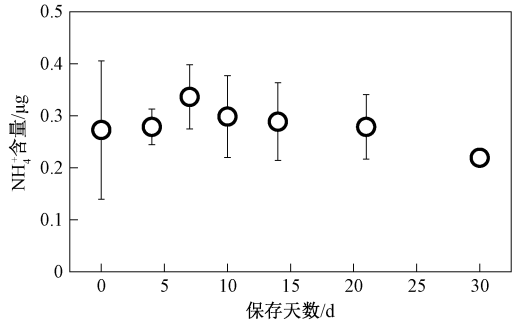


图 5 不同保存时间下吸附膜 NH_4^+ 含量变化

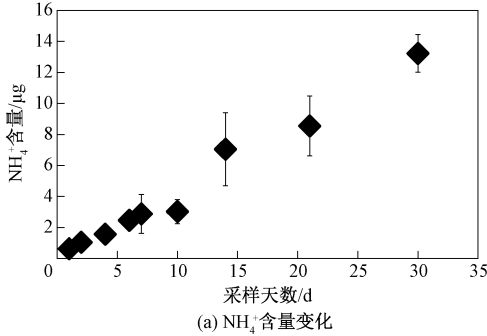
Fig. 5 Variations of NH_4^+ contents in filter sampled at different preservation periods

2.3 被动采样方法采样时间验证

已有研究中, 采用 ALPHA 采样器进行实际观测时的采样时间设置在 60 d 内不等^[51-54]。为探究城市地区基于被动采样器进行 NH_3 浓度监测的最适宜采样天数, 该研究设置了不同采样时间 (1、2、4、6、7、10、14、21、30 d) 的条件实验。图 6 (a) 为不同采样时间下采集的吸附膜的 NH_4^+ 含量变化情况。由图 6 (a) 可知, 随着采样时间增加到 30 d, 吸附膜采集到的 NH_4^+ 含量持续上升, 表明经过 30 d 采样后的吸附膜并未达到吸附饱和。有研究报道, 在京津冀 NH_3 排放热点区域连续采样 60 d 才可能达到饱和^[55], 因此 ALPHA 被动采样法至少可在 30 d 以内进行连续采样。

此外, 该研究采用空白吸附膜的 NH_4^+ 含量 (m_{blk}) 与实际样品的 NH_4^+ 含量 (m_s) 的比例 (m_{blk}/m_s) 来确定最低采样天数。 m_{blk}/m_s 值越低, 表明空白吸附膜的 NH_4^+ 本底含量对测量结果的影响越小。图 6 (b) 显示了不同采样时间下 m_{blk}/m_s 值的变化情况。 m_{blk}/m_s 值随着采样时间的增加呈幂函数递减趋势, 当采样时间超过 6 d 时, m_{blk}/m_s 值降低到 20% 以下; 随着采样时间增加, m_{blk}/m_s 值下降趋势趋于平缓, 当采样时间超过 14 d 时, m_{blk}/m_s 值降低到 10% 以下。上述结果表明: 当采样时间大于 6 d 时, 空白吸附膜 NH_4^+ 本底含量对

样品的影响低于 20%，处于可接受范围，因此城市地区使用 ALPHA 被动采样法测定环境 NH_3 时，建议采样天数不少于 6 d。这与 PUCHALSKI 基于被动采样方法开展环境 NH_3 监测研究中设置的 1~2 周的采样时间相契合^[30]。此外，MENG



等^[52]、CAO 等^[53]和 TANNER 等^[54]使用被动采样器 Ogawa 对北京、西安和香港的 NH_3 进行监测，设置的采样天数均为 7 d。还有研究建议，冬季 NH_3 浓度低，4 周采样一次为宜，夏季 NH_3 浓度高，2~3 周采样一次为宜^[51]。

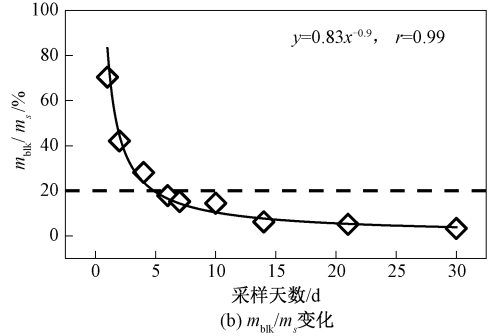


图 6 不同采样时间下的 NH_4^+ 含量变化和 $m_{\text{bk}}/m_{\text{s}}$ 的变化

Fig. 6 Variations of NH_4^+ contents using passive sampling in different sampling periods and ratios of NH_4^+ contents in blank filters to the real sampled NH_4^+ contents

2.4 与主动采样仪器对比验证

基于上述验证结果，开展主、被动同步采样观测。观测期间，在采样温度为 20 °C，采样时长为 168 h 条件下，实验室空白和全程序空白测得的 NH_3 浓度分别为 0.12 ~ 0.26 $\mu\text{g}/\text{m}^3$ 和 0.09 ~ 0.29 $\mu\text{g}/\text{m}^3$ ，测定结果均低于方法测定下限，观测结果可靠。采样时，采样开始时间相同的样品为一组，每组 3 个平行样，相对标准偏差为 20%，方法重复性良好。PAN 等^[40]将被动法与 2 种主动法进行了比对，结果显示，相关系数分别为 0.97 和 0.92，呈强对应关系。图 7(a) 给出了观测期间

ALPHA 被动采样与 MARGA 主动采样获得的 NH_3 浓度变化情况。由图 7(a) 可知，ALPHA 与 MARGA 测得的 NH_3 浓度变化趋势一致性较好，观测期间平均浓度分别为 $(6.82 \pm 2.27) \mu\text{g}/\text{m}^3$ 和 $(6.32 \pm 3.05) \mu\text{g}/\text{m}^3$ ，ALPHA 测得的 NH_3 浓度整体略高于 MARGA。图 7(b) 为主、被动 2 种采样方法测量的 NH_3 浓度对比结果，其线性拟合斜率为 1.16，两者线性拟合的相关系数为 0.87，说明 ALPHA 与 MARGA 的测量结果吻合良好，进一步证明了该研究采用的被动 NH_3 采样方法对环境 NH_3 浓度的测量具有较好的可靠性。

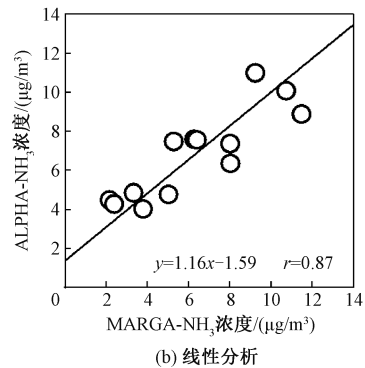
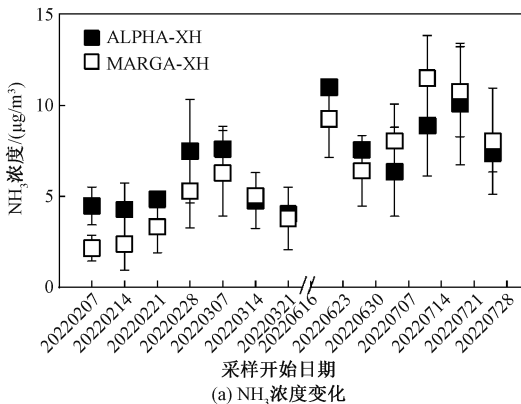


图 7 观测期间被动采样 ALPHA 与主动采样 MARGA 获得的 NH_3 浓度变化与线性分析

Fig. 7 NH_3 concentrations obtained by ALPHA passive sampling and MARGA online measurement and linear analysis

2.5 被动法在城市观测中的应用

图 8 给出 2022 年夏季观测期间上海市总体

NH₃ 浓度变化和不同功能区 NH₃ 浓度变化情况, 以及与其他研究中 NH₃ 浓度观测结果的对比。

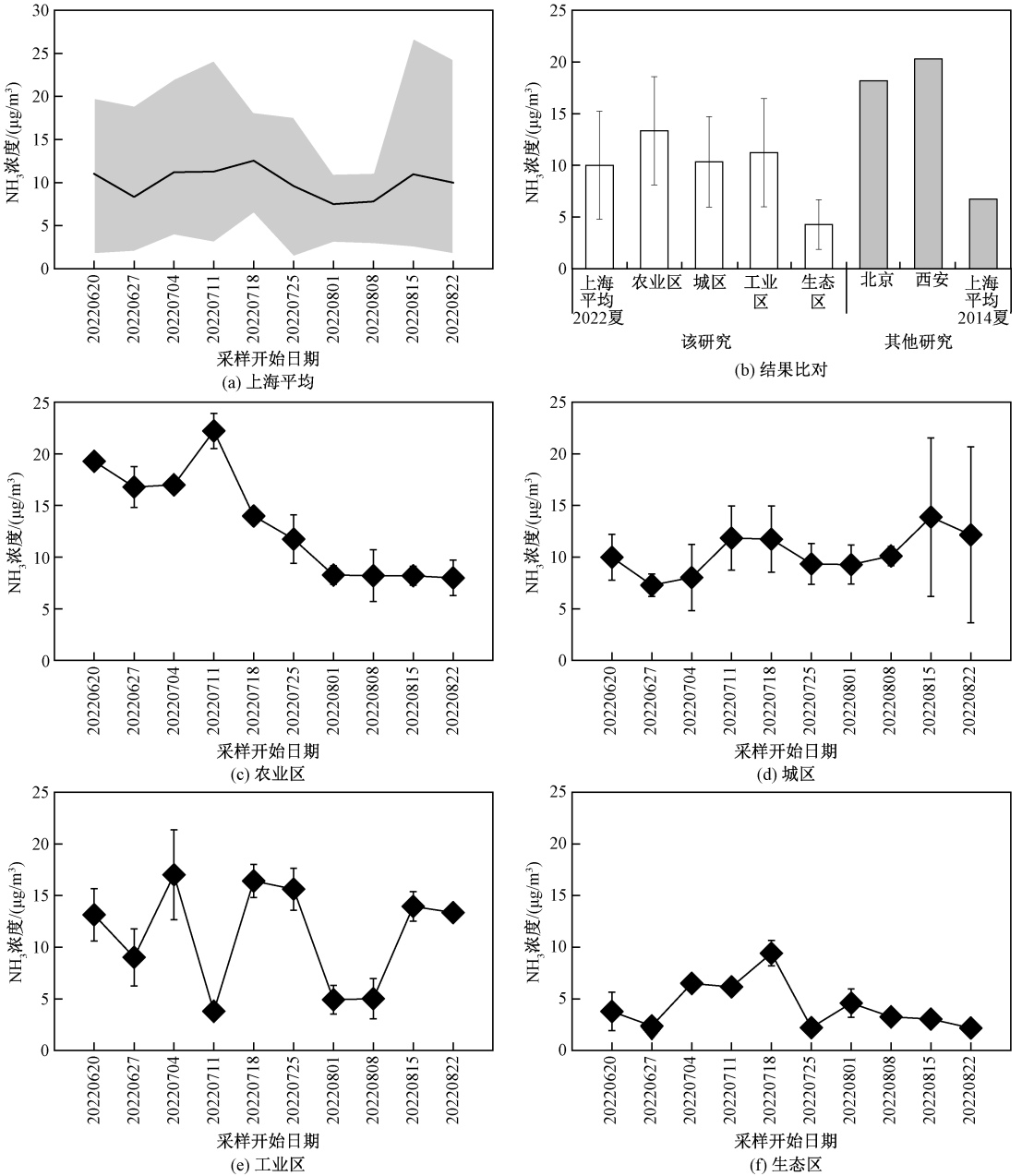


图 8 观测期间的 NH₃ 浓度变化及与其他研究中 NH₃ 浓度变化结果对比

Fig. 8 Variations of NH₃ concentrations during the observation period and comparison with the observed NH₃ concentrations in other studies

观测期间,上海市 NH₃ 周浓度为 1.47 ~ 26.75 µg/m³,平均浓度为 (10.01 ± 5.22) µg/m³. 与其他研究相比 [图 8 (b)],该研究结果高于 CHANG 等^[56] 在 2014 年夏季的观测结果 (6.75 µg/m³),这可能与 2022 年夏季极端高温气候条件^[57] 有关。2022 年夏季,上海市平均气温为 29.6 °C,同比 2014 年高约 3.2 °C;高温日(日最

高温超过 35 °C) 为 38 d,同比 2014 年多 4 d。高温一方面提高农田等面源的 NH₃ 排放速率,导致大气 NH₃ 排放量增加^[58],另一方面使 NH_x (总氨, NH_x = NH₄⁺ + NH₃) 更容易以气态形式存在^[56]。该研究观测结果远低于北京 (18.20 µg/m³)^[59] 和西安 (20.30 µg/m³)^[53] 等中国北部及西北部城市的夏季 NH₃ 浓度,这主要与华北平原地区具有较

高的农业集约化程度以及较高的土壤碱度(以旱田为主)有关,从而导致氮肥和土壤 NH_3 的挥发量较大^[60-61],而长三角城市群的农作物以酸性水稻为主, NH_3 的挥发量相对较小^[62]。

从上海市不同功能区看,农业区、城区、工业区和生态区的 NH_3 平均浓度分别为 (13.36 ± 5.24) 、 (10.35 ± 4.39) 、 (11.22 ± 5.24) 、 $(4.28 \pm 2.40) \mu\text{g}/\text{m}^3$ 。其中农业区的 NH_3 浓度水平最高,较城区和工业区偏高 30% 和 20%,是生态区的 3 倍;城区和工业区的 NH_3 浓度分别高出生态区 6.07、6.95 $\mu\text{g}/\text{m}^3$ 。从不同功能区的 NH_3 浓度周变化看,农业区 NH_3 浓度高值主要出现在 6—7 月,这可能与农田施肥挥发有关^[63]。上海地区普遍在 5—6 月进行第一轮施肥,2022 年受新冠疫情影响,施肥活动相对延后 1 个月左右。夏季高温促进农用肥料快速挥发,从而增加大气 NH_3 排放,使得农业区 NH_3 浓度水平高于其他功能区。LARIOS 等^[64] 和 LI 等^[65] 的研究也表明,在农业活动的监测站点较常出现 NH_3 浓度高值,农业源仍然是 NH_3 的主要来源。值得注意的是,非农业源排放对大气 NH_3 浓度的影响也是不可忽视的^[66-67]。城区 NH_3 排放主要来源于移动源、宠物和人体排放的贡献^[68],而工业区的 NH_3 则更多受燃煤电厂、工业工艺过程、废水处理排放等 NH_3 排放源的影响^[69-70]。工业区最终观测的 NH_3 浓度受周边排放源影响大,与站点位于上海化学工业区内的联合路旁边,更直接地受到园区内部排放源的影响密切相关。从全国排污许可证管理信息平台了解到,园区内一些主营有机化学原料制造的公司进行生产活动和废物处理时会排放大量 NH_3 (如其硝酸装置 SCR 尾气排口直接排放的 NH_3 与厂界的无组织排放等)。使用 SCR 进行脱硝尾气处理所用的还原剂主要是液氨或尿素分解出的 NH_3 ,因此在还原过程中,不可避免会剩余还原剂而带来 NH_3 的逃逸或泄漏。工业源 NH_3 排放还涉及氮肥、硝酸等工业原料生产过程,来自工业源的 NH_3 排放与生产活动频率密切相关^[71-72]。

3 结论

1) 基于酸浸渍法制备的吸附膜 NH_4^+ 含量均值为 $(0.27 \pm 0.13) \mu\text{g}$,比未处理吸附膜的 NH_4^+ 含

量高约 8%,不同操作过程对吸附膜的 NH_4^+ 本底含量影响不大;酸浸渍法可在膜液比为 1:4~8:4 范围内增加膜的单次浸渍数量,从而降低酸浸渍法吸附膜制备的溶剂使用量;当采样温度为 20 $^{\circ}\text{C}$,采样时长为 168 h 时,被动法测定环境 NH_3 的方法检出限为 0.08 $\mu\text{g}/\text{m}^3$ 。采用密实袋双层密封、4 $^{\circ}\text{C}$ 冷藏、保存时间不超过 30 d 的保存方式,并未显著增加吸附膜的 NH_4^+ 含量本底值,可适用于空白吸附膜和样品膜的保存。当采样时间大于 6 d 时,空白吸附膜 NH_4^+ 本底含量对样品的影响低于 20%,处于可接受范围,同时经过 30 d 采样后的吸附膜并未达到吸附饱和。因此,城市地区使用 ALPHA 被动采样法测定环境 NH_3 时,建议采样时间不少于 6 d 且至少可在 30 d 内进行连续采样。

2) ALPHA 被动采样法与主动采样法的 NH_3 浓度观测结果变化趋势较一致,测量结果吻合良好(相关系数为 0.87,斜率为 1.16),进一步证明了该研究采用的被动采样方法对环境 NH_3 浓度的测量具有较好的可靠性。

3) 基于被动法开展上海市环境空气中 NH_3 浓度观测的应用研究发现,上海 2022 年夏季的环境大气 NH_3 平均浓度为 $(10.01 \pm 5.22) \mu\text{g}/\text{m}^3$ 。农业区 NH_3 浓度最高,浓度值为 $(13.36 \pm 5.24) \mu\text{g}/\text{m}^3$,城区和工业区次之,生态区的 NH_3 浓度最低。说明虽然与农业活动相关的监测站点的 NH_3 浓度高值显著,但城区和工业区的非农业源排放对 NH_3 浓度的影响同样不可忽视。这表明 ALPHA 被动采样方法能较好捕捉城市不同功能区的 NH_3 浓度特征,可满足城市环境 NH_3 浓度的观测应用。

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