

1 **Modeling greenhouse gas emissions from riverine systems: a review**

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5 **Abstract**

6 Despite the recognized importance of flowing waters in global greenhouse gas (GHG) budgets, riverine
7 GHG models remain oversimplified, consequently restraining the development of effective prediction
8 for riverine GHG emissions feedbacks. Here we elucidate the state of the art of riverine GHG models
9 by investigating 148 models from 122 papers published from 2010 to 2021. Our findings indicate that
10 riverine GHG models have been mostly data-driven models (83%), while mechanistic and hybrid
11 models were uncommonly applied (12% and 5%, respectively). Overall, riverine GHG models were
12 mainly used to explain relationships between GHG emissions and biochemical factors, while the role
13 of hydrological, geomorphic, land use and cover factors remains missing. The development of complex
14 and advanced models has been limited by data scarcity issues; hence, efforts should focus on developing
15 affordable automatic monitoring methods to improve data quality and quantity. For future research, we
16 request for basin-scale studies explaining river and land-surface interactions for which hybrid models
17 are recommended given their flexibility. Such a holistic understanding of GHG dynamics would
18 facilitate scaling-up efforts, thereby reducing uncertainties in global GHG estimates. Lastly, we propose
19 an application framework for model selection based on three main criteria, including model purpose,
20 model scale and the spatiotemporal characteristics of GHG data, by which optimal models can be
21 applied in various study conditions.

22 **Keywords:** Greenhouse gas, river, stream, driving factor, modeling

23 **List of acronyms**

- 24 A: Watershed area
- 25 Chl-a: Chlorophyll a
- 26 C_{CO_2} : CO_2 concentration
- 27 $C_{CO_2_{gw}}$: CO_2 molarity in the groundwater
- 28 $C_{CO_2_{atm}}$: CO_2 molarity in the atmosphere
- 29 C_{NO_3} : Nitrate concentration
- 30 $C_{N_2O_{rip}}$: Nitrite concentration in the riparian zone
- 31 $C_{N_2O_{soil}}$: Nitrite concentration in the soil area
- 32 CI: Confidence interval
- 33 d_{50} : Median grain size of streambed sediments
- 34 D or h or z: River depth
- 35 Dif: Diffusion coefficient
- 36 Disp: Dispersion coefficient
- 37 DO: Dissolved oxygen
- 38 DOC: Dissolved organic carbon
- 39 DIC: Dissolved inorganic carbon
- 40 DIN: Dissolved inorganic nitrogen
- 41 ER: Emission rate
- 42 EcoR: Ecosystem respiration
- 43 $F * N_2O$: N_2O emission flux
- 44 F_{WC} : Molar flux of CO_2 from water column
- 45 F_{he} : Molar flux of CO_2 from hyporheic zone respiration
- 46 g: Gravity force
- 47 GPP: Gross primary production
- 48 K_{600} : Gas exchange rate normalized to a Schmidt number of 600
- 49 K_{CO_2} : Reaeration coefficient of CO_2
- 50 K_h : Stream hydraulic conductivity
- 51 K_{NIT} : Rate constant for nitrification
- 52 L_{st} : Stream length
- 53 L_{DIN} : DIN load
- 54 MF: Methane formation
- 55 NPP: Net primary production
- 56 NO_2 : Nitrite
- 57 NO_3 : Nitrate
- 58 NH_4 : Ammonium
- 59 OM: Organic matter

- 60 PPF_D: Photosynthetic photon flux density
- 61 Pop_Density: Population density
- 62 P_{N₂O_denrip}: Rate of production of N₂O
- 63 pCO₂: Particulate CO₂
- 64 Q: Discharge
- 65 R_{autotrophic}: River autotrophic respiration
- 66 R_{heterotrophic}: River heterotrophic respiration
- 67 R_{hyporheic}: River hyporheic respiration
- 68 S_o: Average slope gradient
- 69 SIM: Suspended inorganic matter
- 70 SOM: Suspended organic matter
- 71 SSS: Sea surface salinity
- 72 SST: Sea surface temperature
- 73 t_m: Time of turbulent vertical mixing
- 74 T_{air}: Air temperature
- 75 T_w: Water temperature
- 76 TCG: Total carbon gas concentration (CO₂ + CH₄)
- 77 TN: Total nitrogen
- 78 TP: Total phosphorous
- 79 V or u: River velocity
- 80 V_{den}: Uptake rate of denitrification
- 81 W or B: River width
- 82 Y_{DIN}: DIN yield
- 83 Ø1: Arrhenius coefficient
- 84 α_{ox}: Water column methane oxidation rate
- 85 τ₅₀: Median hyporheic residence time
- 86 τ_D: Time of denitrification

87 **1. Introduction**

88 Rivers have recently become recognized as an important component of the carbon (C) cycle and
89 represent a potential yet-to-be-quantified feedback of climate change. Global estimates of riverine CO₂
90 emissions range from 0.65 (95% CI: 0.48–0.84) to 2.0 ± 0.2 Pg CO₂ yr⁻¹ (Lauerwald et al., 2015; Liu et
91 al., 2022), equivalent to 33.7% of total anthropogenic emissions from industrial activities and land use
92 change (Drake et al., 2018) and higher than the annual terrestrial carbon sink of 3.6 Pg C yr⁻¹ (Keenan
93 and Williams, 2018). Riverine CH₄ emissions range from 1.5 to 26.8 (5th–95th percentiles: 0.01–160)
94 Tg CH₄ yr⁻¹ (Bastviken et al., 2011; Stanley et al., 2016) equivalent to 15–40% of the emissions from
95 wetlands and lakes combined (Stanley et al., 2016). And riverine N₂O emissions range from 72.8 to
96 291.3 ± 58.6 Gg N₂O yr⁻¹ (Marzadri et al., 2021; Yao et al., 2020), about 1–10% of the global
97 anthropogenic N₂O emissions (Beaulieu et al., 2011; Tian et al., 2020). Significant discrepancies within
98 GHG estimates are reported because of the use of different estimation methods or models, which use
99 datasets with varying characteristics, different data processing techniques, and include diverse
100 assumptions such as the inclusion or exclusion of headwaters in global assessments (Beaulieu et al.,
101 2011; Lauerwald et al., 2015; Marzadri et al., 2021; Rosentreter et al., 2021; Yao et al., 2020). As such,
102 the real potential of riverine systems to contribute to GHG emissions is yet unquantified.

103 By excluding the complexity of riverine ecosystems, current estimation models of riverine emissions
104 are oversimplified with questionable assumptions, hence have been reported to be error-prone. For
105 example, emission factors (EF) assume that emissions are proportional to nitrogen (N) inputs (IPCC,
106 2019, 2006), while upscaling techniques assume that regional fluxes are proportional to point
107 measurements, surface area, and local gas transfer velocities (Bastviken et al., 2011; Cole et al., 2007;
108 Raymond et al., 2013). These oversimplified methods disregard multiple essential drivers, such as land
109 use and cover (LULC) or lateral fluxes, consequently causing errors in estimation of as high as 42%
110 (Yang et al., 2022). To improve the estimation of riverine GHG emission, several modeling approaches
111 have been proposed lately, offering diverse methodologies and knowledge frameworks. However, no
112 review of the models for riverine GHG emissions can be found to analyze their current status, identify
113 challenges and limitations, and guide future developments in this field.

114 In contrast to recent reviews that provide an overview of methods to achieve global-scale estimates
115 (Lauerwald et al., 2023) or focus on GHG emissions modeling in lentic waters (Ion and Ene, 2021;
116 Levasseur et al., 2021), this review centers on critically evaluating the state of the art of riverine GHG
117 models across diverse case studies with varied spatiotemporal scales. As such, we conducted a
118 comprehensive analysis of 148 models obtained from 122 publications published over the past 11 years
119 (2010–2021). The goal of this review is threefold: 1) to provide new insights into the potential
120 challenges and issues associated with existing models; 2) to define their role in quantifying regional
121 and global GHG budget; and 3) to guide future development of modeling techniques. This review

122 focuses on diverse elements of model selection and development, which are progressively scrutinized
123 in three sections. First, we define the three model types and elucidate their properties, advantages, and
124 disadvantages. Second, we characterize these models according to model purposes, model scales, data
125 attributes, modeled factors, and uncertainty analysis. These findings are mapped into a decision tree to
126 facilitate model selection for future studies, considering specific requirements and objectives of
127 researchers. Finally, we critically discuss challenges associated with riverine GHG models and highlight
128 key research needs and future directions to enhance the accuracy and reliability of these models.

129 **2. Methodology**

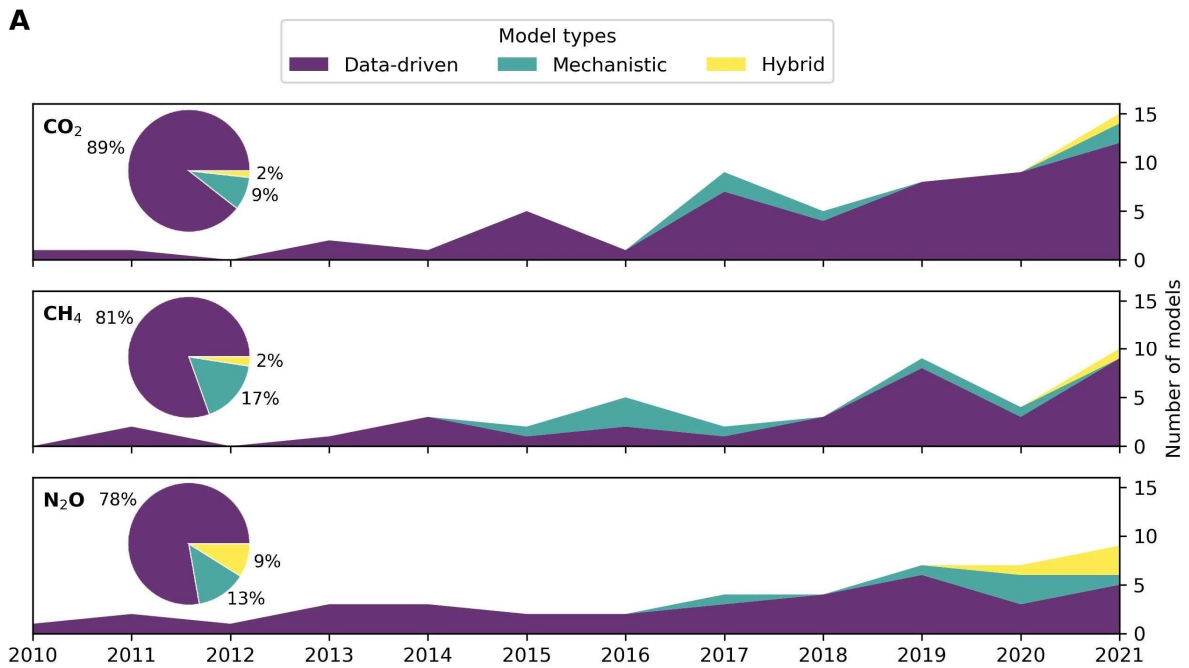
130 To investigate recent studies on riverine GHG emission modeling, we launched a detailed review of the
131 studies published in peer-reviewed journals on the Scopus platform for the timeframe 2010–2021 by
132 applying the query TITLE (river* AND (nitrous* OR "carbon dioxide*" OR "greenhouse gas*" OR
133 CO₂ OR methan* OR CH₄ OR N₂O)) AND PUBYEAR > 2009 AND PUBYEAR < 2022 AND
134 TITLE-ABS-KEY (model* OR method* OR framework* OR estim* OR predict*). In total, 707
135 publications were collected. We scrutinized these studies by eliminating publications on unrelated
136 topics, ultimately obtaining 122 relevant publications, including 148 models almost equally distributed
137 among the main GHGs: CO₂ (40%), CH₄ (29%) and N₂O (31%) (Figure S1 in supplementary material).
138 The studies collected were used to investigate factors of interest, including model types, model
139 purposes, model scales, riverine GHG data attributes, modeled factors, and uncertainty analysis. Based
140 on modeling paradigm, we identified three model types: data-driven, mechanistic, and hybrid models
141 (Figure S2), which, according to their purpose, were subcategorized into explicative and predictive
142 models. Given their scale of application, these models were subclassified into site-, basin-, or global-
143 scale models. Similarly, we investigated data attributes that are used for model development by
144 identifying data collection methods, sampling frequency, and sampling duration. Additionally, we
145 determined driving factors that are commonly used as inputs in riverine GHG models, namely
146 biochemical, hydrological, geomorphic factors, and LULC types. This subclassification of factors is
147 described in Table S3. Finally, we evaluated the use of uncertainty analysis and model validation
148 techniques in riverine GHG models. Note that these characteristics were selected to represent main steps
149 in model selection and development, which can enable us to define the state of the art of riverine GHG
150 models. It is worth mentioning that we excluded the boundary layer method to estimate fluxes via gas
151 exchange as this method was out of scope of our review and was thoroughly investigated in Hall Jr. and
152 Ulseth (2020).

153 **3. Model types**

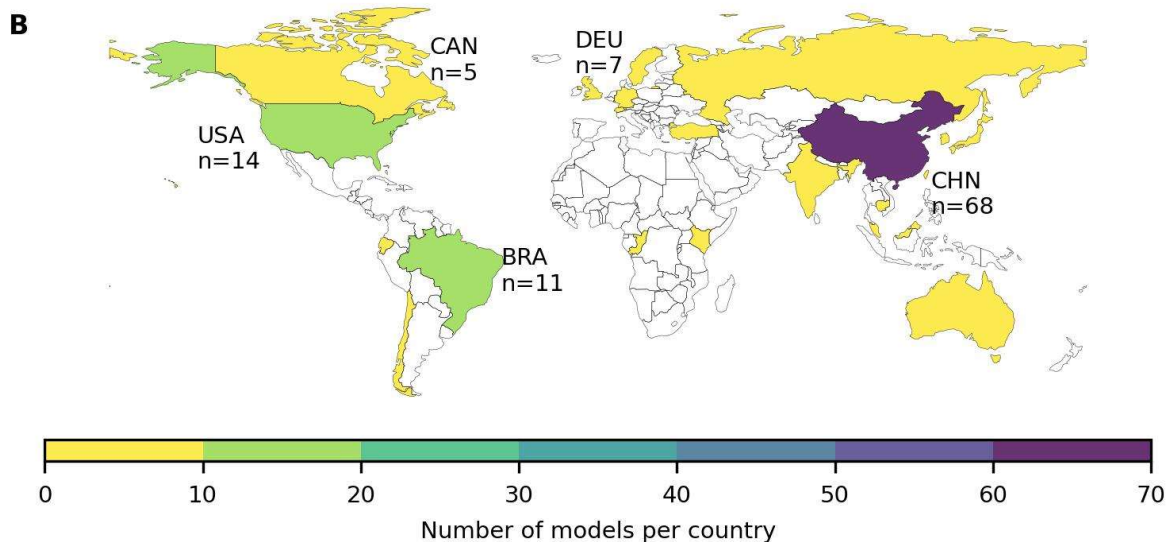
154 Illustrating the distribution of model types from 2010 to 2021, Figure 1A reveals that the majority of
155 riverine GHG models have been data-driven models (83%), while mechanistic and hybrid models have

156 been constructed less frequently (12% and 5%, respectively). Prior to 2015, all riverine GHG models
157 were data-driven, with less than 10 models published per year. However, since 2015, there has been a
158 considerable increase in the number of models, reaching a peak of 34 models in 2021, with a breakdown
159 of 10 models for CO₂, 15 for N₂O, and 9 for CH₄. This increase is accompanied by the growing
160 application of mechanistic and hybrid models, which implies a better understanding of the mechanism
161 and production pathways of riverine GHG dynamics. GHG modeling studies were mainly developed in
162 highly industrialized countries such as China and United States that concentrate ~60% of riverine
163 modeling research (Figure 1B). While tropical areas are missing, especially in Africa and South and
164 Central America, which might be significant given the high concentrations of GHGs reported in these
165 waters (Aufdenkampe et al., 2011). To further shed light on the current state of riverine GHG models, a
166 detailed analysis of the specific characteristics of these models is provided in the following section.

167



168



169

170 *Figure 1. Chronological evolution (A) and spatial distribution (B) in the development of riverine*
 171 *GHG models, including the number of modeling studies in the top-five countries (CHN: China, USA:*
 172 *United States of America, BRA: Brazil, DEU: Germany, CAN: Canada).*

173 3.1. Data-driven models

174 Data-driven models rely on observed data to define relationships between GHG fluxes or concentrations
 175 with driving factors. In our review, we found that these relationships are mainly defined statistically by
 176 applying methods such as principal component analysis (PCA) and regression analysis, or empirically
 177 with EFs and upscaling techniques, while other data-driven methods such as non-linear models have
 178 been scarcely applied (Figure S2). The differences between these main approaches is in their model
 179 structure and purpose. Statistical models can adapt model structure to collected data in order to obtain

180 optimal relationships and model performance, while empirical models have their structure fixed. Due
 181 to this flexibility, statistical models can be used to explore raw data and identify relationships between
 182 model inputs and output (Begum et al., 2021; Xiao et al., 2021). On the other hand, empirical models
 183 assume that GHG emissions are proportional to point measurements in the system. As such, values of
 184 EFs are used to transform N inputs into N₂O emissions and GHG point measurements are converted to
 185 regional and global emissions by multiplying them with surface area and gas transfer velocities
 186 (Aufdenkampe et al., 2011; Hu et al., 2016). Note that, given the diverse conditions of river systems,
 187 different equations of EFs have been obtained to estimate riverine N₂O emissions with diverse
 188 characteristics, such as hydrogeological conditions (Cooper et al., 2017) or climate (Hu et al., 2016).

189 Data-driven models have been applied for modeling site-scale riverine emissions, taking mainly into
 190 account biochemical processes (Table 1 and Figure S3). For instance, CO₂ data-driven models have
 191 focused on chemical equilibria of aquatic inorganic carbon – as such, pH, OC, DO, and Chl-a variables
 192 are included – while CH₄ and N₂O models have accounted for microbial processes, thereby using
 193 different forms of nutrients. Data-driven models are preferred due to their flexibility. Even with limited
 194 datasets, these models can provide initial insights and practical predictions, which can be valuable for
 195 making informed decisions or guiding further data collection efforts (Gu et al., 2021). However, the
 196 performance of data-driven models heavily relies on quality, quantity, and representativity of data.
 197 Therefore, the captured relationships are strongly dependent on the characteristics of collected data.
 198 Specifically, in riverine research, sampling campaigns have been conducted often under different
 199 climatic conditions, locations, seasons, and sampling periods, consequently, leading to datasets and
 200 models containing distinct characteristics (Xia et al., 2014). Moreover, the experimental design, such
 201 as sampling methods and measurement techniques, introduce further variation in data (Bastviken et al.,
 202 2022). Due to this strong dependence on datasets, data-driven models are limited to provide general
 203 comprehensive results, and their ability to make predictions beyond the observed data is restricted.

204 *Table 1. Summary of the data-driven models riverine GHG models encountered in this review. ns: not*
 205 *specified.*

System	Equation	R ²	Reference
Regression analyses			
CO₂			
Amazon Estuary, Brazil	$p\text{CO}_2 = 0.05 \cdot \text{SSS}^2 + 34.81 \cdot \text{SST}^2 + 19.71 \cdot \text{SSS} \cdot \text{SST} + 48792.07 - 560.47 \cdot \text{SSS} - 2694.56 \cdot \text{SST}$	0.74	Valerio et al. (2021)
River Kelvin, UK	$F_{\text{CO}_2} = 1.01 \cdot Q + 0.17$ $p\text{CO}_2 = 0.09 \cdot Q - 0.10$	0.64 0.96	Gu et al. (2021)
Upper Yangtze River, China	For the Taohua river $p\text{CO}_2 = -3637 \cdot \text{pH} + 280 \cdot \text{DOC} + 30587$	0.84	Tang et al. (2021)
	For the Nan river $p\text{CO}_2 = -1341 \cdot \text{pH} + 12640$	0.40	

	For the Puli river $p\text{CO}_2 = -2535 \cdot \text{pH} + 392 \cdot \text{Chl-a} + 21896$	0.78	
	For winter season $p\text{CO}_2 = -2712 \cdot \text{pH} + 308 \cdot \text{DOC} + 22810$	0.87	
	For summer season $p\text{CO}_2 = -3022 \cdot \text{pH} + 214 \cdot \text{Chl-a} + 26165$	0.83	
	For all seasons $p\text{CO}_2 = -3092 \cdot \text{pH} + 130 \cdot \text{Chl-a} + 46 \cdot \text{CFU} + 26704$	0.85	
Tanswei River, Northern Taiwan	$p\text{CO}_2 = 1.88 \cdot \text{turbidity} + 10160.507 \cdot \text{SOM} + 71.930 \cdot \text{SIM} - 46.157 \cdot \text{NO}_3 + 3705.831$	ns	Yang et al. (2015)
Global	$\text{Log}(p\text{CO}_2) = -3.192 + 9.372 \cdot \text{Pop_density} - 0.279 \cdot \text{log}(S_o) + 1.343 \cdot T_{\text{air}} + 0.279 \cdot \text{NPP}$	0.47	Lauerwald et al. (2015)
Boreal River	$\text{Log}(p\text{CO}_2) = -2.76 + 0.28 \cdot \text{Log}(\text{DOC}) - 0.22 \cdot \text{Log}(V)$	0.38	Campeau and Del Giorgio (2014)
CH₄			
Upper Yangtze River, China	When urban land proportion < 2% $p\text{CH}_4 = 8493 - 973 \cdot \text{pH}$	0.27	Tang et al. (2021)
	When 2% ≤ Urban land proportion < 20% $p\text{CH}_4 = 1430 + 929 \cdot \text{TN} - 27 \cdot \text{DO} - 388 \cdot \text{Chl-a} + 3620 \cdot \text{TP}$	0.75	
	When 20% ≤ Urban land proportion ≤ 46% $p\text{CH}_4 = 7191 + 3498 \cdot \text{TN} - 8598 \cdot \text{NO}_3$	0.96	
	For all land use types $p\text{CH}_4 = 1679 + 1411 \cdot \text{TN} - 10153 \cdot \text{NH}_4 + 9432 \cdot \text{TP} - 708 \cdot \text{NO}_3$	0.59	
River Kelvin, UK	$F_{\text{CH}_4} = 2.53 \cdot Q + 3.70$	0.46	Gu et al. (2021)
	$p\text{CH}_4 = 0.17 \cdot Q - 0.17$	0.91	
Flooding event Indigirka River, Siberia	$p\text{CH}_4 = -1.90 \cdot (\text{reflectance}) + 1.02$	0.94	Morozumi et al. (2019)
Tanswei River, Northern Taiwan	$p\text{CH}_4 = 84.463 \cdot \text{SIM} + 864.274 \cdot \text{NH}_4 - 456.171$	ns	Yang et al. (2015)
Boreal River in Québec, Canada	$\text{Log}(\text{CH}_4)/\text{TCG} = -2.90 + 0.06 \cdot T_w$	0.39	Campeau and Del Giorgio (2014)
N₂O			
Saitama, Japan	$p\text{N}_2\text{O} = 0.34 \cdot \text{NO}_2 - 0.30 \cdot \text{pH} + 0.22 \cdot \text{NH}_4 + 0.26 \cdot \text{NO}_3 + 0.23 \cdot \text{DOC}$	0.64	Mishima et al. (2021)
Xiaoyue River, China	$\text{FN}_2\text{O} = 4810.3e^{-0.26 \cdot \text{DO}}$	0.70	Wang et al. (2020)
Mara River, Kenya	When forest land use proportion > 70% $p\text{N}_2\text{O} = 0.23 + 0.10 \cdot p\text{CO}_2 + 1.71 \cdot \text{NH}_4 - 0.03 \cdot \text{DOC}$	0.59	Mwanake et al. (2019)

	When agricultural land use proportion > 70% $pN_2O = 1.49 + 0.27 * pCO_2 - 0.18 * DO - 0.05 * DOC$	0.77	
	When livestock land use proportion > 70% $pN_2O = 1.52 - 0.42 * pCO_2 - 0.22 * DO$	0.45	
Changjiang River estuary, China	$pN_2O = f(NO_3) * Q$ $Log(N_2O) = -0.39 + 0.69 * Log(NO_3)$	0.52	Yan et al. (2012)
Empirical models			
CO₂			
Global	$F_{CO_2} = \sum A * k * pCO_2$ $F_{CO_2} = \sum A * F_{CO_2}$		Aufdenkampe et al. (2011)
CH₄			
Global	$F_{CO_2} = \sum A * F_{CH_4}$		Stanley et al. (2016)
N₂O			
Global	For freshwater systems $EF_{5r} = 0.0026$ (kg N ₂ O per kg of N inputs to rivers) $EF_{5r} = N_2O/NO_3$		IPCC (2019)
Rivers Avon, Eden, and Wensum, UK	For unconfined chalk hydrogeological conditions $EF_{5r} = 0.00036$; $EF_{5r} = N_2O/NO_3$		Cooper et al. (2017)
	For semi-confined chalk hydrogeological conditions $EF_{5r} = 0.00020$; $EF_{5r} = N_2O/NO_3$		
	For confined chalk hydrogeological conditions $EF_{5r} = 0.00016$; $EF_{5r} = N_2O/NO_3$		
Global	General equations $ER_{N_2O} = 0.0034 * Y_{DIN}^{-0.169}$ $L_{DIN} = 0.0034 * Y_{DIN}^{0.831} * A$ $ER_{N_2O} = 0.0138 * Y_{DIN}^{-0.417}$ $L_{DIN} = 0.0138 * Y_{DIN}^{0.583} * A$		Hu et al. (2016)
	For subtropical and tropical rivers $ER_{N_2O} = 0.0044 * Y_{DIN}^{-0.179}$ $L_{DIN} = 0.0044 * Y_{DIN}^{0.821} * A$ $ER_{N_2O} = 0.0112 * Y_{DIN}^{-0.355}$ $L_{DIN} = 0.0112 * Y_{DIN}^{0.645} * A$		
	For temperate rivers $ER_{N_2O} = 0.0041 * Y_{DIN}^{-0.230}$ $L_{DIN} = 0.0041 * Y_{DIN}^{0.770} * A$ $ER_{N_2O} = 0.0198 * Y_{DIN}^{-0.521}$ $L_{DIN} = 0.0198 * Y_{DIN}^{0.479} * A$		

206

207 3.2. Mechanistic models

208 Based on model structure and complexity, three types of mechanistic models are observed: conceptual,
209 mass-balance biochemical, and mass-balance hydraulic models (Table 2). Conceptual models apply
210 simplified forms of physical or chemical principles to define relationships between GHG fluxes or
211 concentrations with driving factors. For instance, Marzadri et al. (2017) estimated N₂O emissions at a

212 basin scale, based on two denitrification Damköhler numbers, $Da_{D_{HZ}}$ and $Da_{D_{S}}$. The first model accounts
 213 for emissions from streams where hyporheic and benthic processes play an important role, while the
 214 second simulates emissions from rivers where processes in the water column are more important. Mass-
 215 balance biochemical models are usually one-dimensional models that estimate the time-variant
 216 transformation of C and N sources into riverine GHGs. For example, Newcomer et al. (2018) applied a
 217 mass-balance model to study nutrient transformation in the hyporheic zone, including storage and
 218 release of C and N in biomass and biogenic CO_2 and N_2 to the atmosphere, driven by fluctuations in
 219 groundwater levels, antecedent hydrological conditions, riverbed sediment characteristics, and DOC
 220 delivery.. Mass-balance hydraulic models are two-dimensional models that simulate the spatial- and
 221 time-variant concentration of C and N components along the river network, including transformation
 222 processes in the water column and the interaction of these with lateral sources. Mass-balance hydraulic
 223 models include two major modules: flow and reactive transport. The flow module simulates the
 224 propagation of flow in a channel, while the reactive transport module simulates the quantity and fate of
 225 GHG components using transport coefficients, such as diffusion and dispersion (Akella and
 226 Bhallamudi, 2019). Mass-balance hydraulic models are particularly useful to evaluate interactions of C
 227 and N components carried by the river with groundwater inputs and point effluents at different locations,
 228 thereby providing a detailed modeling framework for predicting hotspots of GHG emission and
 229 production (Saccardi and Winnick, 2021).

230 Mechanistic models use fundamental knowledge to describe via mathematical expressions and physical
 231 principles, temporal and/or spatial changes in C, N, and resulting GHG components. Mechanistic
 232 models are more comprehensive than data-driven models, being suitable to provide new insights into
 233 system processes and mechanisms and extrapolate beyond observed data (Pfeiffer-Herbert et al., 2019).
 234 However, the extensive system representativity of mechanistic models can lead to complex calculations
 235 and overparameterization, which increases substantially required data (Ho et al., 2019). As a result,
 236 river modelers often appeal to certain assumptions on model parameters and boundary conditions, such
 237 as denitrification conversion ratio or zero initial GHG concentrations (Saccardi and Winnick, 2021;
 238 Stets et al., 2017; Vanderborgh et al., 2002). These assumptions often distort the representation of the
 239 real system, introducing biases into modeling results.

240 *Table 2. Summary of the mechanistic riverine GHG models encountered in this review.*

System	Equation	Reference
Conceptual models		
N₂O		
Upper Mississippi River basin, USA	$\sum_{i=1}^{NC} ER_{N_2O,i} = \sum_{i=1}^{NC} V * DIN_i * F^* N_2O * W_i * L_{St,i}$ When river width ≤ 10 m $F^* N_2O_{HZ} = 1.55 * 10^{-7} * (Da_{D_{HZ}})^{0.43}$	Marzadri et al. (2020, 2017)

	When $10 \text{ m} < \text{river width} \leq 175 \text{ m}$ $F^*N_2O_{BZ} = 1.91 * 10^{-8} * (Da_{DHz})^{0.58}$	
	When river width $W > 175 \text{ m}$ $F^*N_2O_{WC} = 4.56 * 10^{-6} * (Da_{DS})^{0.72}$	
	$Da_{DHz} = \tau_{50}/\tau_D = 17.810 * g^*D^*V_{fden}/(K_h * V^2)$	
	$Da_{DS} = t_m/\tau_D = 14.925 * V_{fden}/(g^*D^*S_o)^{1/2}$	
CH₄		
Saar River, Germany	$MF_{Z_1T} = \left(a_1 * e^{\frac{z}{z_1}} + a_2 * e^{\frac{z}{z_2}} + a_3 \left(\frac{1}{1 + e^{-b_3 z_3 + c_1}} - 1 \right) \right) a_4 T^{b_4}$	Wilkinson et al. (2015)
Mass-balance biochemical models		
CO₂		
Connecticut River, USA	$\Delta DO_{i,d} = \left(\frac{GPP_d}{D_{i,d}} \times \frac{PPFD_{i,d}}{PPFD_d} \right) + \left[\left(\frac{EcoR_d}{D_{i,d}} \right) + f_{i,d}(K_{600d})(DO_{sat,i,d} - DO_{i,d}) \right] \times \Delta t$ $DIC_t = DIC_{t-1} - K_{CO_2} * (CO_{2,t-1} - CO_{2,sat}) - GPP_{DIC,t-1} + EcoR_{DIC,t-1}$	Aho et al. (2021)
Russian River, USA	$\frac{dCO_2}{dt} = GPP - R_{autotrophic} - R_{heterotrophic} + R_{hydropneic} \pm Dif$	Newcomer et al. (2018)
N₂O		
Seine River, France	$P_{N_2O_denrip} = \frac{N_2O}{N_2O + N_2} * \Delta C_{NO_3_denrip} * Q$ $Q \times C_{N_2O_rip} = Q \times C_{N_2O_soil} + P_{N_2O_denrip} + kvs \times A_{rip} \times (C_{N_2O_soil} - C_{eq}) - kvs \times A_{rip} * (C_{N_2O_rip} - C_{eq})$	Billen et al. (2020)
CH₄		
Cambridge Bay estuary, Canada	$C_{CH_4,t+1} = (C_{CH_4,t} V_{box} + F_{riv,t} + F_{ice,t} + F_{gasex,t} + F_{in,t} + F_{out,t} + F_{ox,t})/V_{box}$ $F_{riv,t} = V_{riv,t} * C_{CH_4_riv,n,t}$ $F_{ice,t} = V_{ice,t} * C_{CH_4_ice,n,t}$ $F_{in,t} = (V_{riv,t} + V_{ice,t}) * C_{CH_4,n-1,t-1}$ $F_{out,t} = -(V_{riv,t} + V_{ice,t}) * C_{CH_4,n,t}$ $F_{gasex,t} = K_{CH_4,t}(C_{CH_4,eq,t} + C_{CH_4,n,t}) * V_{box} * dt$ $F_{ox,t} = -K_{ox,t} * C_{CH_4,t} * V_{box} * dt$	Manning et al. (2020)
Mass-balance hydraulic models		
CO₂		
East River, USA	$\frac{dC_{CO_2}}{dt} = -V \frac{dC_{CO_2}}{dx} + \frac{1}{A} \frac{dQ}{dx} (C_{CO_2gw} - C_{CO_2}) - k_{CO_2}(C_{CO_2} - C_{CO_2atm}) + F_{wc} + F_{he}$	Saccardi and Winnick, (2021)
N₂O		
Tyne River, UK	$\frac{\partial D}{\partial t} + D \frac{\partial V}{\partial x} + V \frac{\partial D}{\partial x} + \frac{D * V}{W} \frac{dW}{dx} = \frac{Q_L}{W * \Delta x}$	Akella and Bhallamudi (2019)

	$\frac{\partial \text{NH}_4}{\partial t} + V \frac{\partial \text{NH}_4}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} \left(A * \text{Disp}_x \frac{\partial \text{NH}_4}{\partial x} \right) + \left(\frac{Q_L}{A} \right) \text{NH}_{4\text{Lat}} + \frac{R_{\text{Ammon}}}{h} - K_{\text{NIT}} \text{NH}_4 \theta_1^{T-20} - K_{\text{Alg-up}} \text{NH}_4$ $\frac{\partial \text{NO}_3}{\partial t} + V \frac{\partial \text{NO}_3}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} \left(A * \text{Disp}_x \frac{\partial \text{NO}_3}{\partial x} \right) + \left(\frac{Q_L}{A} \right) \text{NO}_{3\text{Lat}} - K_{\text{NIT}} \text{NO}_3 \theta_1^{T-20}$ $\frac{\partial \text{N}_2\text{O}}{\partial t} + V \frac{\partial \text{N}_2\text{O}}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} \left(A * \text{Disp}_x \frac{\partial \text{N}_2\text{O}}{\partial x} \right) + \left(\frac{Q_L}{A} \right) \text{N}_2\text{O}_{\text{Lat}} + \frac{0.25}{100} * K_{\text{NIT}} * \text{N}_2\text{O} * \theta_1^{T-20} - \alpha (\text{N}_2\text{O} - \text{N}_2\text{O}_{\text{atm}})$	
CH₄		
Columbia River, USA	$Q_{j,k} = V_{j,k} * \Delta y * \Delta z$ $A \frac{\partial C_{\text{CH}_4}}{\partial t} = \frac{\partial}{\partial x} \left[Q_R C_{\text{CH}_4} + A * \text{Dif}_H \frac{\partial C_{\text{CH}_4}}{\partial x} \right] + A * \left[\frac{K_{\text{CH}_4}}{H} (C_{\text{CH}_4\text{sat}} - C_{\text{CH}_4}) - \alpha_{\text{OX}} C_{\text{CH}_4} + \text{CH}_{4\text{Lat}} \right]$	Pfeiffer-Herbert et al. (2016)

241 3.3. Hybrid models

242 Hybrid models combine data-driven models and mechanistic models to leverage their strengths and
243 potentially provide more comprehensive and accurate assessments. This model type is able to integrate
244 diverse knowledge realms, data sources, and formats into its calculations, thereby providing a holistic
245 analysis of the system (Jia et al., 2020). A holistic approach is highly required in riverine GHG research,
246 as land-surface and riverine processes need to be integrated to simulate the entire cycle of GHG
247 dynamics and accurately estimate the fate and transport of C, N, and GHG components (Borges et al.,
248 2015).

249 Table 3 shows hybrid models collected in this review. What is noticeable is the flexibility of this model
250 type, as a data-driven model can be used to either complement the outputs of a mechanistic model or
251 provide input variables. This characteristic is particularly useful in riverine GHG research as well-
252 established mechanistic models can be used to simulate processes such as C and N biogeochemical
253 transformations in the river (Ho et al., 2021) or hydrology driving the transport of C and N components
254 from land-surface to riverine systems (Gao et al., 2020). In the meantime, a data-driven model can be
255 used to predict riverine GHG emissions from the outputs of a mechanistic model, thereby providing a
256 holistic approach of the cycling of water, C, N, and GHGs. Additionally, data-driven models can also
257 provide inputs for a mechanistic GHG model, thereby creating tools to estimate global N₂O emissions
258 (Marzadri et al., 2021).

259 Despite these advantages, hybrid models face challenges that hinder their application. These challenges
260 include complexity, specialized knowledge requirements, discrepancies in temporal and spatial scales
261 of models, and concerns regarding the interpretability of their outcomes (Kratzert et al., 2019).
262 Integrating diverse data sources and model types demands for substantial computational resources and
263 expertise, posing time and cost barriers (Willard et al., 2020). Moreover, the accuracy and
264 interpretability of hybrid models remains disputed, as these models usually rely on physical constraints
265 of mechanistic components to provide transparency to their calculations, which might be unrealistic or

266 insufficient to explain model output (Chen et al., 2022). Furthermore, the lack of interpretative tools to
 267 validate the accuracy of hybrid models contributes to their characterization as black-box models
 268 (Schneider et al., 2022).

269 *Table 3. Description of the hybrid riverine GHG models encountered in this review.*

System	Model 1	Model 2	Reference
CO₂, CH₄, and N₂O			
Cuenca River basin, Ecuador	Mechanistic model: River Water Quality Model No.1 (RWQM1) and Activated Sludge Model No.1 (ASM1)	Data-driven model: fuzzy models to evaluate risk of GHG accumulation in the river	Ho et al. (2021)
N₂O			
Naoli River basin, China	Mechanistic SWAT hydrological model	Data-driven N ₂ O regression model	Gao et al. (2020)
Global	Data-driven models to calculate hydrological and morphological factors: W, D, V, S, d ₅₀ , K _h , L _{st} , V _{fden} , τ ₅₀ , τ _D , t _m	Mechanistic N ₂ O emission model	Marzadri et al. (2021)
Manistee and Tippecanoe River basins, USA	Data-driven models to calculate hydrological and morphological factors: W, D, V, S, d ₅₀ , K _h , L _{st} , V _{fden} , τ ₅₀ , τ _D , t _m	Mechanistic N ₂ O emission model	Tonina et al. (2021)

270 **4. Current status of riverine GHG models**

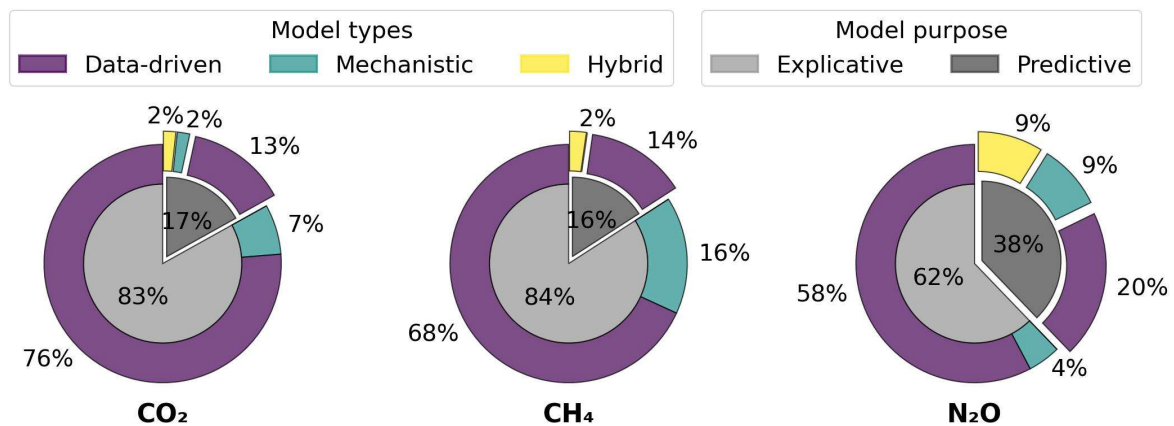
271 **4.1. Model purposes**

272 Regarding model purposes, riverine GHG models can be classified into explicative or predictive (Figure
 273 2). Explicative models aim to explain the relationships and underlying mechanisms between driving
 274 factors of GHGs. Examples include statistical causal analyses, such as multiple linear regressions (Hao
 275 et al., 2021) and PCA analyses (Shen et al., 2020), and mechanistic models that validate the hypothesis
 276 of GHG dynamics (Pfeiffer-Herbert et al., 2016). Predictive models, on the other hand, forecast the
 277 value of GHG concentrations or fluxes based on the status of driving factors. Their focus is to develop
 278 models that can extrapolate precisely to unseen data. Examples include regression models used to
 279 forecast global CO₂ emissions using changes in basin population density, slope of the river, air
 280 temperature, and net primary production (Lauerwald et al., 2015), or mechanistic models used to
 281 simulate scenarios to determine the optimal allocation of wastewater effluents in tidal rivers (Akella
 282 and Bhallamudi, 2019). Note that studies also combined explicative and predictive techniques, such as
 283 PCA to determine the principal drivers of GHG production, followed by regression models that use
 284 these factors for prediction (Tang et al., 2021).

285 Figure 2 shows that explicative models are more commonly applied than predictive models, reflecting
 286 the ongoing interest of researchers in understanding the causal relationships between driving factors

287 and GHG emissions. Among explicative models, the data-driven approach prevails in CO₂ (76%), CH₄
 288 (68%) and N₂O (58%) models, followed by much fewer applications of mechanistic models at 7%, 16%
 289 and 4% in CO₂, CH₄ and N₂O, respectively. Predictive models also show a dominance of data-driven
 290 approaches (13%, 14% and 20%), while mechanistic (2%, 0% and 9%) and hybrid models (2%, 2% and
 291 9%) are less commonly applied. This data reveals the researcher preference for applying data-driven
 292 models, likely due to less data requirements, and for predicting N₂O emissions, which might be
 293 explained by the early concern over anthropogenic N inputs to river systems (Baulch et al., 2011;
 294 Seitzinger and Kroeze, 1998).

295



296

297 *Figure 2. Description of riverine GHG models according to the model purpose.*

298 4.2. Model scales

299 Riverine GHG modeling research is mostly applied at specific site-scale conditions, whereas the
 300 analysis of larger-scale systems (basin or global) is scarcely proposed (Figure 3). Site-scale studies
 301 apply either data-driven or mechanistic models, basin-scale studies apply either mechanistic or hybrid
 302 models, and global-scale studies apply data-driven, mechanistic, and hybrid models. This can be related
 303 to the distinct advantages that each model type offers at different scales.

304 Data-driven models are suitable either at the site or global scale. At the site scale, data-driven models
 305 excel at defining relationships between biochemical factors that locally affect GHG production and
 306 emissions. As shown in Section 3.1, multiple data-driven models are proposed to model chemical
 307 equilibria of aquatic inorganic carbon or microbial nutrient transformations. At the global scale, data-
 308 driven models are applied due to their flexibility in using datasets from heterogeneous systems without
 309 requiring to satisfy any physical constraint. Therefore, a single model can be applied simultaneously to
 310 multiple (and even ungaged) basins (Lauerwald et al., 2015). On the contrary, at the basin scale, data-
 311 driven models require extensive datasets because basin-scale processes are characterized by
 312 geomorphological heterogeneity and time-dependent relationships. For example, depending on
 313 antecedent hydrological conditions, such as accumulated precipitation and soil water content of the

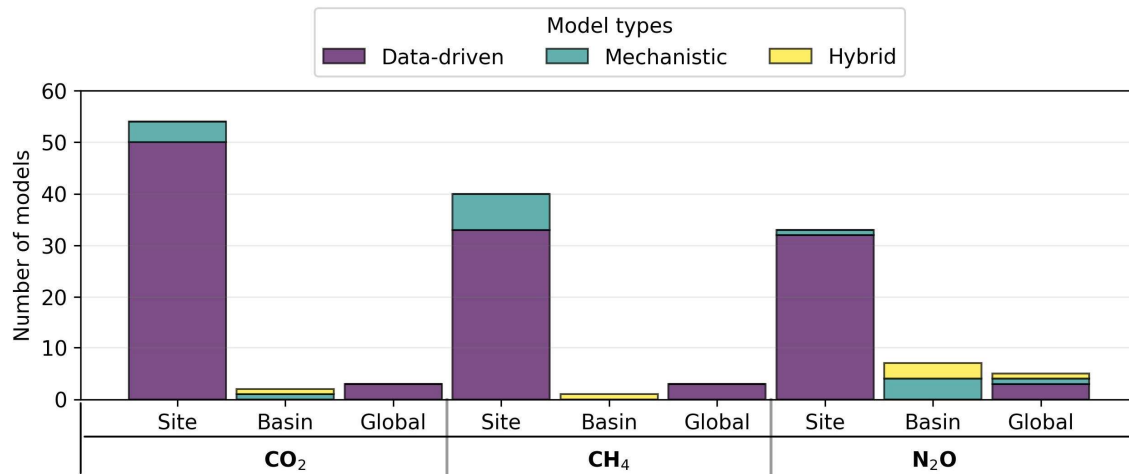
314 basin before precipitation events, generated runoffs can either carry great soil CO₂ to a river triggering
315 riverine emissions or conversely dilute CO₂ concentrations with rapid runoff to a river (Zhang et al.,
316 2020). Since available riverine GHG datasets rarely satisfy this demand, more parsimonious
317 mechanistic models are preferred for basin-scale practical applications.

318 Mechanistic models are able to simulate dynamics occurring at multiple temporal and spatial scales
319 therefore being useful at any scale of analysis. At the site scale, these models provide detailed
320 simulations of underlying physical and chemical processes, which allows researchers to understand
321 processes where data is difficult to obtain. For example, mechanistic models were used to explain
322 nitrification and denitrification processes in hyporheic zones, contributing to our understanding of the
323 complexities of GHG fluxes (Hu et al., 2021). However, as the model size increases, required data and
324 computational power also increase significantly. For instance, Yao et al. (2020) proposed a mechanistic
325 model that integrates surface and subsurface hydrological and biogeochemical processes to estimate
326 global riverine N₂O emissions. This model requires extensive data to define critical parameters, such as
327 ratio of riverine N₂O production, thickness of the hyporheic zone, and surface area of streams and rivers,
328 which are not available in global datasets, constituting great uncertainties in the model outcomes.

329 Contrary to data-driven and mechanistic models, hybrid models offer advantages across multiple
330 scales by combining the strengths of different modeling approaches. They can integrate data-driven
331 and mechanistic models to capture both site-scale biochemical processes and basin-scale land-surface
332 processes. For instance, in [Gao et al. \(2020\)](#), the basin-scale model SWAT, originally designed to
333 model hydrological, soil, and plant physiological processes, was complemented with a data-driven
334 model to also account for biochemical riverine transformations of nutrients into N₂O fluxes. In other
335 words, hybrid models offer the possibility of complementing well-established mechanistic basin-scale
336 models, whose parameters and capabilities are largely investigated in the literature. Hybrid models are
337 also applied at the global scale. For instance, Marzadri et al. (2021) designed data-driven models to
338 derive parameters from globally available datasets that subsequently are inputted to mechanistic
339 conceptual GHG models. Differently from fully data-driven global models, hybrid global models
340 offer a knowledge-based background that explain, to a certain extent, the outcomes of the model.

341 However, it must be noted that at the global scale, models oversimplify processes, likely omitting
342 important sources and sinks of GHGs, such as wastewater inputs or drainages from urban and arable
343 areas. Therefore, global models need to report uncertainties implied in their methodology (e.g., Yao et
344 al., 2020).

345



346

347 *Figure 3. Characterization of the model scale of river GHG models. Site-scale models are applied*
 348 *locally to specific spots in the basin, while basin- and global-scale models combine data from*
 349 *multiple points into a single modeling framework.*

350 4.3. Riverine GHG data attributes

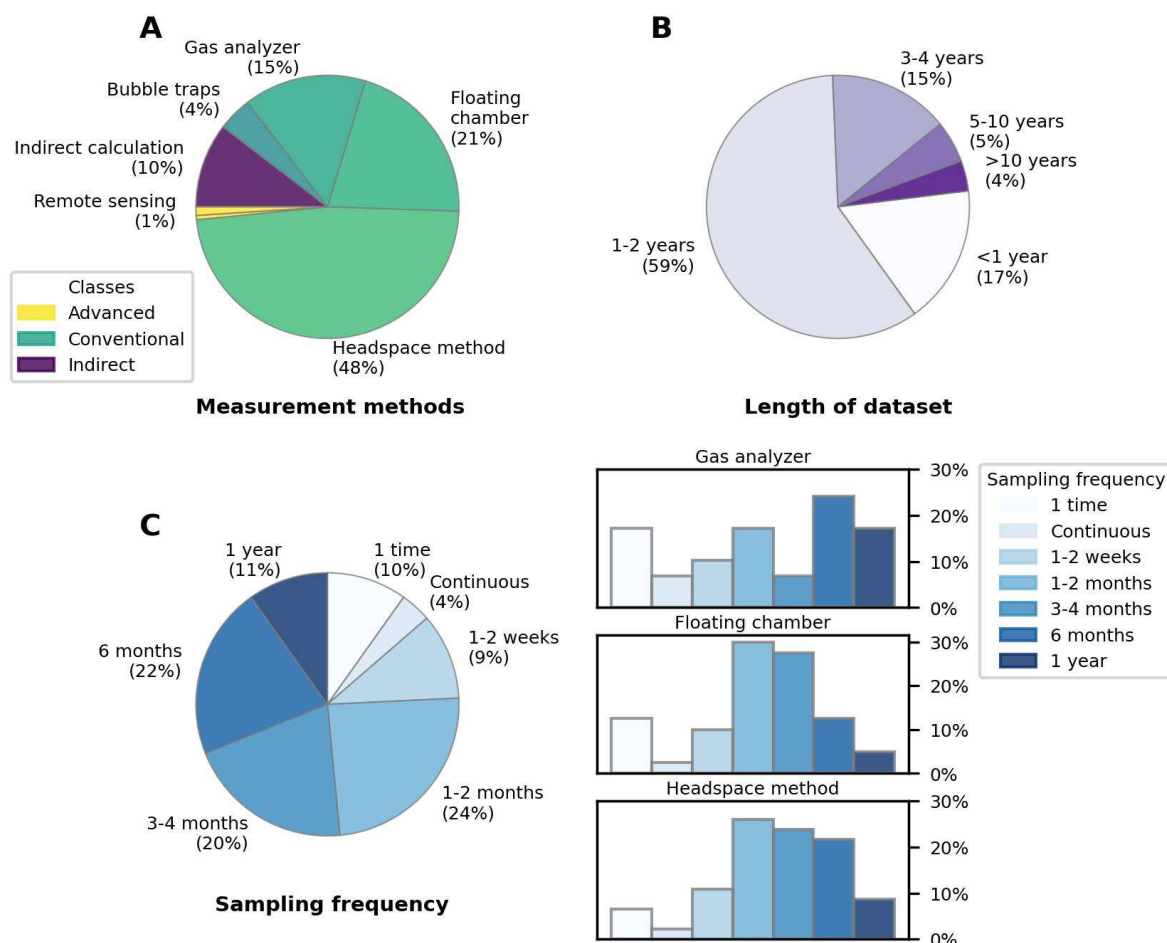
351 The attributes of measurement methods and datasets used for riverine GHG model development is
 352 shown in Figure 4. The measurement methods are categorized based on data acquisition processes,
 353 namely indirect calculations and conventional and advanced measurements (Figure 4A). The first
 354 category uses chemical equilibria of aquatic inorganic C to calculate dissolved CO₂ concentration
 355 (*p*CO₂) (Nordstrom et al., 1979). Typical calculations of *p*CO₂ include the DIC-pH-temperature method
 356 (Abril et al., 2015; Hunt et al., 2011), the alkalinity-pH-temperature method (Hunt et al., 2011; Li et al.,
 357 2013; Liu et al., 2020) as well as software tools like CO2SYS (Lewis and Wallace, 1998) or PHREEQC
 358 (Parkhurst and Appelo, 2013). Conventional measurements correspond to manual methods used to
 359 collect data at specific site spots, such as floating chambers, the headspace method, bubble traps, and
 360 gas analyzers. Advanced measurements encompass non-invasive techniques that cover larger areas
 361 compared to conventional methods, such as hydroacoustic surveys and remote sensing techniques.
 362 Further details on these methods can be found in Bastviken et al. (2022). It is important to note that
 363 remote sensing techniques, including satellite surveys, face challenges in directly measuring GHGs in
 364 riverine systems due to detection limits, sample frequencies, and spatial coverage (Palmer et al., 2018;
 365 Thorpe et al., 2017). Consequently, proxies for GHGs are identified, such as reflectance or surface water
 366 temperature, which are then utilized to indirectly predict riverine GHG concentrations and fluxes
 367 (Morozumi et al., 2019; Valerio et al., 2021; Wilkinson et al., 2019).

368 Figure 4A indicates that 84% of the models are based on conventional measurements, namely the
 369 headspace method (48%), floating chamber (21%), and gas analyzers (15%). The extensive use of the
 370 first two techniques can be attributed to their lower costs and easier deployment compared to expensive
 371 gas analyzers and time-consuming bubble traps (4%) (Bastviken et al., 2022; Wilkinson et al., 2015).
 372 In addition to conventional methods, indirect calculations are employed (10%) despite their

373 acknowledged systematic errors due to overestimation of $p\text{CO}_2$ in acidic, organic-rich freshwaters
374 (Abril et al., 2015; Hunt et al., 2011; Liu et al., 2020). Furthermore, it appears that riverine GHG models
375 barely use data collected from advanced methods, which might be related to the high costs of
376 hydroacoustic surveys and technical difficulties of satellite surveys in rivers.

377 The majority of riverine GHG models (77%) are based on data collected over a period longer than a
378 month (Figure 4C). The low frequency of sample collection can be attributed to the prevalence of
379 conventional manual methods, such as the headspace method and floating chambers (Figure 4A).
380 Although the headspace method is simple to perform, increased sampling frequency requires multiple
381 displacements of human resources to the study site, whereas combining this method with automated
382 water collection systems is problematic due to difficulties in preserving samples unaltered, e.g., issues
383 regarding degassing in the sampled bottle (Johnson et al., 2010). In addition to multiple displacements
384 to the field, floating chambers also require a significant amount of deployment time, making it labor-
385 intensive to collect samples at shorter intervals (Thanh Duc et al., 2020). The few studies that obtained
386 higher temporal resolutions (1–2 weeks or continuous) involved either dedicated efforts by researchers
387 using manual methods or the use of automated methods that combined gas analyzers (Figure 4C). The
388 limited frequency of GHG data collection poses significant challenges in establishing comprehensive
389 relationships between GHGs and the drivers that influence emissions at high temporal resolution (Xia
390 et al., 2014). For instance, sporadic precipitation events cause the interruption of aquatic metabolism
391 processes, therefore changing the diurnal variation of CO_2 emissions from rivers (Zhang et al., 2020).

392 Furthermore, GHG data are often of short duration (Figure 4B), which can be attributed to the
393 aforementioned challenges associated with costly deployment and equipment. Overall, more than 90%
394 of riverine GHG models were built based on a dataset of less than 4 years, with the majority (59%)
395 using a dataset of 1–2 years. The use of short-term datasets hampers the comprehensive investigation
396 of the long-term effects that driving factors have on riverine GHG emissions, which likely fails to
397 capture a full range of GHG emissions from riverine systems (Borges et al., 2015). For instance, the
398 identification of seasonal trends and patterns of riverine GHG emissions and other environmental
399 factors is unlikely to be revealed with the absence of long-term datasets (Ran et al., 2021).



400

401

402 *Figure 4. Percentage of riverine GHG models across distinct measurement methods (A), length of*
 403 *dataset (B), and sampling frequency (C). Figure C describes the sampling frequency of the three most*
 404 *frequently used measurement methods.*

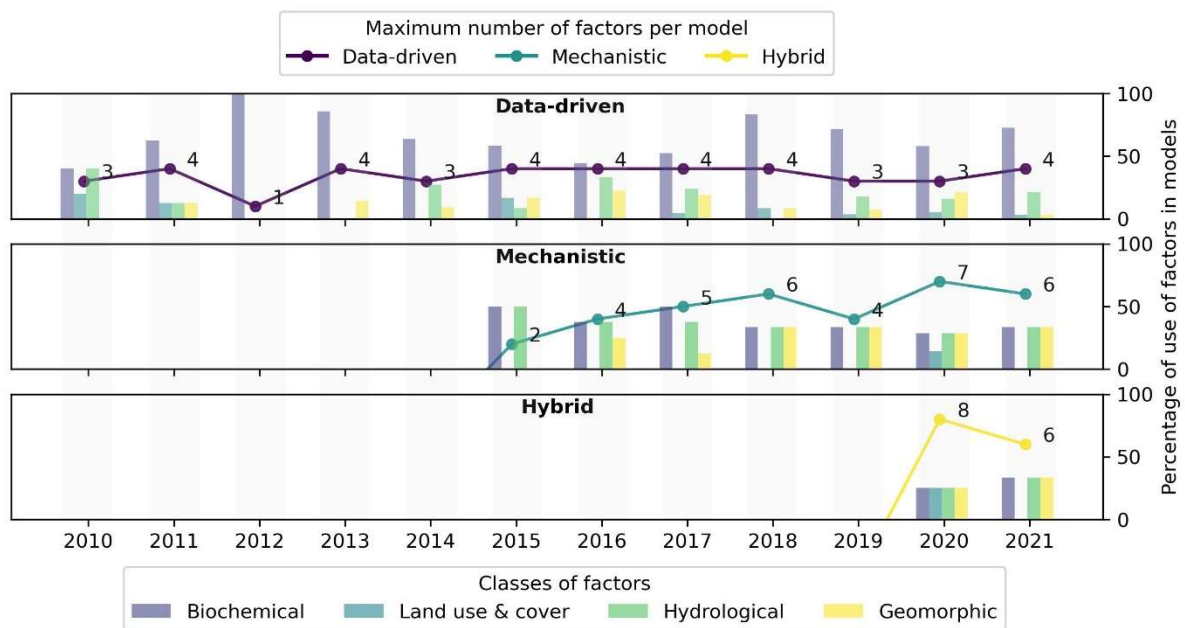
405 **4.4. Modeled factors**

406 This section elucidates the complexity of riverine GHG models by examining the number of factors that
 407 are incorporated in model development, namely biochemical, hydrological, geomorphic, and LULC
 408 factors (Figure 5). Integrating multiple factors is crucial in riverine GHG modeling, as overlapping
 409 effects of factors can create emission hotspots (Quick et al., 2019; Stanley et al., 2016). For instance,
 410 areas in which the river flows from low to high slopes can become emission hotspots as a result of OM
 411 accumulation, which is commonly driven by an increase in hydrological flow paths after precipitation
 412 events (Rocher-Ros et al., 2019).

413 Based on the number of modeled factors, the complexity of riverine GHG models increases from data-
 414 driven models to mechanistic and hybrid models (Figure 5). Data-driven models have incorporated one
 415 to four factors, focusing mostly on biochemical factors in contrast to infrequent use of hydrological,

416 geomorphic, and LULC factors. This degree of complexity of data-driven models remained steady from
 417 2010 to 2021. On the other hand, mechanistic and hybrid models exhibit an increasing complexity by
 418 incorporating up to seven and eight factors, respectively. Although these models are able to integrate
 419 more hydrological and geomorphic factors, LULC factors have been rarely used.

420 The lack of integration of LULC factors might be explained by the difficulties in accurately representing
 421 this factor in existing models. LULC data is usually reported in maps where each grid is representative
 422 of a class or category (categorical spatial data). This troubles its integration with data-driven models
 423 that are based on point measurements (Mallast et al., 2020). For instance, LULC factors are currently
 424 represented into data-driven models simply as a percentage of the basin area, losing valuable spatial
 425 information through converting map details into numerical values (Tang et al., 2021). Contrarily, the
 426 mass-balance calculation scheme of mechanistic models allows the integration of LULC factors, but
 427 this can make the model and required data considerably more complex and lead to uncertain outcomes
 428 (Hu et al., 2021).



429

430 *Figure 5. Description of model complexity across diverse model types. Line plots show the maximum*
 431 *number of factors used per year, while bar plots show the classes of these factors.*

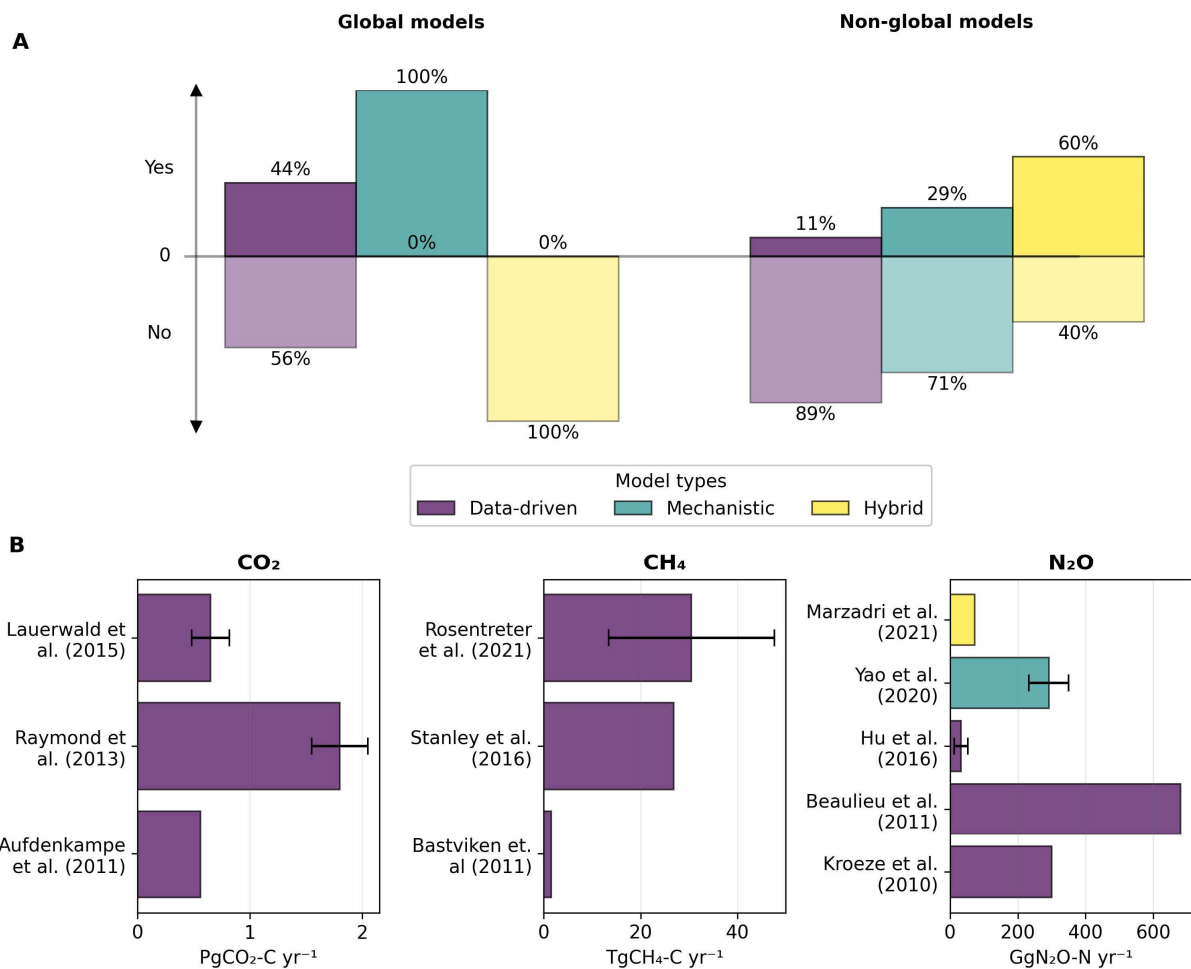
432 4.5. Uncertainty analysis

433 Reporting uncertainties associated with model outcomes is indispensable to increase the transparency
 434 of GHG emission inventories, thereby enabling realistic feedbacks of anthropogenic climate change
 435 (Benveniste et al., 2018). Uncertainty information is often provided as a range, reflecting uncertainties
 436 related to data limitations, parameter values, and/or model structure, helping to identify the most
 437 influential model components and therefore bottlenecks in model development and outcomes (Hu et al.,
 438 2021). This information is crucial for a comprehensive understanding and comparison within the

439 outcomes provided by different modeling approaches. However, uncertainty evaluation techniques have
 440 often been omitted in riverine GHG models (Figure 6A). Only few publications that evaluated model
 441 uncertainties applied either Monte Carlo analysis (Rosentreter et al., 2021), error propagation (Borges
 442 et al., 2019), or generalized likelihood uncertainty estimation (Ho et al., 2021).

443 Large discrepancies exist in global estimates of riverine GHG emissions, however uncertainty ranges
 444 are overlooked in 56% of the cases (Figure 6B). For instance, significant discrepancies in riverine CO₂
 445 emissions have been observed due to the inclusion of headwaters in some models (Raymond et al.,
 446 2013) and exclusion in others (Aufdenkampe et al., 2011; Lauerwald et al., 2015). Similarly,
 447 discrepancies in riverine N₂O emission estimates have been reported when incorporating headwaters
 448 (Yao et al., 2020) and hydromorphological effects in models (Marzadri et al., 2021). Furthermore,
 449 estimating global riverine CH₄ emissions remains challenging due to substantial flux variability within
 450 and between aquatic ecosystems. For instance, CH₄ empirical data distribution is skewed towards higher
 451 values making estimations sensitive to modeling assumptions and methods (Rosentreter et al., 2021).
 452 Additionally, determining surface areas of aquatic ecosystems, crucial for most riverine global models,
 453 carries significant uncertainties (Rosentreter et al., 2021; Yao et al., 2020).

454



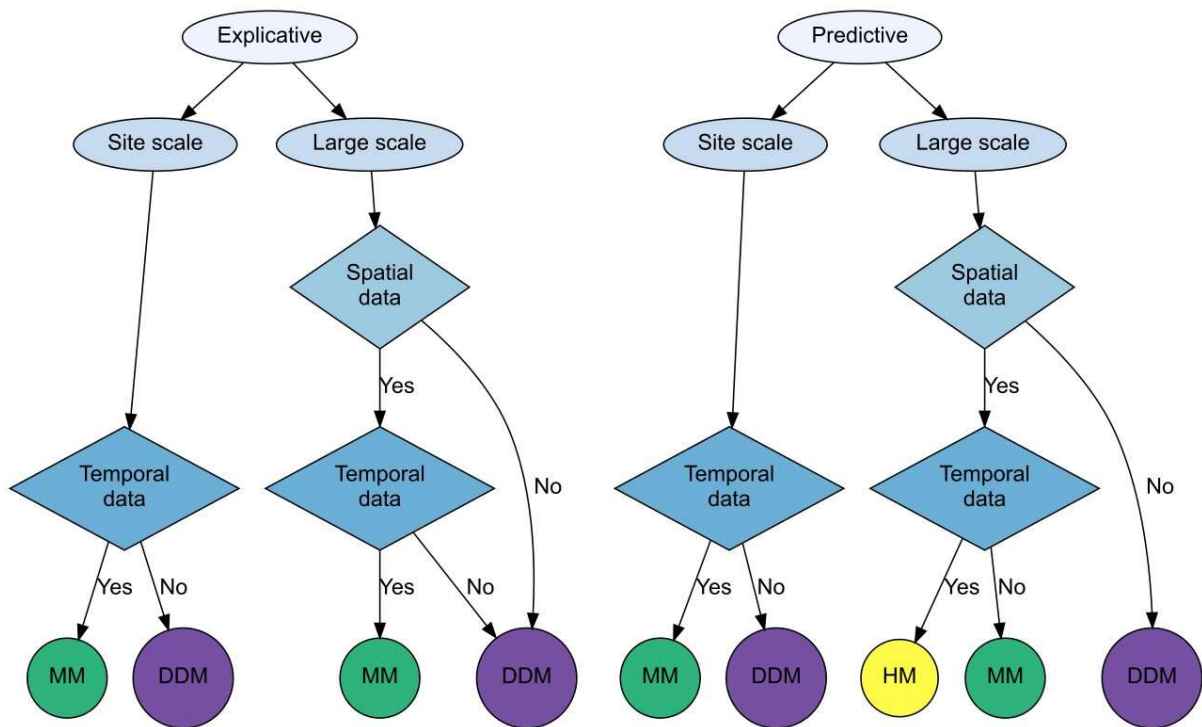
455

456 *Figure 6. Application of uncertainty analysis in global and non-global riverine GHG models (A),*
 457 *including global estimates of riverine GHG emissions with uncertainty ranges when reported (B).*

458 **5. Application framework of riverine GHG models**

459 Based on the characteristics of riverine GHG models, a decision tree is provided in Figure 7 to guide
 460 model selection. Specifically, model selection is based on three main criteria, including model purpose,
 461 model scale, and the spatiotemporal characteristics of GHG data. Overall, low complexity of data-
 462 driven models allows for its simple application, making these models applicable even when data is
 463 scarce. The development of more complex data-driven models, such as machine learning algorithms in
 464 GHG riverine research, is still limited by data availability. However, the use of such complex data-
 465 driven models is gradually being implemented in GHG riverine research through their combination in
 466 hybrid models, e.g., for determining catchment characteristics for global-scale predictions (Marzadri et
 467 al., 2021). Given the extensive representation of the system of mechanistic models, these can simulate
 468 temporal and spatial dynamics of GHGs being relevant for explicative or predictive purposes when
 469 sufficient spatiotemporal resolution is available to validate model outcomes. However, a fully
 470 mechanistic approach needs abundant data for large-scale applications. Then, hybrid models are
 471 particularly valuable as they can combine existent mechanistic models, such as hydrological models
 472 with a data-driven component for GHG emission calculation, therefore providing a framework suitable
 473 for combining processes occurring at different temporal and spatial scales, such as land-surface and
 474 riverine processes.

475



476

477
478

Figure 7. Decision tree for riverine GHG model selection. DDM: Data-driven models; MM: Mechanistic models; HM: Hybrid models.

479 **6. Current challenges and future directions**

480 After meticulously reviewing numerous research articles in multidisciplinary studies, we created a
481 comprehensive summary outlining the factors that have restricted the advancement of riverine GHG
482 models (Table 4). These factors are categorized into drawbacks in data availability and model
483 development, including specific knowledge gaps described per GHG. This compilation encompasses
484 implications and potential research directions that we strongly advocate for acknowledgment during
485 this epoch of prolific model development.

486 Table 4. Main drawbacks and potential research directions for riverine GHG modeling.

487

Findings	Implications	Potential research directions
Drawbacks in data availability and quality		
86% of modeling studies are carried at the site scale.	- Biochemical factors are vastly studied with data-driven models, however the interplay of these local factors at larger scales is unknown. Consequently, it remains uncertain if the factors identified as significant at the site scale also apply across the entire river network.	- More basin-scale studies are needed to depict the complex interactions of in-stream biochemical factors and basin-scale LULC and geomorphological heterogeneities, together with time-dependent hydrological relationships. For this purpose, mechanistic and hybrid models are suitable, especially hybrid models that can integrate available knowledge of in-stream biochemical controls with missing basin-scale processes.
	CO₂: - Current studies fail to define relationships of riverine CO ₂ evasion with basin-scale hydrological flow paths that transport DOC from organic-rich areas (e.g., croplands) and geogenic DIC to rivers (Gu et al., 2021; Liu et al., 2021; Stewart et al., 2022). Likely, transition areas from high to low slopes might support high CO ₂ effluxes (Rocher-Ros et al., 2019). As such, catchment land use, geology, geomorphology and alkalinity might be relevant for predicting CO ₂ emissions.	- More research is needed to explain the influence of catchment hydrology and geogenic C sources on riverine CO ₂ emissions. Moreover, these factors need to be characterized and integrated into riverine GHG models, to improve scaling-up efforts and facilitate more reliable regional and global estimates.
	CH₄: - Current studies are unable to constrain river hydrological connectivity with organic-rich areas that input dissolved CH ₄ (McGinnis et al., 2016; Siczko et al., 2016; Teodoru et al., 2015), or to determine the potential effects of hydrological exchanges on CH ₄ oxidation in the hyporheic zone (Villa et al., 2020). Moreover, basin geomorphology might drive patterns of sediment deposition in river channels, creating CH ₄ hotspots (Sawakuchi et al., 2014).	- Researchers must apply basin models to elucidate the potential effects of hydrology and hydrodynamics in creating hotspots of CH ₄ production and emissions.
	N₂O: - Catchment geology affects significantly the transport of N inputs from land surface to rivers, with low permeable aquifers	- It would be interesting to combine spatially distributed measurements of GHG fluxes and isotope analysis with hydrological

	<p>promoting complete denitrification, whereas permeable aquifers are linked to high N₂O effluxes (Cooper et al., 2017). Additionally case studies might miss to determine the overall effect of riparian zones in regional and global reports (Billen et al., 2020; Saggarr et al., 2013; Yao et al., 2020).</p>	<p>modeling. While flux and isotope measurements would help explain production pathways and sources (Ho et al., 2023), hydrological models would elucidate hydrological flow paths, depicting relationships between aquifer residence times and denitrification processes. This can be also applied to elucidate riparian buffer effects. The overall goal must be to characterize catchment geology, geomorphology and hydrology in order to conceptualize hyporheic and riparian denitrification rates, which are highly required for upscaling calculations.</p>
<p>77% of riverine GHG models are based on data collected over periods longer than a month.</p>	<p>- Manual measurements are vastly reported while automated measurements are missing. Consequently, datasets have low temporal resolution and are of short duration. This hampers the comprehensive investigation of factors that influence riverine GHG emissions at high temporal resolution or have long-term effects on riverine emissions. Consequently, global estimates fail to incorporate seasonal trends and elucidate feedback patterns.</p> <p>CO₂: - Short datasets might overlook important shifts in C sources to rivers, for instance the interconnection of rivers and floodplains during high-flow periods might lead to peaks in fluxes (Gu et al., 2021; Scofield et al., 2016), whereas during low-flow periods groundwater inputs might be of great importance (Aho et al., 2021; Hotchkiss et al., 2015; Saccardi and Winnick, 2021).</p> <p>CH₄: - Current datasets fail to capture seasonal fluctuations in CH₄ emissions pathways. For instance, low-flow periods are associated with hyporheic CH₄ generation (Sawakuchi et al., 2014; Villa et al., 2020; Wang et al., 2018). Additionally, sporadic events are also missing, such as abrupt changes in water levels promoting CH₄ ebullition (Ho et al., 2021). Spatial variability in inundated and air-exposed sediments might also play an important role missing in current datasets (Bednařík et al., 2019; Villa et al., 2020).</p> <p>N₂O: - With the current GHG data resolution, the study of seasonal hydrological flow paths causing the shift in N₂O production from the hyporheic zone to the water column is incomplete (Cornejo-D'ottone et al., 2019; Hu et al., 2021; Marzadri et al., 2017). It is therefore likely that datasets might not capture important N inputs from croplands during intensive agricultural periods (Gao et al., 2020; Yao et al., 2020).</p>	<p>- Automated and affordable data collection systems are needed. Moreover, standardized protocols and guidelines must be proposed for data collection in riverine systems which include biochemical, hydro- and geomorphological data (Ho and Goethals, 2022). This will provide compatible datasets, thereby enabling the analysis of large-scale relationships between factors, reducing data uncertainties in upscaling approaches.</p> <p>- Automated measurements would generate higher GHG data resolution, which must be combined with hydrological mechanistic models to explain system flow connections and dynamics. Until these automated systems become available, researchers must prioritize experimental designs with systematic temporal measurements, including standardized protocols, with a main goal: to integrate antecedent hydrological conditions into CO₂ evasion prediction.</p> <p>- In addition to combining automated GHG measurements with mechanistic models to explain catchment dynamics, CH₄ models require to associate advanced remote sensing methods to include the variability of inundated-exposed river areas. As currently, advanced methods are not able to provide such data at adequate resolutions, synergies between advanced and conventional methods are needed. While advanced methods provide long-term data at large scales, yet at coarse spatiotemporal resolution (Huang et al., 2019), conventional methods offer high resolution data at site-specific locations (Wilkinson et al., 2019).</p> <p>- Apart from automated measurement techniques and modeling, more isotope mixing models and mapping analysis are required to investigate potential nitrate sources to riverine systems, such as precipitation, soil N, chemical fertilizers, and manure and sewage (Barthel et al., 2022).</p>

Drawbacks in model development

Although data-driven models have yielded valuable insights into the dynamics of riverine GHG emissions, there is still room for improvement.

- Data-driven models mostly incorporated biochemical factors, whereas basin factors are missing. If data is limited, data-driven models have implicit difficulties to integrate spatial information (e.g., maps) with point measurements of GHGs without substantially losing information. For instance, LULC emissions, including deforestation and reforestation, are excluded in current figures of regional and global emissions. The few cases in which LULC factors are included used numerical values of percentage of the basin area, yet were unable to accurately capture the impact of LULC on riverine emissions.

- We recommend more mechanistic and hybrid models to target basin-scale simulations. Given the flexibility of hybrid models, they are able to integrate multiple drivers and data sources at diverse scales of analysis, for example, the integration of mechanistic models that simulate lateral exports from land-surface to rivers with data-driven models (existing) that simulate site-scale riverine GHG production and emissions. Such hybrid models can provide a holistic simulation of the system, especially at the basin level where the complex effects of LULC factors can be captured and models can be better constrained. Likewise, this flexibility of hybrid models makes it easy to update results when new data become available.

Large discrepancies exist within global estimates of riverine GHG emissions; yet, uncertainty ranges are overlooked in 56% of the cases.

- Overlooking uncertainty ranges hampers a comprehensive understanding of the estimates obtained from different approaches (different methodologies, assumptions, factors and data), because the potential errors, limitations and/or variability associated with each approach remain unknown.

- Incorporating uncertainty ranges must be mandatory for reporting purposes, as this facilitates more informed decision-making and helps in evaluating the robustness and effectiveness of the applied methodologies.

488

489 7. Conclusions

490 This review investigated the progress of riverine GHG models over the past 11 years. Three main model
491 types have been applied: data-driven, mechanistic, and hybrid models, among which data-driven models
492 have been predominated. These models mainly explore biochemical processes in site-scale studies,
493 while the role of geomorphological, hydrological factors, and land use types remains largely
494 overlooked. Limited insights and data prevent the existing models from simulating complex interaction
495 between influencing factors, which ultimately results in uncertainties in GHG global budgets. To
496 advance this field, we proposed an application framework for model selection in which advantages and
497 disadvantages of the model types regarding purposes, scales, and data availability can be found.
498 Moreover, we outlined the factors restricting model development, emphasizing the lack of basin-scale
499 studies to explain the interplay of river-land dynamics triggering riverine GHG emissions. We highlight
500 the need for automated data collection systems and improved experimental designs to systematically
501 gather GHG, biochemical, hydro- and geomorphological data, to cover these knowledge gaps.

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506 **Open Research**

507 Datasets for this research are available online at <https://data.mendeley.com/datasets/2tvm63grb7/1>

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