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环境科学

ENVIRONMENTAL SCIENCE

ISSN 0250-3301 CODEN HCKHDV

HUANJING KEXUE

中国主要城市土壤重金属累积特征与风险评价

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■ 主办 中国科学院生态环境研究中心

■ 出版 科学出版社



2022年1月

第43卷 第1期
Vol.43 No.1

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基于流量和溶存浓度的河流水系氧化亚氮释放量估算

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摘要: 随着活性氮污染负荷增加, 河流已成为许多地区重要的氧化亚氮(N_2O)释放源。由于许多研究的监测数据较少以及现行方法存在中间参数估算困难和难以表达时空变异性等不足, 估算河流水系 N_2O 释放量尚存在较大不确定性。以浙江永安溪水系为研究对象, 基于2016-06~2019-07对10个监测断面的逐月监测结果, 分析了河流 N_2O 溶存浓度 $[\rho(N_2O)]$ 和释放通量的时空分布特征及其影响因素, 建立了河流 N_2O 释放通量估算的二元回归模型。结果表明, 永安溪水系 $\rho(N_2O)$ (0.03~2.14 $\mu g \cdot L^{-1}$) 和释放通量 $[1.32 \sim 82.79 \mu g \cdot (m^2 \cdot h)^{-1}]$ 呈现1~2个数量级的时空变异性。河流 $\rho(N_2O)$ 的时空变化主要受硝态氮、氨氮和可溶性有机碳无机氮质量比影响, 而 N_2O 释放通量主要受流量和 $\rho(N_2O)$ 影响。基于河流流量和 $\rho(N_2O)$ 建立的二元回归模型能解释河流 N_2O 释放通量90%的时空变异性, 具有较高精度。模型估算的整个永安溪水系 N_2O 释放量为 $3.67 t \cdot a^{-1}$, 其中29%来源于干流和71%来源于支流。IPCC(联合国政府间气候变化专门委员会)的排放因子推荐值方法会高估受人类活动影响小的河流 N_2O 释放量, 但会低估受人类活动影响大的河流 N_2O 释放量。研究结果推进了对河流水系 N_2O 释放规律的定量认识, 为较准确地估算河流水系 N_2O 释放量提供了借鉴方法。

关键词: 河流; 氧化亚氮; 溶存浓度; 释放通量; 模型

中图分类号: X16 文献标识码: A 文章编号: 0250-3301(2022)01-0369-08 DOI: 10.13227/j.hjks.202105005

Estimation of Nitrous Oxide Emission from River System Based on Water Discharge and Dissolved Nitrous Oxide Concentration

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Abstract: Due to increasing active nitrogen pollution loads, river systems have become an important source of nitrous oxide (N_2O) in many areas. Due to the lack of monitoring data in many studies as well as the difficulty in estimating intermediate parameters and expressing temporal-spatial variability in current methods, a high level of uncertainty remains in the estimates of riverine N_2O emission quantity. Based on the monthly monitoring efforts conducted for 10 sampling sites across the Yonganxi River system in Zhejiang Province from June 2016 to July 2019, the temporal and spatial dynamics of riverine N_2O dissolved concentrations $\rho(N_2O)$, N_2O fluxes, and their influencing factors were addressed. A multiple regression model was then developed for predicating riverine N_2O emission flux to estimate annual N_2O emission quantity for the entire river system. The results indicated that observed riverine $\rho(N_2O)$ (0.03-2.14 $\mu g \cdot L^{-1}$) and the N_2O fluxes $[1.32-82.79 \mu g \cdot (m^2 \cdot h)^{-1}]$ varied by 1-2 orders of magnitude of temporal-spatial variability. The temporal and spatial variability of $\rho(N_2O)$ were mainly influenced by the concentrations of nitrate, ammonia, and dissolved organic carbon, whereas the N_2O emission fluxes were mainly affected by river water discharges and $\rho(N_2O)$. A multiple regression model that incorporates variables of river water discharge and $\rho(N_2O)$ could explain 90% of the variability in riverine N_2O emission fluxes and has high accuracy. The model estimated N_2O emission quantity from the entire Yonganxi River system of $3.67 t \cdot a^{-1}$, with 29% from the main stream and 71% from the tributaries. The IPCC default emission factor method might greatly overestimate and underestimate N_2O emission quantities for rivers impacted by low and high pressures of human activities, respectively. This study advances our quantitative understanding of N_2O emission for the entire river system and provides a reference method for estimating riverine N_2O emission with more accuracy.

Key words: river; nitrous oxide; dissolved concentration; emission flux; model

随着活性氮污染负荷增加, 河流已成为很多地区大气氧化亚氮(N_2O)的重要来源^[1~3]。明确河流水系的 N_2O 释放量是实施区域 N_2O 高效减排的关键科学基础。然而, 与土壤和湖泊等静态环境介质相比, 河流具有较大流动性, 使得河流 N_2O 释放通量的时空变异性更加强烈, 准确估算河流水系的 N_2O 释放量较为困难。例如, 不同研究对全球河流 N_2O 的年度释放量估算结果为 $0.19 \sim 2.10 Tg \cdot a^{-1}$ ^[4~7], 存在

1个数量级的巨大差异。因此, 准确估算河流水系 N_2O 释放量是当前准确制定全球或区域人为 N_2O 释放清单的关键^[6,8,9]。

收稿日期: 2021-05-01; 修订日期: 2021-06-11

基金项目: 国家自然科学基金项目(41877465); 浙江省杰出青年基金项目(LR19D010002)

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目前,河流水系 N_2O 释放通量的估算主要采用排放因子法、漂浮通量箱法、水-气交换模型法和乙炔抑制法等^[10]. 乙炔抑制法仅考虑反硝化产生的 N_2O ^[11],且难以描述野外真实状况^[12]. 排放因子法是当前全球或区域尺度估算河流水系 N_2O 释放量的主要方法,基于淋溶和径流流失氮污染负荷与排放因子相乘间接估算河流 N_2O 释放量^[13]. 尽管联合国政府间气候变化专门委员会(IPCC)对排放因子推荐值作了多次修正(现行的推荐值为0.0026)^[14],但是单个排放因子推荐值忽略了巨大的时空异质性,难以适用于某一河流水系的估算^[15]. 漂浮通量箱法是利用漂浮通量箱中的气体浓度动态变化直接估算 N_2O 释放通量的方法. 尽管漂浮通量箱法的监测结果能较为真实地反映研究河流断面实时的 N_2O 释放情况,但人力成本高,易受野外条件限制,难以对整个河流水系进行监测^[16]. 水-气模型法是基于 N_2O 溶存浓度 $[\rho(N_2O)]$ 和水-气界面的气体交换速率间接估算 N_2O 释放通量的方法^[17]. 尽管水-气交换模型法能克服野外条件限制^[10],但气体交换速率的估算需要风速、流速和水深等水文气象数据,而在实际应用中往往缺乏这些水文气象的实测数据,导致估算结果存在较大不确定性^[18].

总体而言,由于监测成本高,数据获取困难,目前许多有关河流水系 N_2O 释放量估算的研究对 N_2O 释放通量或 $\rho(N_2O)$ 的监测次数较少(<50 次)和时间较短(<2 a)^[19-25],难以较为全面地反映河流水系 N_2O 产生及释放过程的时空变异性,影响估算结果可靠性. 因此,在加强监测基础上,进一步发展实用且可靠方法是提高河流水系 N_2O 释放量估算结果可靠性的关键.

本文以我国东南地区典型河流水系——永安溪水系为研究对象,基于逐月的水文水质及 $\rho(N_2O)$ 和释放通量监测结果,分析了 $\rho(N_2O)$ 和释放通量变化特征及其主要影响因素,构建了 N_2O 释放通量估算的二元回归模型,估算了永安溪水系 N_2O 年释放量. 本研究结果对推进我国东南地区典型河流水系 N_2O

释放规律定量认识具有重要借鉴意义.

1 材料与方法

1.1 研究区概况

永安溪(120°21'29"~121°03'38" E, 28°30'48"~28°52'43" N)为浙江省椒江水系上游区域,位于浙江省台州市,自仙居县经缙云县,下游出口处距台州湾55 km. 永安溪水系具有“源短流急、下游感潮”的特征,是我国东南地区河流水系的典型代表^[26]. 永安溪流域面积约为2 474 km²,属于亚热带季风气候,年平均气温约为17.4℃. 年平均降雨量约为1 400 mm,5~10月为丰水期,其降雨约占全年的65%. 流域内主要土地利用类型为林地、农地和城乡、工矿和人居地等发展用地,其中农地约占流域面积的17%,林地约占76%,城乡、工矿和居民用地约占5%,水域和草地约占2%. 随着城市化进程的不断加快,林地、水域和草地面积不断减少,建设用地面积不断增加. 1980~2015年,永安溪柏枝岙断面氮污染加剧, $\rho(TN)$ 、 $\rho(NH_4^+-N)$ 和 $\rho(NO_3^--N)$ 分别增加了68%、126%和402%^[27].

1.2 采样与分析

本研究选取永安溪水系布设的10个水文水质监测断面(图1),其对应集水区的农地和人居地面积比例范围分别为5%~34%和1%~31%(表1). 2016-06~2019-07每4~8周对所有监测断面(图1)完成1次监测分析. 现场使用便携式水质检测仪(YSI Profession Plus,美国YSI公司)测定溶解氧(DO)和水温等的指标,利用StarlogV4(Unidata Inc.)测定各监测断面的流量. 现场采集各监测断面多点混合水样1 L置于聚乙烯瓶中,作为室内水质分析样品. 现场采集各监测断面多点混合的水样25 mL置于提前装有6滴0.5 g·mL⁻¹氯化锌的血清瓶中^[28],作为水体 $\rho(N_2O)$ 分析样品. 所有水样置于放有冰块的恒温箱($<4^\circ\text{C}$)中,并于24 h内送往实验室完成相关指标测定.

表1 永安溪水系各监测断面对应集水区的基本属性

Table 1 Basic catchment properties of mainstream and tributaries in Yonganxi River system

监测断面名称	类型	集水区土地利用类型占比/%			河流流量 /m ³ ·s ⁻¹
		农地	林地	人居地	
柏枝岙(BZA)	干流	16	80	4	60.6
河埠(HB)	干流	11	85	2	44.4
下张(XZ)	干流	14	81	4	47.5
横溪(HX)	干流	8	90	1	13.4
沙家洋(SJY)	支流	31	64	4	4.8
航管(HG)	支流	34	32	31	1.8
下张支流(XZT)	支流	13	84	2	8.8
官路(GL)	支流	7	90	2	5.0
埠头(BT)	支流	6	92	1	2.5
圳口(ZK)	支流	5	93	1	3.5

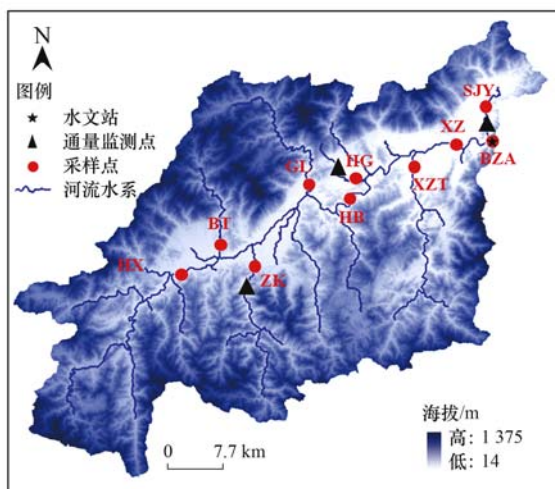


图1 永安溪水系区位与监测断面分布示意

Fig. 1 Location map and sampling sites of the Yong'an River system

水样中硝氮浓度 $[\rho(\text{NO}_3^- - \text{N})]$ 测定采用紫外分光光度法(HJ/T 346-2007),氨氮浓度 $[\rho(\text{NH}_4^+ - \text{N})]$ 测定采用靛酚蓝比色法(HJ 536-2009),总氮(TN)和可溶氮(DN)浓度测定采用碱性过硫酸钾消解紫外分光光度法(GB 11894-89),可溶性有机碳(DOC)浓度采用 TOC 总氮/可溶氮分析仪(Jena multi N/C3100)测定。

水样中 $\rho(\text{N}_2\text{O})$ 的测定采用顶空平衡法^[29]:首先向血清瓶中注入一定体积的高纯氮气,并抽出等体积的水样,形成瓶内顶部空间;剧烈振荡血清瓶,使瓶内气液相平衡;最后从瓶内抽出一定体积的气体样品,并测定 N_2O 浓度。按照式(1),基于振荡环境参数及气体溶解度计算水样中 $\rho(\text{N}_2\text{O})$:

$$c_w^0 = p_g \times (\beta RT + V_g/V_w) / RT \quad (1)$$

式中, c_w^0 为平衡前血清瓶中水相 N_2O 浓度($\text{mol} \cdot \text{m}^{-3}$); p_g 为顶空气体分压(Pa); β 为 N_2O 的本生系数; R 为气体常量 $[8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}]$; T 为振荡温度(K); V_g 为气相体积(mL); V_w 为水相体积(mL)。

2018-07、2018-08、2019-07、2019-08 和 2021-01 分别利用漂浮通量箱法现场测定 SJY、HG 和 ZK 支流 N_2O 释放通量。将参考 Minami 等^[30]设计的漂浮通量箱置于各个监测断面水面上(每个监测断面沿横截面左中右位置放置 2~3 个箱体),每隔 15 min 抽取 1 次通量箱内的气体,每次抽取 100 mL 气体于密封气袋并置于恒温箱($<4^\circ\text{C}$)中,带回实验室测定。利用每个样点的 4 次气体样品浓度差计算 N_2O 释放通量^[28]。水样 $\rho(\text{N}_2\text{O})$ 和气体样品 N_2O 浓度均采用顶空-气相色谱法(GC-2010,日本岛津)测定^[31],每个样品设置 3 次重复。

1.3 数据分析

本研究采用 ANOVA 单因素方差分析及多重比较方法(Turkey 检验, $P < 0.05$ 表示有显著性)分析河流 $\rho(\text{N}_2\text{O})$ 和释放通量以及各常规水质指标的时空差异显著性;采用 Spearman 相关系数法进行河流 $\rho(\text{N}_2\text{O})$ 和释放通量与各影响因素之间的相关性分析($P < 0.05$ 表示显著相关);采用多元回归分析方法建立河流 N_2O 释放通量与相关影响因素及其组合之间的回归模型。所有统计分析采用 SPSS 18.0 软件(SPSS, Inc., USA)。基于 Google earth 影像,采用人工解译方法估算河流水系面积。本研究中各类作图采用 Prism 8.0 (GraphPad Software Inc.) 和 DataGraph (Visual Data Tools Inc.) 软件。

2 结果与讨论

2.1 河流 N_2O 溶存浓度时空变化特征

2016-06~2019-07 永安溪水系各个监测断面的平均 $\rho(\text{N}_2\text{O})$ 为 $0.50 \mu\text{g} \cdot \text{L}^{-1}$,存在 2 个数量级的时空变异性($0.03 \sim 2.14 \mu\text{g} \cdot \text{L}^{-1}$,表 2)。与很多已有研究结果类似^[21,32,33],永安溪流域河流 $\rho(\text{N}_2\text{O})$ 与 $\rho(\text{NO}_3^- - \text{N})$ ($r = 0.50$, $P < 0.01$)和 $\rho(\text{NH}_4^+ - \text{N})$ ($r = 0.36$, $P < 0.01$)呈显著正相关。以上结果表明,永安溪水系河流溶存的 N_2O 可能主要通过硝化作用和反硝化作用产生^[34,35]。河流 $\rho(\text{N}_2\text{O})$ 与可溶性有机碳和无机氮质量比(C/N, $r = -0.16$, $P < 0.05$)呈显著负相关关系(图 2)。由于硝化作用细菌通常为化能自养型细菌,但在环境 C/N 较高的条件下,异养细菌竞争 NH_4^+ 的能力更强,使得硝化细菌缺少反应底物,从而降低硝化速率,减少了 N_2O 产生^[36]。

从时间变异性上看,永安溪水系 $\rho(\text{N}_2\text{O})$ 在春季和冬季(均值: $0.51 \mu\text{g} \cdot \text{L}^{-1}$;范围: $0.10 \sim 2.14 \mu\text{g} \cdot \text{L}^{-1}$)显著高于夏季和秋季(均值: $0.40 \mu\text{g} \cdot \text{L}^{-1}$;范围: $0.03 \sim 1.39 \mu\text{g} \cdot \text{L}^{-1}$, $P < 0.05$,图 3)。这主要与河流氮污染的季节性差异有关(表 2)。永安溪水系春季和冬季的 $\rho(\text{NO}_3^- - \text{N})$ 和 $\rho(\text{NH}_4^+ - \text{N})$ 均显著高于夏季和秋季的($P < 0.05$)。由于春季和冬季的温度偏低,植被覆盖较少,因此,不同景观对氮的同化能力较低,导致河流氮污染加重^[37]。同时,春季和冬季时,河流处于平水期或枯水期,而夏季和秋季河流处于平水期或丰水期,即受到稀释作用影响,使得春季和冬季的河流 $\rho(\text{N}_2\text{O})$ 相对较高。

从空间变异性上看,永安溪水系支流监测断面的 $\rho(\text{N}_2\text{O})$ (均值: $0.55 \mu\text{g} \cdot \text{L}^{-1}$;范围: $0.16 \sim 2.14 \mu\text{g} \cdot \text{L}^{-1}$, $P < 0.05$,表 2)显著高于干流的(均值:

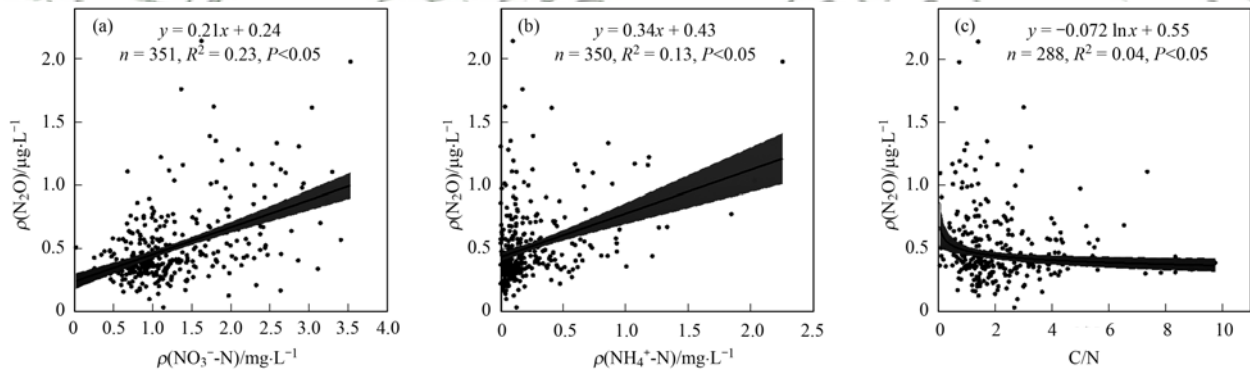
0.44 $\mu\text{g}\cdot\text{L}^{-1}$; 范围:0.03 ~ 1.76 $\mu\text{g}\cdot\text{L}^{-1}$). 相对于干流,由于支流的流量较小和水深较浅,单位水体体积的河床接触面积较大,且稀释作用较小,使得硝化和反硝化反应速率较高,导致 N_2O 产生速率及 $\rho(\text{N}_2\text{O})$ 较大^[7,38,39]. 从不同支流监测断面的差异性上看,对应集水区农地和人居地面积比例较高的监测断面 (SJY 和 HG) 河流 $\rho(\text{N}_2\text{O})$ (均值:0.69

$\mu\text{g}\cdot\text{L}^{-1}$; 范围:0.16 ~ 1.98 $\mu\text{g}\cdot\text{L}^{-1}$) 显著高于面积比例较低的河流 (ZK、XZT、GL 和 BT, 均值:0.48 $\mu\text{g}\cdot\text{L}^{-1}$; 范围:0.17 ~ 2.14 $\mu\text{g}\cdot\text{L}^{-1}$, $P < 0.05$). 由于人类活动的影响,集水区农地和人居地面积比例较大的支流监测断面的 $\rho(\text{NO}_3^- - \text{N})$ 和 $\rho(\text{NH}_4^+ - \text{N})$ 显著高于面积比例较低的支流 (表 2),从而直接影响 $\rho(\text{N}_2\text{O})$ 的差异性.

表 2 永安溪水水质指标及 $\rho(\text{N}_2\text{O})$ 的时空分布特征¹⁾

Table 2 Temporal and spatial variations in water quality indexes and $\rho(\text{N}_2\text{O})$ in Yonganxi River system									
季节	监测断面类别	$\rho(\text{NO}_3^- - \text{N})/\text{mg}\cdot\text{L}^{-1}$		$\rho(\text{NH}_4^+ - \text{N})/\text{mg}\cdot\text{L}^{-1}$		$\rho(\text{N}_2\text{O})/\mu\text{g}\cdot\text{L}^{-1}$		C/N	
		范围	均值	范围	均值	范围	均值	范围	均值
春	干流	0.25 ~ 1.83	0.96 ± 0.29de	0.001 ~ 0.55	0.17 ± 0.14c	0.30 ~ 1.76	0.51 ± 0.26bc	1.99 ~ 5.62	0.51 ± 0.26bc
	支流 1	0.99 ~ 3.53	2.07 ± 0.73ab	0.04 ~ 2.26	0.58 ± 0.62a	0.26 ~ 1.98	0.78 ± 0.45a	0.50 ~ 3.91	1.79 ± 1.00cde
	支流 2	0.02 ~ 1.67	0.78 ± 0.36e	0.02 ~ 2.03	0.21 ± 0.39c	0.29 ~ 1.16	0.48 ± 0.24bc	0.06 ~ 8.91	4.12 ± 2.45a
夏	干流	0.57 ~ 1.81	1.05 ± 0.30cd	0.001 ~ 0.80	0.14 ± 0.18c	0.17 ~ 0.76	0.39 ± 0.14c	0.68 ~ 5.62	2.57 ± 1.37bc
	支流 1	0.80 ~ 3.30	1.93 ± 0.76b	0.001 ~ 1.21	0.20 ± 0.25c	0.16 ~ 1.30	0.52 ± 0.33bc	0.61 ~ 4.08	1.69 ± 1.03cde
	支流 2	0.26 ~ 2.57	1.04 ± 0.52cd	0.001 ~ 1.26	0.16 ± 0.27c	0.17 ~ 1.39	0.45 ± 0.24bc	0.42 ~ 9.75	3.44 ± 2.68a
秋	干流	0.49 ~ 2.29	1.23 ± 0.48c	0.01 ~ 0.93	0.17 ± 0.20c	0.03 ~ 0.85	0.42 ± 0.18c	0.50 ~ 4.56	1.84 ± 1.04cd
	支流 1	1.01 ~ 3.14	2.14 ± 0.61ab	0.01 ~ 1.33	0.39 ± 0.41ab	0.16 ~ 1.33	0.77 ± 0.37a	0.34 ~ 2.09	1.09 ± 0.52de
	支流 2	0.34 ~ 1.46	0.89 ± 0.25de	0.01 ~ 0.38	0.11 ± 0.10c	0.20 ~ 0.70	0.43 ± 0.14c	0.74 ~ 4.24	2.17 ± 0.96cd
冬	干流	0.74 ~ 1.76	1.22 ± 0.26c	0.04 ~ 0.85	0.22 ± 0.21bc	0.20 ~ 0.79	0.45 ± 0.14bc	0.12 ~ 5.44	1.41 ± 1.19de
	支流 1	0.99 ~ 3.41	2.33 ± 0.66a	0.09 ~ 0.95	0.47 ± 0.34a	0.31 ~ 1.61	0.78 ± 0.36a	0.07 ~ 1.23	0.70 ± 0.38e
	支流 2	0.52 ~ 1.99	1.15 ± 0.44cd	0.006 ~ 1.82	0.24 ± 0.39bc	0.20 ~ 2.14	0.57 ± 0.43b	0.08 ~ 5.00	1.71 ± 1.24de

1) 支流 1 表示集水区农地和人居地面积占比较高的采样点 (SJY 和 HG), 支流 2 表示集水区农地和人居地面积占比较低的采样点 (ZK、XZT、GL 和 BT); 同一列中不同小写字母表示同一指标平均值的显著差异 ($P < 0.05$)



阴影部分为回归关系 95% 置信区间

图 2 永安溪水系 $\rho(\text{N}_2\text{O})$ 与 $\rho(\text{NO}_3^- - \text{N})$ 、 $\rho(\text{NH}_4^+ - \text{N})$ 和碳氮比 (C/N) 的相关关系

Fig. 2 Relationships between $\rho(\text{N}_2\text{O})$, $\rho(\text{NO}_3^- - \text{N})$, $\rho(\text{NH}_4^+ - \text{N})$, and carbon to nitrogen ratio in Yonganxi River system

2.2 河流 N_2O 释放通量空间变化特征

2018-07 ~ 2021-01 永安溪水系 SJY、HG 和 ZK 监测断面 5 次通量箱法监测的 N_2O 释放通量均值为 23.93 $\mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$, 存在 1 个数量级的变异性 [范围:1.32 ~ 82.79 $\mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$]. 河流 N_2O 释放通量与 $\rho(\text{N}_2\text{O})$ ($r = 0.93$, $P < 0.05$) 和流量 ($r = 0.34$, $P < 0.05$) 呈显著正相关, 但与 $\rho(\text{NO}_3^- - \text{N})$ 和 $\rho(\text{NH}_4^+ - \text{N})$ 等因素相关性低 ($P > 0.05$), 这意味着河流 N_2O 释放通量可能主要受释放能力影响^[40, 41]. 河流 $\rho(\text{N}_2\text{O})$ 直接决定了水体的 N_2O 饱和度以及水-气界面 $\rho(\text{N}_2\text{O})$ 梯度, 从而影响 N_2O 从河流水体向大气的释放强度. 随着河流流量增大, 水体物理扰动增

强, 从而促进 N_2O 的逃逸, 提高 N_2O 释放通量^[42]. 尽管无显著性差异 (可能由于监测样本较少), 但是对应集水区农地和人居地面积比例较大的监测断面, N_2O 释放通量总体高于农地和人居地面积占比较小的监测断面位, 这主要是受不同监测断面的 $\rho(\text{N}_2\text{O})$ 差异性影响 (图 4 和表 1).

2.3 河流 N_2O 释放通量预测模型构建

以上的分析结果表明, 永安溪水系 N_2O 释放通量主要受河流流量与 N_2O 浓度的影响. 因此, 应用多元回归统计方法, 综合分析了多种河流流量和 N_2O 浓度作为自变量的组合形式, 按照拟合精度 (R^2 和 NSE 系数值), 筛选出以下基于幂函数形式的二元

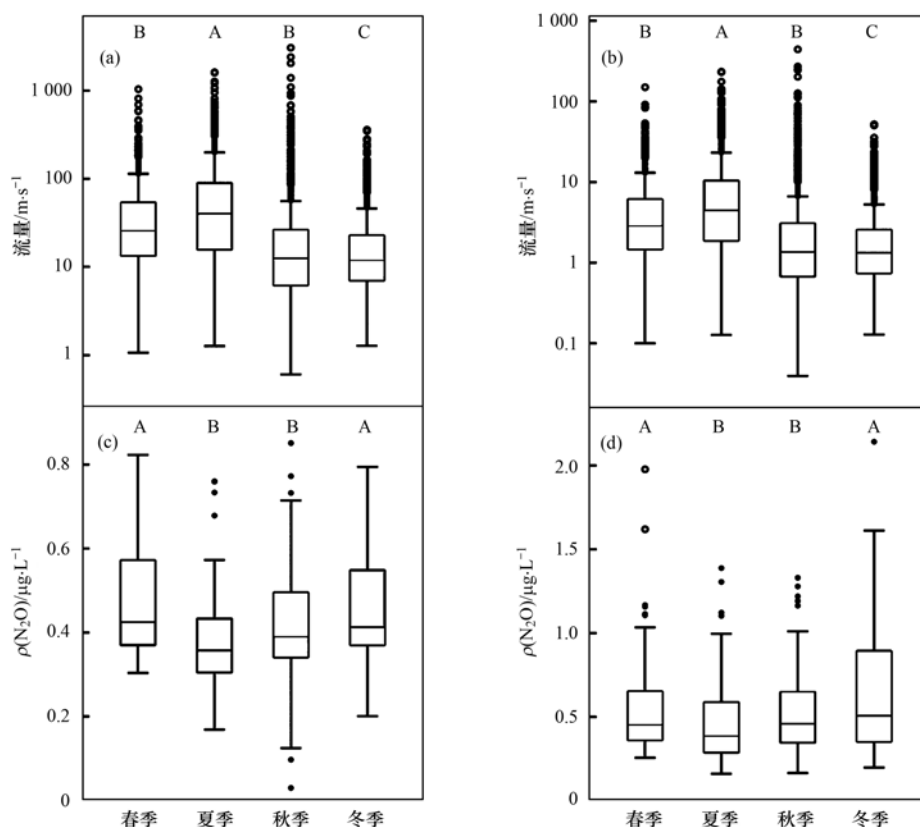


图3 永安溪水系干流和支流的流量和 $\rho(\text{N}_2\text{O})$ 的季节性差异

Fig. 3 Seasonal differences in river water discharge and $\rho(\text{N}_2\text{O})$ for mainstream and river water discharge and $\rho(\text{N}_2\text{O})$ for tributaries in Yonganxi River system

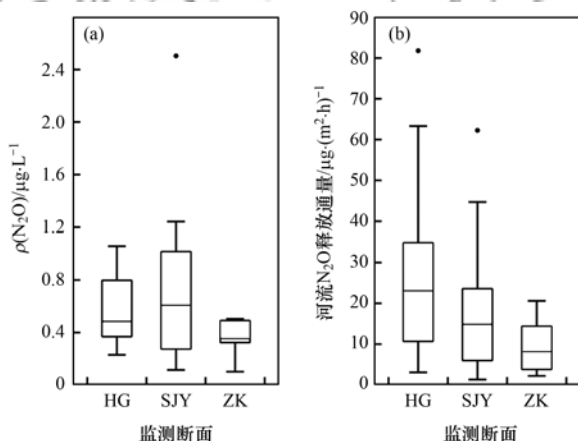


图4 永安溪水系部分监测断面的 $\rho(\text{N}_2\text{O})$ 及 N_2O 释放通量空间差异性

Fig. 4 Spatial differences of $\rho(\text{N}_2\text{O})$ and flux across several sampling sites in Yonganxi River system

回归模型为最优:

$$f = 68.20\rho^{1.56}Q^{0.03} \quad (2)$$

式中, f 为 N_2O 释放通量 [$\mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$], ρ 为 N_2O 浓度 ($\mu\text{g}\cdot\text{L}^{-1}$), Q 为河流流量 ($\text{m}^3\cdot\text{s}^{-1}$).

式(2)模拟的河流 N_2O 释放通量值与实测值之间的 $R^2 = 0.90$ 且 $\text{NSE} = 0.82$ ($n = 26$), 意味着模型具有较高的精度[图 5(a)]. 与排放因子法相比, 式

(2)综合考虑了河流 N_2O 浓度和水文等条件,使得估算结果更加可靠. 与漂浮通量箱法相比,式(2)克服了应用漂浮通量箱法过程中人力成本高和受野外条件限制等缺点. 与水-气交换模型法相比,式(2)克服了水气交换系数估算的不确定性. 与应用 SWAT-F(N_2O)模型估算 Naoli 河流水系 N_2O 释放量的研究相比 ($R^2: 0.51 \sim 0.79$, $\text{NSE}: 0.45 \sim 0.65$)^[43],式(2)不仅形式简单,所需数据少,而且具有较高精度.

2.4 河流 N_2O 年际释放量估算

式(2)模拟的 2016-06 ~ 2019-07 永安溪水系 N_2O 释放通量为 $(27.60 \pm 27.58) \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$ [范围: $0.31 \sim 224.95 \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$], 其中干流的年均 N_2O 释放通量为 $(22.02 \pm 17.82) \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$ [范围: $0.31 \sim 181.38 \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$], 支流的年均 N_2O 释放通量为 $(31.42 \pm 32.10) \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$ [范围: $3.83 \sim 224.95 \mu\text{g}\cdot(\text{m}^2\cdot\text{h})^{-1}$]. 相对于干流,支流的流量低及水位浅,使得水-气交换速率较快,且其各类氮浓度总体较高(表 2). 因此,同一河流水系的支流 N_2O 释放通量显著高于干流的,即随着河流级数的增加 N_2O 释放通量降低^[38, 44].

为估算未监测支流的 N_2O 释放量,对集水区中

农地 + 人居地面积比例 > 35% 的未监测支流, 采用式(2)模拟的 SJY 和 HG 支流释放通量平均值估算; 对农地 + 人居地面积比例 < 35% 的未监测支流, 采用式(2)模拟的 XZT、GL、BT 和 ZK 支流的释放通量平均值估算. 基于以上假设及式(2)模拟结果, 估算的永安溪水系 N_2O 年均释放量为 $3.67 \text{ t} \cdot \text{a}^{-1}$ (表 3). 干流水面面积占全水系总水面面积的 38%, 贡献了 29% 的 N_2O 释放量; 各支流总水面面积占全水系总水面面积的 62%, 贡献了 71% 的 N_2O 释放量. 因此, 支流是永安溪水系 N_2O 减排的重点. 然而, 基于 IPCC 排放因子推荐值(0.002 6)估算的永安溪水系

N_2O 年均释放量为 $11.94 \text{ t} \cdot \text{a}^{-1}$, 这是基于式(2)估算结果的 3.25 倍. 尤其是干流, 基于 IPCC 排放因子推荐值的 N_2O 释放量估算值是式(2)估算结果的 6.48 倍. 从不同支流看(表 3), IPCC 排放因子推荐值的方法大大低估了集水区农地和人居地面积比例较高的支流(SJY 和 HG)的 N_2O 释放量, 而大大高估了集水区农地和人居地面积比例较低的支流(ZK、XZT、GL 和 BT). 以上研究结果表明, IPCC 的排放因子推荐值方法忽略了时空异质性, 会高估受人类活动影响较小河流的 N_2O 释放量, 但低估了受人类活动影响较大河流的 N_2O 释放量^[3,45].

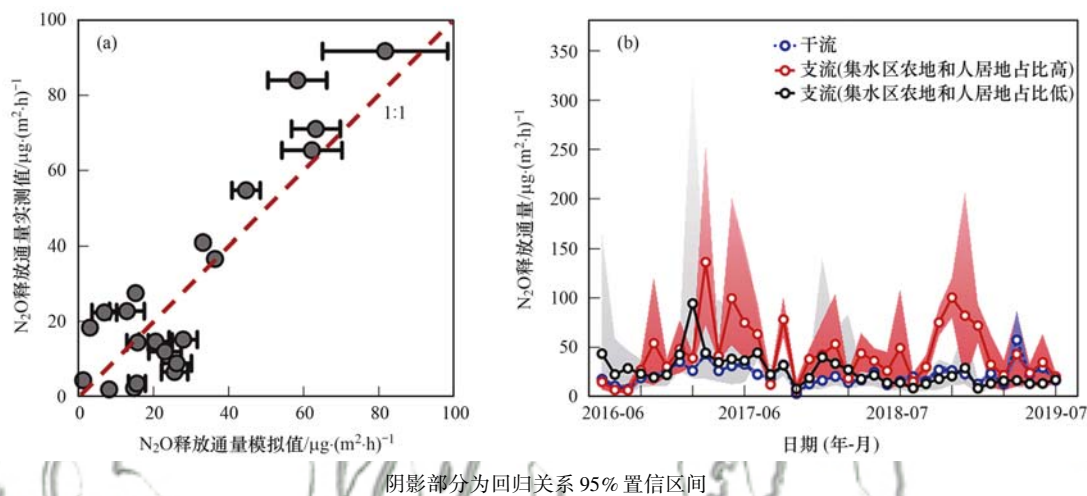


图 5 永安溪水系 N_2O 释放通量实测值与模拟值拟合关系及 N_2O 释放通量模拟结果

Fig. 5 Relationship between measured and modeled N_2O emission fluxes and temporal variation of modeled N_2O emission fluxes in Yonganxi River system

表 3 基于式(2)和 IPCC 释放因子推荐值的永安溪水系干支流 N_2O 释放量估算结果比较

Table 3 Estimated annual N_2O emission quantities from mainstream and tributaries of the Yonganxi River system based on the formula (2) and the default value of emission factor recommended by IPCC

类型		水面面积/ km^2	N_2O 释放量	
			基于式(2)/ $\text{t} \cdot \text{a}^{-1}$	基于 IPCC 推荐值/ $\text{t} \cdot \text{a}^{-1}$
干流		5.50	1.06	6.87
集水区农地和人居地 面积比例较大的支流	SJY	0.44	0.18	0.14
	HG	0.28	0.08	0.04
	未监测支流	3.21	1.25	1.07
	XZT	0.78	0.14	0.27
集水区农地和人居地 面积比例较小的支流	GL	0.33	0.09	0.12
	BT	0.02	0.01	0.04
	ZK	0.14	0.02	0.05
	未监测支流	3.81	0.84	3.38

3 结论

(1) 永安溪水系监测的 $\rho(\text{N}_2\text{O})$ 具有 2 个数量级的时空变异性, 总体为: 冬季和春季 > 夏季和秋季; 支流 > 干流, 主要受 $\rho(\text{NO}_3^- - \text{N})$ 、 $\rho(\text{NH}_4^+ - \text{N})$ 和 C/N 的影响. 对应集水区农地和人居地面积比例较大的监测断面 $\rho(\text{N}_2\text{O})$ 显著高于面积比例较小的.

(2) 永安溪水系监测的 N_2O 释放通量存在 1 个数量级的时空变异性, 主要受 $\rho(\text{N}_2\text{O})$ 和流量的影响. 对应集水区农地和人居地面积比例较大的监测断面的 N_2O 释放通量高于面积比例较小的.

(3) 基于河流流量和 $\rho(\text{N}_2\text{O})$ 建立的二元回归模型具有较高的精度, 克服了人力成本高、受野外条件限制和中间参数估算困难等不足, 为较准确地

估算河流水系 N_2O 释放通量提供了参考方法。

(4) 永安溪水系的 N_2O 年均释放量为 $3.67 \text{ t} \cdot \text{a}^{-1}$ (29% 来自于干流, 71% 来自于支流)。支流 N_2O 释放通量显著高于干流的, 是河流水系 N_2O 减排的关键。IPCC 的排放因子推荐值方法会高估受人类活动影响小的河流 N_2O 释放量, 但会低估受人类活动影响大的河流 N_2O 释放量。

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