



# Measuring CH<sub>4</sub> Fluxes From Lake and Reservoir Sediments: Methodologies and Needs

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Accurately quantifying the diffusive flux of CH<sub>4</sub> between sediments and the overlying water column is crucial when constructing CH<sub>4</sub> budgets in lakes and reservoirs. Although a variety of *ex situ* and *in situ* techniques exist for determining this flux, no reviews have provided a comprehensive, comparative overview of these approaches or discussed implications of measurement method on flux estimation. Here, we critically review methods applied in 163 peer-reviewed studies to estimate diffusive CH<sub>4</sub> fluxes from lake sediments, including sediment incubations, benthic chambers, and modeling approaches applied in the sediment or water column. For each method, we summarize the approach, discuss limitations and advantages, and summarize published comparisons between different methods. In addition, we examine how method limitations have likely shaped knowledge gaps in current understanding of lake CH<sub>4</sub> dynamics. Finally, we call for the development and application of new methods, along with additional testing and intercomparison of existing methods, in order to advance understanding of lake CH<sub>4</sub> fluxes.

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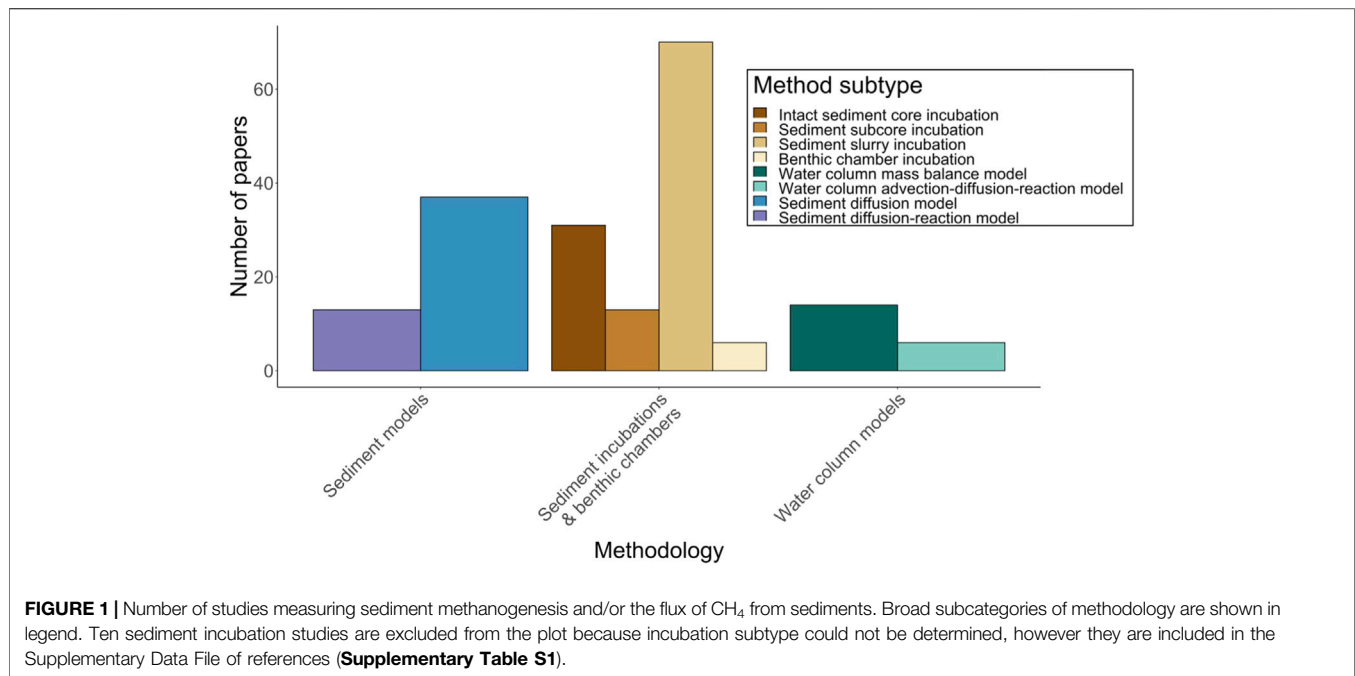
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## 1 INTRODUCTION

Lakes and reservoirs are collectively responsible for an estimated 9%–27% (70–175 Tg) of global methane (CH<sub>4</sub>) emissions annually (Rosentreter et al., 2021). The majority of CH<sub>4</sub> in these ecosystems is thought to be produced in sediments (Peeters et al., 2019), where high organic carbon availability and anoxic conditions favor methanogenesis (Bastviken, 2009). Methane in sediments can then cross the sediment-water interface (SWI) via diffusion or ebullition (bubbling) into the water column, from whence it may ultimately reach the atmosphere. Typically, up to 50% of CH<sub>4</sub> emissions from lakes and reservoirs occurs via diffusion rather than ebullition (Bastviken et al., 2004; Bastviken et al., 2008; Deemer et al., 2016). Although bubbling from sediments is certainly an important pathway for CH<sub>4</sub> transport (DelSontro et al., 2010; Beaulieu et al., 2016), here we focus on the diffusive flux of CH<sub>4</sub> from sediments, which is a critical component of understanding lentic greenhouse gas cycling and emissions.

Methane diffusion from lake and reservoir sediments is highly variable in both space and time. In a synthesis of measurements from 23 lakes and reservoirs, diffusive CH<sub>4</sub> fluxes across the SWI varied up to three orders of magnitude across and within systems (Adams, 2005). The wide variability in rates is due, in part, to physical and biological factors that influence rates of CH<sub>4</sub> production (methanogenesis) and oxidation (methanotrophy) within sediments, as well as controls on the diffusive transport of CH<sub>4</sub> out of sediments. For example, greater sediment CH<sub>4</sub> production rates have been linked to higher lake productivity (West et al., 2016; D'Ambrosio and Harrison, 2021), warmer temperatures (Duc et al., 2010), organic matter availability (Berberich et al., 2019; Praetzel



et al., 2020), and anoxic conditions above and within sediments (Liikanen and Martikainen, 2003; Huttunen et al., 2006). Methane oxidation, which can consume significant amounts of CH<sub>4</sub> at the SWI or deeper in the sediment profile, is controlled by the availability of CH<sub>4</sub> and electron acceptors such as oxygen, nitrate, iron oxides, manganese oxides, and sulfate (Kuivila et al., 1988; Clayer et al., 2016; van Grinsven et al., 2020). The diffusive release of CH<sub>4</sub> out of sediments is, in turn, influenced by the net supply of CH<sub>4</sub> (i.e., production—oxidation), and can be affected by conditions and processes above sediments such as the CH<sub>4</sub> concentration in water overlying sediments, oxidation at the sediment surface (Bosse et al., 1993; Rolletschek, 1997), near-bed turbulence (D'Ambrosio, 2022), surface waves (Hofmann et al., 2010), and sediment resuspension (Bussmann, 2005).

The wide range of methods used to measure the CH<sub>4</sub> diffusion from sediments may play an important role in the large variability in reported fluxes. Approaches such as sediment incubations, sediment models, and water column models have differing spatiotemporal resolutions, sampling requirements, and limitations, all of which influence resulting flux measurements. Although explicit comparisons of multiple approaches for measuring CH<sub>4</sub> emission across the air-water interface have been extensive (St. Louis et al., 2000; Schubert et al., 2012; Deemer et al., 2016), there is no similar synthesis of methods for measuring for CH<sub>4</sub> diffusion across the SWI. A critical examination of methodologies used to estimate this flux is needed to: 1) understand the advantages and disadvantages of current approaches; 2) recognize how limitations of common techniques shape gaps in our current view of CH<sub>4</sub> dynamics in lakes and reservoirs; and 3) identify future method developments needed to advance understanding of the supply and transport of CH<sub>4</sub> in lacustrine systems.

Here, we critically review methodologies from 163 studies reporting CH<sub>4</sub> diffusive flux and/or methanogenesis in lake or reservoir sediments (references provided in the **Supplementary Data File**). From these studies, we classify typical methods for measuring this flux into three broad categories: sediment incubations and benthic chambers, modeling approaches applied in the sediment, and modeling approaches applied in the water column. We summarize each approach, describe the utility, advantages, and disadvantages for each, and examine previous studies explicitly comparing measurements from multiple techniques. Finally, we discuss how existing approaches have shaped knowledge gaps in lacustrine CH<sub>4</sub> cycling, and we provide recommendations for future methodological developments needed to improve the quantification of sediment CH<sub>4</sub> flux and its role in lake and reservoir carbon budgets.

## 2 METHODOLOGIES

### 2.1 Sediment Incubations & Benthic Chambers

#### 2.1.1 Approach Summary

Sediment incubations have historically been the most common approach for estimating diffusive CH<sub>4</sub> fluxes from lake sediments (**Figure 1**). Incubation-based estimates can be categorized as *ex situ* sediment incubations, typically performed in the lab, or *in situ* incubations, usually performed by deploying benthic chambers to the lakebed.

*Ex situ* incubations are the most common and measure CH<sub>4</sub> flux *in vitro* from intact sediment cores, subcores, or sediment-water slurries (**Figure 1**). Intact cores can be collected via piston, gravity, or box coring, and may be segmented into smaller

subcores prior to incubation (Mudroch and MacKnight, 1991). Slurries are subsampled from a core or sediment grab and then homogenized prior to incubation, often through mixing with lake water or deionized water. Sediment cores, subcores, or slurries are placed in incubation chambers, such as acrylic tubes for cores (Sturm et al., 2014) or glass vials for subcores or slurries (Wagener et al., 1990), then sealed with gastight stoppers. Vial headspaces above sediments may be filled partially or completely with lake water or deionized water. Anoxic or oxic conditions are then established in the chambers prior to incubation, depending on the study objectives. Anoxic incubations are often flushed and evacuated with an inert gas (e.g., N<sub>2</sub> or He; Liikanen et al., 2002a; Praetzel et al., 2020), whereas oxic incubations use air (Sweerts et al., 1991; Chmiel et al., 2016). Incubations usually take place either in a temperature-controlled water bath (Kelly and Chynoweth, 1981) or at *in situ* depth in the water column (Algesten et al., 2005). Core incubation chambers are often, although not always, equipped with a magnetic stirrer that gently mixes water above the core without disturbing the SWI (Frenzel et al., 1990; Leal et al., 2007). Some core incubations also use constant flow-through systems that pump lake water from an outside reservoir into the overlying water of cores. This maintains oxic or anoxic conditions throughout the incubation and prevents the accumulation or depletion of compounds that may alter CH<sub>4</sub> production or consumption rates (Liikanen et al., 2002d; Bussmann, 2005).

A small subset of incubations is performed *in situ* using a benthic chamber approach (sometimes called a static chamber; **Figure 1**). Benthic chambers are open-bottomed boxes or cylinders constructed of acrylic, steel, or plastic, and are implanted several centimeters into the sediment for *in situ* incubation (Viollier et al., 2003). Chambers can be installed manually with scuba divers (Duchemin et al., 1995) or using a benthic lander, which is designed to implant the chamber remotely after being lowered to a lake bottom (Devol, 1987; Kuivila et al., 1988; Urban et al., 1997; Maerki et al., 2009). Chamber designs often include pumps or paddles that continuously circulate water within a chamber throughout the incubation (Devol, 1987; Colas et al., 2021).

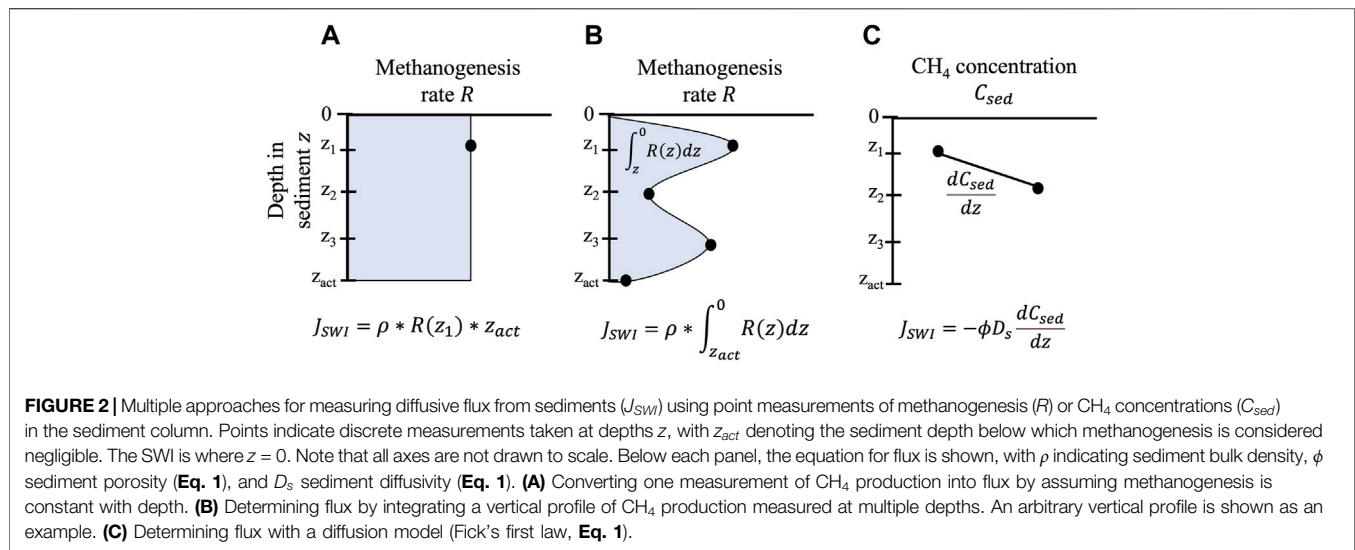
Incubation duration varies substantially, in part as a function of technique. *Ex situ* incubations typically last days (Jones et al., 1982; Hershey et al., 2015) to weeks (Liikanen et al., 2002b; Dan et al., 2004); however some can last months (Martinez-Cruz et al., 2017; Valle et al., 2018) to years (Nozhevnikova et al., 2007; Isidorova et al., 2019). Benthic chamber deployments are usually shorter, lasting from hours to a day (Kuivila et al., 1988; Urban et al., 1997). Incubations are generally sampled at multiple time points to determine CH<sub>4</sub> concentrations, with the rate of change in concentrations over time used to calculate fluxes. For *ex situ* incubations, headspace gas or water overlying sediment can be sampled using syringes, or flow from an external reservoir may be used to push water out of the incubation chamber to be sampled. For benthic chambers, samples of water are extracted either manually via tubing/pumps to the surface (Yavitt et al., 1992; Duchemin et al., 1995) or automatically with programmable syringes (Devol, 1987; Kuivila et al., 1988; Urban et al., 1997; Maerki et al., 2009).

Samples collected during incubations are analyzed for CH<sub>4</sub> concentration using gas chromatography or laser absorption spectrometry. Samples in the gas phase can be analyzed immediately. Samples in liquid phase are first prepared using headspace equilibration, a technique which injects an inert gaseous headspace (often ultrapure helium), and then agitates the water in order to equilibrate dissolved CH<sub>4</sub> with the gaseous phase prior to analysis (McAuliffe, 1971; Magen et al., 2014). Henry's law is then used to determine the amount of CH<sub>4</sub> originally present in the liquid phase.

The rate at which CH<sub>4</sub> is produced in the incubation over time is used to estimate sediment diffusive flux. In benthic chambers, intact core, and some subcore incubations, the production rate is typically expressed in areal units (i.e., CH<sub>4</sub> produced per m<sup>2</sup> of core horizontal cross-sectional area incubated) and therefore assumed to be equivalent to diffusive CH<sub>4</sub> flux across the SWI ( $J_{SWI}$ ). In slurry and some subcore incubations, production rates are typically measured in gravimetric or volumetric units (i.e., CH<sub>4</sub> produced per liter or gram of dried sediment). Volumetric or gravimetric production rates can be converted to a flux by assuming rates are constant over a specified sediment depth of active methanogenesis ( $z_{act}$ ), then multiplying by the sediment bulk density ( $\rho$ ). In some cases, one point measurement of CH<sub>4</sub> production is assumed to be representative of the active zone of methanogenesis in the sediment profile (**Figure 2A**; West et al., 2016; Berberich et al., 2019). In other cases, vertical changes in methanogenesis are accounted for by integrating measurements of gravimetric or volumetric CH<sub>4</sub> production made at multiple depths throughout the sediment profile (**Figure 2B**; Murase and Sugimoto 2002; Liu et al., 2019).

### 2.1.2 Approach Advantages

Incubations and benthic chambers provide a highly controlled, customizable environment for researchers to manipulate environmental conditions, and thus they are often used to evaluate drivers of CH<sub>4</sub> processing (**Table 1**). For example, previous incubation studies have investigated how sediment CH<sub>4</sub> flux and/or methanogenesis rates respond to shifting temperatures (Zeikus and Winfrey, 1976; Duc et al., 2010), nutrient concentrations (Stadmark and Leonardson, 2007; Rodriguez et al., 2018), organic matter deposition (West et al., 2012; Grasset et al., 2018), oxygen availability (Liikanen et al., 2002c; Liikanen and Martikainen, 2003), and supply of electron acceptors likely to be involved in CH<sub>4</sub> oxidation (Karvinen et al., 2015; Rissanen et al., 2017). These experimental manipulations are impractical or impossible to apply in most benthic chamber experiments, yet they are important for identifying which environmental drivers exert control on methanogenesis and methanotrophy within lake sediments (Bastviken, 2009; Borrel et al., 2011). Additionally, incubations are unique in that they can be used to partition out gross rates of CH<sub>4</sub> production and oxidation, rather than net rates. This is usually done by injecting the incubation with isotopically-labeled methanogenic or methanotrophic substrate (e.g., <sup>14</sup>C-labeled acetate/bicarbonate or <sup>14</sup>CH<sub>4</sub>, respectively) and tracking the radioactivity and concentration of CH<sub>4</sub> in the incubation over time (Kuivila et al., 1989; Nüsslein et al., 2001; Pimenov et al., 2010).



**TABLE 1** | Summary of procedures, recommended applications, and limitations of each method used to measure diffusive CH<sub>4</sub> flux from lake sediments.

Methodology	Procedure	Recommended Applications	Limitations
Sediment incubations & benthic chambers	Measure CH <sub>4</sub> accumulation or consumption in benthic chambers or <i>ex situ</i> incubations of intact cores, subcores, or sediment slurries	<ul style="list-style-type: none"> <li>- Evaluate effects of potential drivers on relative rates of sediment flux</li> <li>- Compare relative fluxes between multiple sites or time periods</li> </ul>	<ul style="list-style-type: none"> <li>- Possible stimulation/inhibition of methanogenesis/methanotrophy</li> <li>- Sediment disturbance artifacts</li> <li>- Isolation from water column and BBL processes, altered physical mixing</li> </ul>
Sediment models	Estimate flux using profile of CH <sub>4</sub> concentrations in sediment column	<ul style="list-style-type: none"> <li>- Diffusion models: Fast, simple flux estimates to compare across study sites or time periods</li> <li>- Diffusion-reaction models: Depth-specific information on zones of sediment methanogenesis &amp; methanotrophy</li> </ul>	<ul style="list-style-type: none"> <li>- Error associated with concentration gradient estimation near SWI</li> <li>- Excludes sediment surface processes</li> <li>- Sediment disturbance artifacts</li> </ul>
Water column models	Estimate flux based on CH <sub>4</sub> concentration profiles in the water column	<ul style="list-style-type: none"> <li>- Mass balance models: Construct lake-wide CH<sub>4</sub> budget</li> <li>- Advection-diffusion-reaction models: Examine long-term (e.g., seasonal) changes in lake-wide CH<sub>4</sub> cycling</li> </ul>	<ul style="list-style-type: none"> <li>- Little information on drivers behind CH<sub>4</sub> dynamics</li> <li>- Assumptions of spatial homogeneity</li> <li>- Potentially data-intensive</li> </ul>

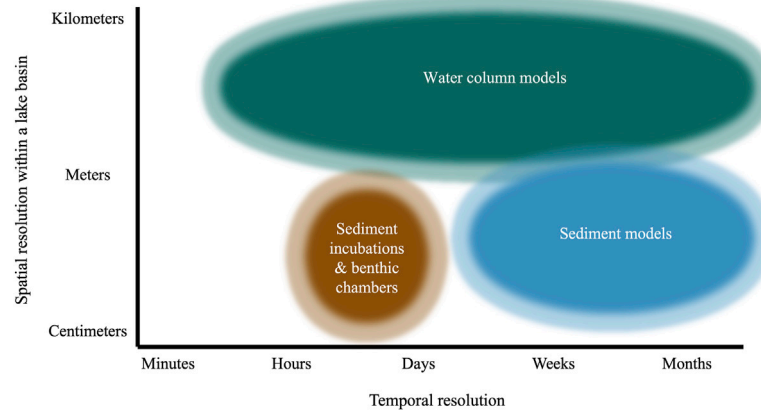
Incubations are also popular in part due to their simplicity, reproducibility, and relatively simple sampling requirements. Benthic chambers and/or *ex situ* incubation containers are generally constructed from low-cost materials and incubations can be repeated with sediments from (or at) multiple sampling locations, time points, and study systems (**Table 1**). Furthermore, CH<sub>4</sub> flux from an incubation can be determined from just a few samples of CH<sub>4</sub> concentrations over time, typically just a few hours to a day, or less. Other approaches, such as water column models (**Section 2.3**), often require significantly more data such as sediment ebullition estimates, temperature profiles in the water column, and/or CH<sub>4</sub> oxidation measurements.

Lastly, although here we focus on methods for measuring CH<sub>4</sub> diffusion from sediments, an advantage of incubations is that some set-ups can be modified to measure diffusion and ebullition simultaneously (Liikanen et al., 2002c). While a full discussion of

these incubation designs is beyond the scope of this review, the capacity to measure diffusive and ebullitive flux from sediments can be advantageous given bubbling is an important CH<sub>4</sub> transport pathway in many lakes and reservoirs (DelSontro et al., 2011, 2015).

### 2.1.3 Approach Limitations

An important limitation of incubations and benthic chambers is that they provide a spatiotemporal snapshot of CH<sub>4</sub> diffusion from sediments. Rates from this method are relevant to the sediment incubated, which typically has a surface area of a few square centimeters to a square meter or less (**Figure 3**). Assumptions that flux estimates based on incubations are applicable lake-wide are questionable, given previous work has found significant differences in sediment CH<sub>4</sub> production and fluxes between profundal and littoral sites (Liikanen et al., 2003;



**FIGURE 3** | Conceptual map showing the typical temporal and spatial resolution of common methodologies included in **Figure 1**. Temporal resolution represents the typical time period over which measurements from each method are made or averaged over. Spatial resolution indicates the spatial scale over which measurements from each method are made or averaged across within an individual lake basin.

Li et al., 2021) or between locations with different organic matter inputs (Berberich et al., 2019; Praetzel et al., 2020). Rate estimates based on incubations also represent a flux averaged only over the incubation duration, usually hours or days (**Figure 3**). Incubations therefore do not generally account for temporal shifts across seasons (Nüsslein and Conrad, 2000; Itoh et al., 2015) or during lake stratification and mixing (Liikanen et al., 2002b; Vachon et al., 2019). Additionally, volumetric or gravimetric CH<sub>4</sub> production rates measured in incubations are often converted into a flux by assuming rates are constant over a specified active layer depth (**Figure 2A**). This assumption runs counter to many studies demonstrating that methanogenesis changes significantly with lake sediment depth (Chan et al., 2005; Lofton et al., 2015; Yang et al., 2017; Praetzel et al., 2020).

*Ex situ* incubations and benthic chambers also largely isolate sediments from lake-scale processes that may influence flux across the SWI (**Table 1**). For example, internal waves can drive fluctuations in turbulence and mixing in the boundary layer overlying sediments (Henderson, 2016). These fluctuations in near-bed conditions have been demonstrated to influence fluxes of oxygen, nitrate, and CH<sub>4</sub> across the SWI on hourly to daily time scales (Lorke et al., 2003; Brand et al., 2008; Bryant et al., 2010; D'Ambrosio, 2022). Internal waves can also drive redox changes at the SWI, which may influence within-sediment rates of methanogenesis and methanotrophy (Frindte et al., 2013; Frindte et al., 2015). The effects of such boundary layer and surface sediment dynamics on flux are not considered within traditional incubation setups. Furthermore, although surface waves and sediment resuspension have also been tied to variations in diffusive CH<sub>4</sub> release from lake sediments (Bussmann, 2005; Hofmann et al., 2010), only one study has simulated the effects of resuspension in their incubation microcosm design (Bussmann 2005).

For *ex situ* incubations specifically, sampling artifacts from sediment collection and preparation are important to consider (**Table 1**). Previous work has posited that sediment slurring can

stimulate methanogenesis (Kelly and Chynoweth, 1980; Frenzel et al., 1990) or inhibit methanotrophy (Su et al., 2019) compared to *in situ* rates (**Table 1**). In contrast, intact and subcore incubations avoid slurring in order to preserve sediment layering and structure, in part because methanogenesis and methanotrophy change significantly with sediment depth (Chan et al., 2005; Martinez-Cruz et al., 2018). However, in gas-rich sediments, stratigraphy can be significantly disturbed by core sampling due to changes in hydrostatic pressure and temperature during core withdrawal (Düeck et al., 2019b). It is similarly challenging to collect cores in soft-bottom sediments without altering sediment structure (Blomqvist, 1991). Given these limitations, incubations are best suited for measuring relative (rather than absolute) rates of diffusive CH<sub>4</sub> release from sediments (**Table 1**).

Lastly, fluxes estimated with incubations are sensitive to incubation duration because conditions within the chamber can change over time. For example, oxygen may be depleted over the course of benthic chamber incubations (Duchemin et al., 1995), which may affect rates of CH<sub>4</sub> production and oxidation given the sensitivity of methanogens and methanotrophs to oxygen availability (Borrel et al., 2011; Thottathil et al., 2019). Such oxygen depletion can be avoided by limiting the duration of benthic chamber deployments (Urban et al., 1997) and by monitoring oxygen concentrations in benthic chambers. For *ex situ* incubations, an initial lag phase of CH<sub>4</sub> production may also occur as methanogens or methanotrophs acclimate to vial conditions and/or compete with other microorganisms present (Torres et al., 2011; Grasset et al., 2021). However, lag phases are not observed in all incubations (Chan et al., 2005; Valle et al., 2018; Li et al., 2020). Furthermore, CH<sub>4</sub> production may decrease over time in long-term incubations (Isidorova et al., 2019), likely due to the gradual depletion of methanogenic precursors such as acetate. Consequently, *ex situ* incubations that are shorter than a typical lag phase or long enough to deplete methanogenic substrates may underestimate rates of CH<sub>4</sub> release from sediments.

## 2.2 Sediment CH<sub>4</sub> Models

### 2.2.1 Approach Summary

Modeling CH<sub>4</sub> in the sediment column is a common method for estimating CH<sub>4</sub> flux across the SWI of lakes and reservoirs (Figure 1). Sediment models for estimating CH<sub>4</sub> fluxes across the SWI can be considered as falling into one of two main categories: 1) diffusion models, which estimate CH<sub>4</sub> flux solely based on molecular diffusion; and 2) diffusion-reaction models, which also account for the effects of microbial reactions and/or bioirrigation on CH<sub>4</sub> flux (Figure 1). In the former case, flux is estimated between two discrete depths in the sediment column using Fick's first law of diffusion (Figure 2C):

$$J = -\phi D_s \frac{dC_{sed}}{dz} \quad (1)$$

where  $J$  is CH<sub>4</sub> flux in the sediment,  $\phi$  is sediment porosity,  $D_s$  is diffusivity of CH<sub>4</sub> in the sediment, and  $\frac{dC_{sed}}{dz}$  is the CH<sub>4</sub> concentration gradient across sediment depth  $z$  (Berner, 1980). For  $J$  to be representative of flux across the SWI ( $J_{SWI}$ ), the CH<sub>4</sub> concentration gradient should be measured as close to the SWI as possible. Sediment porosity is either measured directly or estimated based on literature values, which typically range from 0.8 to 0.99 in lake sediments (Frenzel et al., 1990; Carignan and Lean, 1991; Langenegger et al., 2019). Sediment diffusivity  $D_s$  is determined by correcting the molecular diffusivity of CH<sub>4</sub> in pure water at *in situ* temperature ( $D_0$ ) for sediment tortuosity using the relationship  $D_s = D_0 \phi^2$ . Another approach corrects diffusivity using the relationship  $D_s = \frac{D_0}{\Theta^2}$ , where tortuosity ( $\Theta^2$ ) is estimated as a function of sediment porosity (Lerman, 1979; Berner, 1980). Lastly, the diffusivity of low-solubility compounds such as CH<sub>4</sub> may be increased by the presence of gas voids in the sediment column; in these cases,  $D_0$  can be corrected for sediment porosity and volumetric water content ( $W_c$ ) using the relationship  $D_s = D_0 \frac{W_c^{7/3}}{\phi^2}$  (Flury et al., 2015).

Beyond molecular diffusion considered in Eq. 1, processes such as bioirrigation or microbial reactions may also affect CH<sub>4</sub> distribution in sediments. A more comprehensive diffusion-reaction model can account for how these processes work in concert with molecular diffusion to influence CH<sub>4</sub> concentrations in the sediment. Normally, such a diffusion-reaction model is applied at many discrete vertical layers in the sediment column, rather than the two discrete depths considered in the diffusion model of Eq. 1. First, the effect of molecular diffusion on CH<sub>4</sub> distribution throughout the sediment column is considered, according to Fick's second law of diffusion:

$$\frac{dC_{sed}}{dt} = \frac{d}{dz} \left( \phi D_s \frac{dC_{sed}}{dz} \right) \quad (2)$$

where  $t$  is time. Second, an additional term  $R$  is commonly included to account for how net microbial CH<sub>4</sub> production and/or oxidation in each sediment layer affect the distribution of CH<sub>4</sub> (Rahalkar et al., 2009; Clayer et al., 2018):

$$\frac{dC_{sed}}{dt} = \frac{d}{dz} \left( \phi D_s \frac{dC_{sed}}{dz} \right) + R \quad (3)$$

$R$  can be solved for numerically or analytically. A popular approach involves using differential equation-solving software, such as PROFILE (Berg et al., 1998) or REC (Lettmann et al., 2012), to numerically solve for  $R$  in each layer, given inputs of measured sediment CH<sub>4</sub> concentration profiles.

In some cases, an additional term is added to Eq. 3 to account for the effects of bioirrigation on CH<sub>4</sub> transport (Bartosiewicz et al., 2016, 2021; Clayer et al., 2016). Bioirrigation and bioturbation describe how biologically driven water circulation through sediments and sediment mixing, respectively, affect solute transport between sediment porewater and the overlying water (Kristensen et al., 2012). Burrows serve as conduits between the sediment porewater and the overlying water, creating a concentration gradient that drives additional diffusive transport of CH<sub>4</sub>:

$$\frac{dC_{sed}}{dt} = \frac{d}{dz} \left( \phi D_s \frac{dC_{sed}}{dz} \right) + \phi \alpha (C_0 - C_{sed}) + R \quad (4)$$

where  $\alpha$  is the intensity of bioirrigation and  $C_0$  is the CH<sub>4</sub> concentration measured at the SWI. Estimates of  $\alpha$  for CH<sub>4</sub> in lake sediments can be made based on sediment diffusivity, depth below the SWI, and the radius of the tubes formed by burrowing animals (Boudreau, 1984; Clayer et al., 2016). Lastly, assuming steady state conditions reduces Eq. 4 to:

$$0 = \frac{d}{dz} \left( \phi D_s \frac{dC_{sed}}{dz} \right) + \phi \alpha (C_0 - C_{sed}) + R \quad (5)$$

From Eq. 5, there are multiple routes to calculate a flux across the SWI. Both PROFILE and REC solve for a depth profile of  $R$  in volumetric units, which can be depth-integrated into an flux across the SWI (Figure 2B; Norđi et al., 2013; Bartosiewicz et al., 2016; Clayer et al., 2016). Alternatively, another technique assumes a constant rate for  $R$  in between the SWI and the lower end of the diffusion-reaction zone in the sediment column ( $z_{max}$ , i.e., where the porewater CH<sub>4</sub> concentration remains unchanged with depth). Using these assumptions, Eq. 3 can be solved analytically for flux across the SWI (Epping and Helder, 1997; Müller et al., 2003):

$$J_{SWI} = \phi \sqrt{2RD_s (C_0 - C_{max})} \quad (6)$$

where  $C_{max}$  is the CH<sub>4</sub> concentration at  $z_{max}$  based on measured porewater CH<sub>4</sub> concentration profiles (Pasche et al., 2011; Müller et al., 2012; Steinsberger et al., 2017, 2019).

All sediment models covered here require measurements of CH<sub>4</sub> concentrations in the sediment porewater, which can be obtained a variety of ways. The simplest technique is collecting an intact sediment core, subsampling into core slices by depth, then measuring CH<sub>4</sub> concentration in each subsample using headspace equilibration (Section 2.1.1). Another technique measures CH<sub>4</sub> concentrations using a small probe inserted at various depths in the sediment core (Bussmann and Schink, 2006). Here, methane from the sediment diffuses across the permeable membrane of a probe inserted at a specific sediment depth, and a constant flow of carrier gas to the probe flushes the CH<sub>4</sub> to a gas chromatograph for

determination of concentration. Other approaches rely on the extraction of sediment porewater, which can be analyzed for CH<sub>4</sub> concentration with headspace equilibration (**Section 2.1.1**). Porewater can be extracted with squeezers, metal or plastic devices that use pistons or gas pressure to compress sediment and force out interstitial porewater. Porewater from different depths in a core may be extracted using squeezers on various core subsections (Reeburgh, 1967) or by using squeezers built to compress entire cores and fitted with ports at various sampling depths (Jahnke, 1988). A recently developed technique involves using a modified squeezer to subsample sediment from different depths into copper tubing, then centrifuging aliquots from the tubes to extract the porewater (Tyroller et al., 2016). Alternatively, small, porous Rhizon tubes can be inserted into different depths of the sediment. Porewater is then drawn into the tubes using suction from an attached vacuum pump, syringe, or evacuated test tube. Rhizons were originally developed for use in terrestrial soils, but have subsequently been adapted to sample porewater in saturated sediments from aquatic systems (Seeberg-Elverfeldt et al., 2005).

Porewater may also be sampled without collecting a core by deploying a “peeper” directly into the sediment (Hesslein, 1976). Peepers are acrylic samplers containing an array of small wells spaced several centimeters apart in the vertical. Sampling wells are filled with anoxic water and covered with a permeable membrane made of cellulose-acetate or polysulfone. Peepers are typically left in the sediment for several weeks to equilibrate via dialysis, then sampled and analyzed for CH<sub>4</sub> using headspace equilibration.

### 2.2.2 Approach Advantages

Sediment models are highly customizable depending on the lake system and level of sampling effort required. For example, a simple diffusion model (**Eq. 1**) to estimate flux requires sample collection as basic as measuring one CH<sub>4</sub> concentration gradient close to the SWI. Due to these relatively simple data requirements, sediment diffusion models are often employed as a fast, easy way to compare fluxes across multiple lakes (Adams, 2005; Huttunen et al., 2006), sampling sites (Zhang et al., 2020; Li et al., 2021), or time periods (**Table 1**; Rolletschek 1997).

In contrast, more sophisticated diffusion-reaction models (**Eqs 3–5**) can be constructed to account for the effects of microbial CH<sub>4</sub> production, oxidation, bioturbation, and/or bioirrigation on CH<sub>4</sub> transport out of sediments. Although these more comprehensive models require detailed sampling of CH<sub>4</sub> concentrations in the sediment column, their implementation can be made easier with freely available software used to solve the differential equations involved, such as PROFILE or REC (Berg et al., 1998; Lettmann et al., 2012). Diffusion-reaction models also can be used to solve for depth profiles of methanogenesis and methanotrophy in the sediment, which are powerful tools for examining the locations, controls, and microbial communities involved in CH<sub>4</sub> supply and transport (**Table 1**). For example, comparing rates of CH<sub>4</sub> production and oxidation in the sediment profile with observed fluxes across the SWI can

highlight the importance of methanotrophy in substantially reducing CH<sub>4</sub> release into the hypolimnion (Koschorreck et al., 2008; Rahalkar et al., 2009; Norđi et al., 2013).

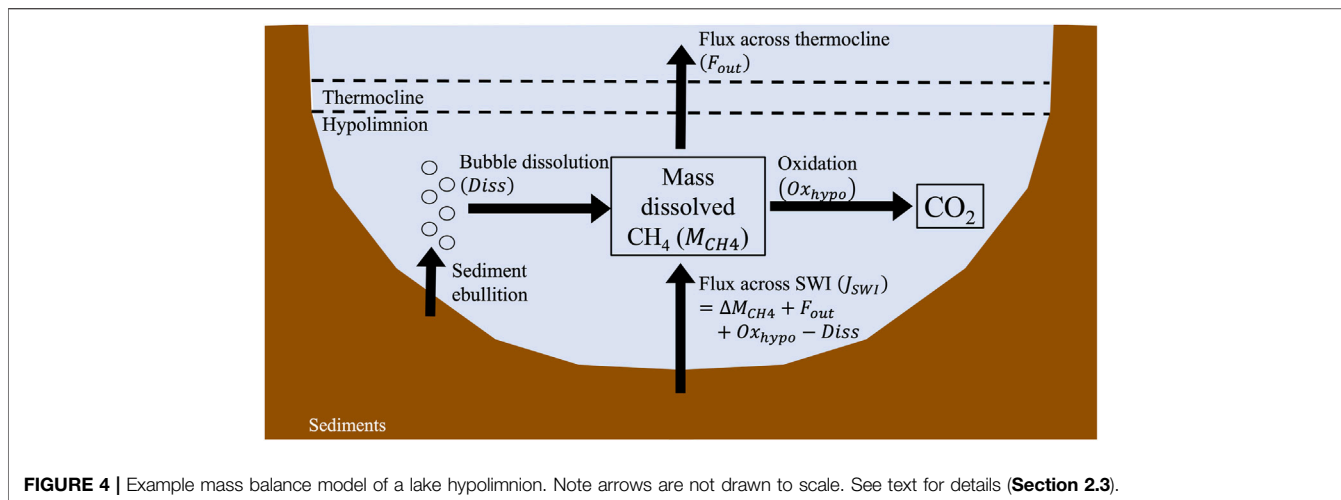
### 2.2.3 Approach Limitations

Estimates from sediment modeling rely on porewater CH<sub>4</sub> concentrations (**Eq. 1**), which are the net result of equilibration with the surrounding sediment column and overlying water. Measurements are therefore only representative of the sediment sampled (usually centimeters to a meter or less) and its close surroundings (likely several meters; **Figure 3**). Accordingly, assumptions that measurements from sediment models characterize fluxes lake-wide should be interpreted with caution, given the significant spatial variability in sediment CH<sub>4</sub> dynamics across different sites within the same lake (**Section 2.1.3**).

Moreover, flux estimates from sediment models should be considered an average across weeks to months (**Figure 3**), the time scale on which equilibration of CH<sub>4</sub> concentrations in sediments typically occurs (Harper et al., 1997). Therefore, similar to incubations, these estimates do not account for short-term fluctuations in processes that may influence CH<sub>4</sub> diffusion across the SWI (**Section 2.1.3**). Unless modeling is repeated across multiple dates and sites, changes across seasons due to changing temperature, deposition of organic matter, or other environmental factors (Thebrath et al., 1993; Murase and Sugimoto, 2002; Yang et al., 2018) are also not considered. This seasonal variability may be particularly pronounced in lakes that thermally stratify and develop seasonal hypolimnetic hypoxia, as the resulting shifts in oxygen availability to surface sediments can profoundly influence sediment CH<sub>4</sub> oxidation and flux (Liikanen et al., 2003).

Typical techniques for measuring CH<sub>4</sub> concentrations in porewater, required for sediment modeling, also come with logistical hurdles and sampling artifacts (**Table 1**). Peepers can be challenging to deploy, since they require 1–3 weeks for equilibration and may need to be installed by scuba divers (Hesslein, 1976; Bufflap and Allen, 1995). Gas loss is a common sampling artifact during sediment core collection (Paull et al., 2000), peeper extraction (Adams, 2005), and headspace equilibration (Tyroller et al., 2016), resulting in underestimated CH<sub>4</sub> concentrations (and therefore inaccurate gradients). Exposure of sediment cores and/or peepers to oxygen during collection (Bufflap and Allen, 1995) is another potential problem that may stimulate methanotrophy and therefore influence sampled concentrations. Applying noble gas tracer (Tyroller et al., 2016) or freeze coring (Dück et al., 2019a) methods to analyze CH<sub>4</sub> concentrations in sediments may address some of these sampling artifacts.

In particular, sediment diffusion models (**Eq. 1**) are inherently limited by the spatial resolution of porewater sampling. The CH<sub>4</sub> gradient used in **Eq. 1** should be measured as close to the SWI as possible, because CH<sub>4</sub> concentrations can change rapidly within just a few millimeters of the sediment surface (Bussmann and Schink, 2006). However, accurately sampling CH<sub>4</sub> concentrations close to the SWI can be challenging with conventional porewater



**FIGURE 4** | Example mass balance model of a lake hypolimnion. Note arrows are not drawn to scale. See text for details (**Section 2.3**).

measurement techniques (**Table 1**). For example, peeper samplers are typically limited to a vertical resolution of a centimeter or more (Harper et al., 1997), making it difficult to accurately measure steep gradients near the SWI. Furthermore, the surface sediments where CH<sub>4</sub> gradients are steepest can be inadvertently lost when using some conventional coring techniques (Shirayama and Fukushima, 1995; Ostrovsky, 2000), especially in soft, unconsolidated sediments (Blomqvist, 1991). To resolve this issue, CH<sub>4</sub> gradients at the SWI are sometimes calculated based on concentrations in the rest of the porewater profile using linear regression or exponential models (Schubert et al., 2011; Maeck et al., 2013; Zhang et al., 2020). Alternatively, a CH<sub>4</sub> gradient measured between the overlying water and the uppermost sampled point in the sediment profile may be a suitable substitute for the SWI gradient (Klump et al., 2009).

## 2.3 Water Column Modeling

### 2.3.1 Approach Summary

The diffusion of CH<sub>4</sub> from sediments is an important component of many models simulating CH<sub>4</sub> dynamics in all or part of the lake water column. Many water column models rely on other methods described in this paper, such as incubations or sediment modeling (**Sections 2.1, 2.2**), to estimate the flux of CH<sub>4</sub> across the SWI and use the measured value as model input. In this section, we focus on water column modeling approaches that estimate CH<sub>4</sub> diffusive flux from sediments through mathematical expressions within the model structure, rather than previously described methods. These water column models can be classified into two groups: 1) mass balances used to calculate CH<sub>4</sub> mass quantities in the water column; and 2) advection-diffusion-reaction models used to simulate CH<sub>4</sub> concentrations in the water column (**Figure 1**).

Mass balances are the most common water column model used to quantify CH<sub>4</sub> diffusion from sediments (**Figure 1**). Researchers applying a mass balance approach create a conceptual model of the sources, sinks, and transformations affecting the mass of CH<sub>4</sub> present in the water column. Most often, this mass balance is focused on the lake hypolimnion

during thermal stratification. The exchange of gases and solutes between the epilimnion and hypolimnion is significantly slowed throughout the stratification period, often resulting in CH<sub>4</sub> accumulation below the thermocline (Eckert and Conrad, 2007). The hypolimnion during stratification can therefore be thought of as a largely closed system with sediments as the primary source of accumulating CH<sub>4</sub>. As an example, a simple conceptual model outlining the sources, sinks, and transformations of CH<sub>4</sub> in the lake hypolimnion during thermal stratification is shown in **Figure 4**. Using this model, a mass balance can be used to link the observed rate of change in the mass of dissolved CH<sub>4</sub> in the hypolimnion over time ( $\Delta M_{CH_4}$ ) to the diffusive flux of CH<sub>4</sub> from sediments ( $J_{SWI}$ ):

$$\Delta M_{CH_4} = J_{SWI} + Diss - F_{out} - Ox_{hypo} \quad (7)$$

where  $Diss$  is the rate of dissolution from CH<sub>4</sub> bubbles present in the hypolimnion,  $F_{out}$  is the CH<sub>4</sub> flux out of the hypolimnion across the thermocline, and  $Ox_{hypo}$  is the rate of CH<sub>4</sub> oxidation in the hypolimnion.  $J_{SWI}$  can therefore be mathematically solved for by determining all the other terms in **Eq. 7** expressed in units of flux (e.g., mmol m<sup>-2</sup> d<sup>-1</sup>).  $Diss$  is typically calculated as a function of ebullition measured from inverted funnel traps (Address and Effler, 1996; Vachon et al., 2019).  $F_{out}$  can be estimated with Fick's first law applied across the thermocline (Kelly et al., 1988):

$$F_{out} = -K_z \frac{dC_{wc}}{dz} \quad (8)$$

where  $K_z$  is the eddy diffusivity within the thermocline and  $\frac{dC_{wc}}{dz}$  is the CH<sub>4</sub> concentration gradient across the thermocline.  $K_z$  is often estimated by measuring heat exchange between the epilimnion and hypolimnion (Powell and Jassby, 1974; Address and Effler, 1996; Matthews et al., 2005). Incubations are often used to quantify  $Ox_{hypo}$  (Rudd et al., 1974; Bastviken et al., 2008). However, some researchers simplify **Eq. 7** by assuming  $Diss$  (Rudd and Hamilton, 1978),  $F_{out}$  (Bédard and Knowles, 1991), and/or  $Ox_{hypo}$  (Vachon et al., 2019) are small enough to be considered insignificant in their lake system.

The  $\Delta M_{CH_4}$  term is determined by tracking the increasing mass of dissolved CH<sub>4</sub> in the hypolimnion throughout the



stratification period. Typically, the hypolimnion is divided into horizontal layers, and CH<sub>4</sub> concentrations are monitored over time at a point within each layer. Water samples are collected periodically from each layer, usually with a Van Dorn sampler or tubing attached to a pump at the surface, then analyzed for CH<sub>4</sub> concentrations using gas chromatography or laser absorption spectrometry. Assuming each layer is horizontally well-mixed,  $\Delta M_{CH_4}$  can therefore be determined over time interval  $\Delta t$ :

$$\Delta M_{CH_4} = \frac{\Delta(\sum C_{wc,i} V_i)}{A_{hypolimnion} \Delta t} \quad (9)$$

where  $A_{hypolimnion}$  is the sediment surface area below the hypolimnion,  $V_i$  is the volume of hypolimnion layer  $i$ , and  $C_{wc,i}$  is the measured CH<sub>4</sub> concentration in layer  $i$  of the water column.

A small subset of water column models that include a term for diffusive CH<sub>4</sub> flux from sediments are advection-diffusion-reaction models. We will provide a brief overview here, however readers are referred to previous detailed descriptions for a full discussion of these models (Durisch-Kaiser et al., 2011; Tan et al., 2015; Stepanenko et al., 2016; Sabrekov et al., 2017; Schmid et al., 2017). These models consider how molecular diffusion affects CH<sub>4</sub> transport in the water column, similar to how diffusion and diffusion-reaction models in the sediment consider the effects of molecular diffusion in the sediment profile (Section 2.2.1). However, unlike sediment models, advection is often included as an important term influencing CH<sub>4</sub> transport in the water column. The diffusive flux of CH<sub>4</sub> from sediments is usually included as a reaction term within the advection-diffusion-reaction model and can be solved for in multiple ways. In models that contain separate modules for the sediment and the water column, flux can be calculated using empirical relationships between methanogenesis and easily-measured sediment characteristics, such as temperature, labile carbon content, and/or pH (Stepanenko et al., 2011; Tan et al., 2015; Sabrekov et al., 2017). Methanogenesis rates can then be depth-integrated to estimate of flux out of sediments (Figure 2B). In models that only contain a water column module, flux can be parameterized by comparing observed and modeled CH<sub>4</sub> concentration profiles in the water column (Durisch-Kaiser et al., 2011; Schmid et al., 2017).

### 2.3.2 Approach Advantages

Water column models are useful for determining the flux of CH<sub>4</sub> across the SWI without relying on direct measurements of CH<sub>4</sub> concentrations within the sediment porewater. Accordingly, these models avoid potential artifacts when sampling sediments for CH<sub>4</sub>, such as the escape of gases, loss of surface sediments, or oxygen exposure during sediment collection (Section 2.2.3). Water column models also provide flux estimates integrated over space and time (Figure 3), which can be advantageous when researchers are more concerned with observing system-wide CH<sub>4</sub> dynamics than quantifying small-scale processes within the sediment or at the SWI (Table 1). For example, coupling CH<sub>4</sub> mass balance information from the hypolimnion with monitoring of surface emissions can track whether CH<sub>4</sub> released from sediments is ultimately stored, oxidized, or emitted (Matthews et al., 2005;

Bastviken et al., 2008). Furthermore, some water column models can simultaneously determine the contribution of diffusion and ebullition to flux from lake sediments (Tan et al., 2015; Stepanenko et al., 2016), which can be advantageous in systems where bubbling is significant. For example, by modeling CH<sub>4</sub> concentrations in the water column of Lake Kinneret, authors determined that ebullition was the primary pathway for surface CH<sub>4</sub> emission and that methanotrophs oxidized the vast majority of dissolved CH<sub>4</sub> in the water column (Schmid et al., 2017).

Another advantage of water column models is that they are highly customizable. On one hand, more terms could be added to the mass balance represented by Eq. 7 as needed, such as source terms for water column CH<sub>4</sub> production (Donis et al., 2017; Günthel et al., 2020) and/or release from CH<sub>4</sub> seeps (Schmid et al., 2007; Bornemann et al., 2016). However, more complicated models may require more sampling effort (Table 1). For example, advection-diffusion-reaction models of CH<sub>4</sub> concentrations in the water column typically require more data than mass balances, such as meteorological information (Tan et al., 2015) and/or detailed temperature profiles (Sabrekov et al., 2017). On the other hand, modeling and sampling effort can sometimes be significantly simplified, for example in lakes where the last three terms in Eq. 7 can be considered negligible. In these cases, a mass balance can be performed with only lake bathymetry information and multiple hypolimnetic CH<sub>4</sub> concentration profiles measured throughout lake stratification (Eq. 9).

### 2.3.3 Approach Limitations

When using water column models, it is important to consider the desired temporal resolution for model output. Water column models can be run on a range of time steps from minutes to months (Figure 3), depending on the level of data input and amount of computational time available. Many models also often assume spatial homogeneity of CH<sub>4</sub> fluxes from sediments (Table 1). For example, mass balances similar to Eqs 7–9 typically provide no information on the flux of CH<sub>4</sub> from sediments not in contact with the hypolimnion, such as shallow littoral regions that can be significant sources of CH<sub>4</sub> in many lakes and reservoirs (Encinas Fernández et al., 2016). Nevertheless, Eqs 7–9 can be adjusted for use in other layers of the water column in order to estimate the diffusive CH<sub>4</sub> flux from sediments lake-wide (Strayer and Tiedje, 1978) or specifically from sediments in contact with the epilimnion and/or metalimnion (Bastviken et al., 2008).

In contrast, advection-diffusion-reaction models applied in the water column focus on the basin-wide distribution of CH<sub>4</sub>, and therefore some do consider spatial heterogeneity in flux. For example, researchers applying an advection-diffusion-reaction model in the water column of Lake Kuivajärvi estimated CH<sub>4</sub> release from sediments for five different depth zones (littoral to profundal) throughout a 6 month period (Stepanenko et al., 2016). Similarly, some advection-diffusion-reaction models account for how methanogenesis rates may vary spatially across sediment layers due to changing substrate quality and quantity (Tan et al., 2015). However, others assume CH<sub>4</sub> diffusion from sediments is spatiotemporally constant throughout the entire

Sediment incubations & benthic chambers			
Sediment models*	11		
Water column models	6	2	
	Sediment incubations & benthic chambers	Sediment models*	Water column models

**FIGURE 5** | Matrix showing number of studies that have compared multiple methodologies for calculating the diffusive flux of CH<sub>4</sub> from sediments. Blue boxes show number of existing studies, with lighter blue indicating fewer studies and darker blue indicating a larger number of studies. Asterisk indicates that there are  $n = 4$  studies, not shown in the matrix here, that compared fluxes between two subtypes of sediment models (diffusion and diffusion-reaction models). All comparative studies are identified in the Supplementary data file (**Supplementary Table S1**).

lake (Durisch-Kaiser et al., 2011), which is not the case in many lakes and reservoirs (Bastviken et al., 2008; Berberich et al., 2019).

Water column models are also limited in their ability to determine drivers of diffusive CH<sub>4</sub> flux from sediments (**Table 1**). Mass balances say little about the possible controls on flux unless they are combined with other data, such as organic carbon deposition rates, temperature profiles, or oxygen concentrations. Similarly, advection-diffusion-reaction models in the water column often rely on model parameterization or empirical equations to calculate flux across the SWI, neither of which directly link CH<sub>4</sub> dynamics to causal drivers. In contrast, other methodologies (such as incubations performed under different experimental conditions) can directly test how CH<sub>4</sub> flux changes with shifting environmental variables.

### 3 METHODOLOGICAL COMPARISONS

As described above, each method for measuring the diffusive flux of CH<sub>4</sub> from lake sediments has particular advantages, limitations, and capacities to answer scientific questions about lacustrine CH<sub>4</sub> cycling. When choosing which method is appropriate for one's work, previous studies explicitly comparing results from multiple approaches are informative. Careful method intercomparisons are useful in that when results from different approaches are comparable, they can build confidence in our ability to estimate CH<sub>4</sub> fluxes. Alternatively, when method intercomparisons reveal vastly divergent flux estimates across different techniques, they can highlight whether certain approaches are associated with systematic biases and indicate important areas for further investigation. Examples of such comparison studies are limited, comprising just 13% of our dataset (**Figure 5**; **Section 4.4**). In this section, we focus on this small subset of comparative studies to highlight a few important insights into the implications of method choice for the estimation of sediment CH<sub>4</sub> fluxes.

#### 3.1 Sediment Diffusion Models and Surface Sediment Processes

Previous comparisons of incubations and diffusion models applied in the sediment (Fick's first law, **Eq. 1**) emphasize the

challenge of accurately measuring processes near the SWI. Compared to sediment incubations, sediment diffusion models are reported to sometimes overestimate (Sweerts et al., 1991; Sinke et al., 1992; Li et al., 2018) and sometimes underestimate (Frenzel et al., 1990; Thebrath et al., 1993) the diffusive flux of CH<sub>4</sub> from sediments. The discrepancy between incubation and diffusion model-based estimates may stem from several causes. For example, sediment concentration profiles cannot capture how rapid processes at the sediment surface may influence flux (Urban et al., 1997) and (**Table 1**). Sediments near the SWI are often an important location for sediment CH<sub>4</sub> oxidation (Frenzel et al., 1990; Schubert et al., 2011; Hershey et al., 2014) or methanogenesis (Winfrey and Zeikus, 1979; Liikanen et al., 2002b; Dan et al., 2004), driving rapid changes in CH<sub>4</sub> concentrations within just a few millimeters or centimeters of the SWI (Bussmann and Schink, 2006). These concentration changes may be unresolvable by the limited spatial resolution of porewater samples (Harper et al., 1997), resulting in measurement error for sediment diffusion model-based estimates (**Table 1**). In contrast, incubation using benthic chambers or intact cores measure CH<sub>4</sub> accumulation above the SWI, and therefore they incorporate the potential effects of rapid surface processes on flux. Intact core incubations or benthic chambers may therefore be preferable to a sediment diffusion modeling approach in systems where significant CH<sub>4</sub> processing in the sediment occurs within several millimeters of the SWI.

#### 3.2 Incubation Effects on Microbial Rates

Comparisons between sediment incubations and other approaches suggest that incubations may overestimate fluxes by stimulating methanogenesis and/or inhibiting methanotrophy. For example, in Lake Constance, sediment fluxes based on slurry incubations were 3–4 times larger than estimates from sediment diffusion modeling (1,400 and 369  $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ , respectively; Frenzel et al., 1990). In a eutrophic maar lake, incubation-based sediment fluxes (16  $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ) were about tenfold higher than sediment diffusion model estimates (1.5  $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ; Fahrner et al., 2008). Similarly, other studies report larger estimates of CH<sub>4</sub> diffusive fluxes from incubations than hypolimnetic mass balances. In Frain's Lake and Third Sister Lake, flux estimates based on incubations performed between 0 and 20 cm sediment depth were 2–5 times higher than flux estimates based on a

hypolimnetic mass balance (Kelly and Chynoweth, 1980). Incubations measured a sediment flux of 2,600  $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  in the profundal zone of Blelham Tarn, 2–10 times higher than flux estimates from a hypolimnetic mass balance (235–1,244  $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ; Jones and Simon 1981). The overestimation of methanogenesis by sediment incubation has also been noted in studies of other flooded soils (Blodau and Moore, 2003), where some incubation-based rates of CH<sub>4</sub> production in peatland soils were found to be more than 10 times larger than estimates from sediment modeling. Sediment collection and handling prior to incubation may disturb sediment microstructure, possibly stimulating methanogenesis by providing better contact for methanogens to access substrate (Kelly and Chynoweth, 1980). Incubation preparation (e.g., sediment slurring or headspace flushing) may also stimulate CH<sub>4</sub> production by degassing or diluting compounds that would otherwise inhibit methanogens (Kelly and Chynoweth, 1980).

Larger sediment fluxes as a result of stimulated methanogenesis may be further compounded by the possible inhibition of CH<sub>4</sub> oxidation by sediment slurring, which may destroy aggregates important for methanotrophs and their syntrophic partners (Su et al., 2019). Methanotrophy is also positively correlated with CH<sub>4</sub> availability (Thottathil et al., 2019), so degassing during sediment core sampling or incubation preparation could slow CH<sub>4</sub> oxidation compared to *in situ* rates. The possible effects of incubation on methanogenesis and methanotrophy suggests that this approach may be more suitable for comparing relative rather than absolute fluxes.

### 3.3 Comparing CH<sub>4</sub> Flux & CH<sub>4</sub> Production

Comparing fluxes across methods also highlights the difference between measurements of CH<sub>4</sub> flux and CH<sub>4</sub> production. Confusingly, these terms are sometimes used interchangeably in the literature, despite the fact that the former technically refers to the rate of CH<sub>4</sub> transport across a plane (e.g., the SWI) and the latter represents a rate of methanogenesis. The confusion in terminology is further compounded by the fact that CH<sub>4</sub> production rates measured at discrete depths throughout the sediment profile can be depth-integrated into a flux out of sediments (Figures 2A,B). Previous studies have reported similar estimates of depth-integrated CH<sub>4</sub> production from sediment diffusion-reaction modeling (Eqs 3–5) and flux across the SWI from sediment diffusion models (Eq. 1; Bartosiewicz et al., 2016; Steinsberger et al., 2019). However, other studies have noted a mismatch between estimates of CH<sub>4</sub> diffusion based on sediment diffusion models and depth-integrated methanogenesis based on sediment diffusion-reaction models, attributing the difference to some produced CH<sub>4</sub> being oxidized anaerobically (Norđi et al., 2013) or forming bubbles (Adler et al., 2011) in the sediment profile before it could diffuse into the water column. Others have calculated sediment ebullition specifically as the difference between depth-integrated methanogenesis and the diffusive CH<sub>4</sub> flux across the SWI (Langenegger et al., 2019).

Depth-integrated production also may not accurately represent flux if the sampling spatial resolution is too coarse

to capture significant changes in methanogenesis within the sediment profile (Figure 2B). Methanogenesis can double or triple within just a few centimeters in the sediment column of some lakes (Chan et al., 2005; Yang et al., 2017), yet depth integration often assumes CH<sub>4</sub> production is constant across sediment layers ranging in thickness from 3 to 5 cm (Bretz and Whalen, 2014; Berberich et al., 2019) to 20 cm or more (West et al., 2016). In these cases, depth-integrated production may be significantly different from flux. The possibility of misrepresenting flux by depth-integrating methanogenesis rates further underscores the advantage of approaches that measure the release of CH<sub>4</sub> from sediments without sampling sediments directly, such as benthic chambers.

### 3.4 Sediment Depth Matters

Lastly, considering what sediment depths are characterized by a method is important when comparing techniques. The majority (60%) of incubation studies in our dataset base sediment CH<sub>4</sub> flux or production measurements on samples taken from a sediment depth  $\leq 20$  cm. This is important because when using methods reliant on sediment sampling, such as sediment modeling or some incubations, fluxes may be underestimated if sampling excludes depths with significant methanogenesis. For example, Kelly and Chynoweth (1980) reported fluxes measured with core incubations sectioned from 0 to 3 cm in the sediment column were 2–4 times lower than fluxes measured with cores sectioned from 0 to 20 cm. Although the authors attribute the stark difference in fluxes to a possible artificial stimulation of methanogenesis in deeper layers of incubated sediment (Section 3.2), there are multiple examples in the literature of active and significant methanogenesis deep in the sediment profile. Production rates from 25 to 30 cm in the sediment profile of oligotrophic Lake Constance were observed to be almost as high as those from surface sediments (Rothfuss et al., 1997). Similarly, methanogenesis from 90 to 130 cm in the sediments of mesotrophic Lake Åtäsö were comparable to rates observed at 10–30 cm (Rissanen et al., 2017), and the highest methanogenesis rates were observed below 50 cm in cores from a thermokarst lake (Heslop et al., 2015) and an acidic lake (Koschorreck et al., 2008).

Taken together, these examples suggest that the common assumption of negligible methanogenesis in deep sediments is incorrect, at least some of the time. Highly organic-rich sediment columns (e.g., those within thermokarst lakes) may exhibit significant methanogenesis beyond surface sediments, whereas sandy, porous sediment columns may not have the carbon stores to support such microbial activity deeper in the profile. Alternatively, highly acidic or basic lakes may contain surface sediments with a pH that inhibits methanogenesis; yet methanogens may be active deeper in the sediment profile where conditions are more favorable. The control that sampled sediment depth exerts on flux estimates from some *ex situ* approaches highlights the advantage of methodologies that consider the entire sediment column in their measurements, such as *in situ* methods or techniques that estimate flux based on water column measurements.

## 4 RECOMMENDATIONS & FUTURE DIRECTIONS

The strengths and limitations of each method for measuring diffusive CH<sub>4</sub> flux from sediments should influence one's choice of approach for different research applications. Thus far, we have focused on limitations of individual methods (Section 2) or between pairs or small groups of methods (Section 3). Here, we take a broader perspective to 1) discuss how limitations across the full suite of approaches have shaped gaps in current understanding of lacustrine CH<sub>4</sub> cycling; and 2) recommend future methodological developments needed to address these gaps.

### 4.1 Short-Term Temporal Variability

Little is known about short-term (sub-hourly) variation in diffusive CH<sub>4</sub> fluxes from sediments, largely because most available approaches operate on hourly to monthly or seasonal time scales (Figure 3). A better characterization of short-term variability is necessary for identifying the implications of temporal resolution on measured fluxes. For example, previous studies have stressed the possibility of under- or over-estimating surface emissions from reservoirs and impounded rivers due to inadequate sampling frequency (Maeck et al., 2014; Wik et al., 2016; Harrison et al., 2017; Marcon et al., 2019). No similar studies exist for CH<sub>4</sub> diffusion from lake sediments, despite recent evidence that diffusive flux can change significantly within hours (D'Ambrosio, 2022). Advancing understanding of short-term variability would therefore be instructive when determining the appropriate method and sampling frequency for future work.

Flux gradient approaches are promising, emerging tools for characterizing short-term variability in CH<sub>4</sub> fluxes. Such methods can be applied to measure fluxes on a time scale of minutes to hours across the lake bottom boundary layer (BBL), a region of the water column extending up to several meters above the lakebed and a zone where currents are affected by friction with sediments (Henderson, 2016). Although flux measured in the BBL is not technically equivalent to flux across the SWI, estimates from the BBL are valuable because they quantify the rate at which CH<sub>4</sub> is transported from sediments into the lake interior, from which it may ultimately be emitted to the atmosphere. Using a flux gradient technique, flux estimates are made *in situ* by combining measurements in the BBL of vertical concentration gradients, turbulent mixing, and temperature stratification (McGillis et al., 2011). Recently, the method has been adapted for use in a lake BBL for the first time (D'Ambrosio, 2022), whereas previous applications have focused on fluxes of momentum, oxygen, or total alkalinity in marine BBLs (Reidenbach et al., 2006; McGillis et al., 2011; Turk et al., 2015; Takeshita et al., 2016). This methodological advancement allowed for the estimation of CH<sub>4</sub> fluxes on an hourly basis within the BBL of a eutrophic reservoir, revealing significant sub-daily variations in CH<sub>4</sub> transport (D'Ambrosio, 2022).

The development of other techniques that operate on a short temporal scale would also be helpful, such as eddy correlation (eddy flux) techniques that have already been developed for fluxes

of other dissolved gases such as CO<sub>2</sub> and O<sub>2</sub> across the SWI (Berg et al., 2013; Kokic et al., 2016). Unfortunately, eddy flux techniques require *in situ* concentration measurements with a temporal resolution <1 s (Donis et al., 2015), which are beyond the capability of dissolved CH<sub>4</sub> instruments at present; response times for aqueous CH<sub>4</sub> sensors are, at this writing, limited to 12 s–40 min response times (Damgaard and Revsbech, 1997; Webb et al., 2016; Xiao et al., 2020). The development of aqueous CH<sub>4</sub> sensors with faster response times would facilitate the development of eddy correlation approaches for measuring CH<sub>4</sub> flux from lakebeds. Alternatively, relaxed eddy accumulation techniques avoid the need for fast-response sensors and have been used to measure fluxes of oxygen, temp, and suspended matter across the SWI in a shallow riverine lake (Lemaire et al., 2017). However, both eddy flux and relaxed eddy accumulation approaches perform best in consistently turbulent conditions, and therefore may be of limited utility in lakes and reservoirs where near-bed turbulence is intermittent (Simpson et al., 2011; Henderson, 2016). Flux gradient approaches, adapted for use in moderately stratified lake BBLs (D'Ambrosio, 2022), may be the best alternative in these cases.

### 4.2 Boundary Layer Dynamics

Methodological limitations have also obscured the relationship between BBL conditions and SWI CH<sub>4</sub> diffusion. In stratified lakes and reservoirs, internal waves and seiches can drive changes in BBL mixing and biogeochemistry that occur on timescales of minutes to hours (Wüest and Lorke, 2003; Bernhardt et al., 2014). It is well-established that such periodic changes in BBL turbulence exert significant control on the diffusive flux of other redox-active solutes to and from sediments, such as oxygen and nitrate (Lorke et al., 2003; Brand et al., 2008, 2009; Bryant et al., 2010). However, most available approaches for measuring CH<sub>4</sub> diffusion from sediments cannot capture how such boundary layer processes influence flux. Current techniques largely rely on *ex situ* analyses (Table 1) performed on hourly to seasonal time scales (Figure 3). Consequently, boundary layer conditions have been largely overlooked as a potential factor influencing the diffusive flux of CH<sub>4</sub> out of sediments.

Future work that couples BBL observations with CH<sub>4</sub> flux measurements from sediments in space and time is needed to investigate how boundary layer dynamics may influence the rate and timing of CH<sub>4</sub> transport into the water column. For example, flux gradient approaches do not isolate sediments from lake-scale processes in the boundary layer that may influence flux (D'Ambrosio, 2022), unlike *ex situ* techniques such as sediment incubations. Application of the flux gradient approach has illustrated how fluctuations in BBL turbulent mixing may exert an important control on CH<sub>4</sub> transport from sediments into the water column (D'Ambrosio, 2022). The development of eddy flux and/or relaxed eddy accumulation techniques may also be helpful in this regard (Section 4.1). However, further measurements in other lake systems and a closer examination of potential causal links between boundary layer dynamics and CH<sub>4</sub> transport are still needed. For example, on seasonal time scales, methanotrophs can regulate the upwards flux of CH<sub>4</sub> in the water column by

responding readily to changes in concentrations of CH<sub>4</sub> and electron acceptors (Graf et al., 2018; Mayr et al., 2020a; Mayr et al., 2020b). On shorter time scales, it is unknown if methanotrophs exert a similar control on CH<sub>4</sub> flux from sediments in response to fluctuating concentrations of CH<sub>4</sub> and electron acceptors in the BBL.

### 4.3 Developing Modeling Approaches

Available methods for measuring diffusive CH<sub>4</sub> flux across the SWI rely on direct sampling of the sediments or the water column. Our capacity to measure flux is therefore limited in lakes that are remote, seasonally inaccessible, or ice-covered. Moreover, a sampling bias towards measurements made over short-term deployments and during the summer months is likely, as noted in the literature of surface CH<sub>4</sub> emissions from lakes (Wik et al., 2016; Jansen et al., 2020). Consequently, current estimates of the diffusive flux of CH<sub>4</sub> from sediments are focused on physically accessible lakes and reservoirs, likely during the warmer months. Expanding the spatiotemporal coverage of measurements would provide novel insight into the variability and controls on CH<sub>4</sub> release from lake sediments in a wide variety of lakes and reservoirs.

Developing models that estimate CH<sub>4</sub> diffusion from sediments using easily-measured lake characteristics, rather than measurements of CH<sub>4</sub> concentrations in the sediments and/or water column, could improve the spatiotemporal coverage of methane flux estimates. Multiple models of surface CH<sub>4</sub> emissions from easily-measured lake characteristics have been created (Bastviken et al., 2004; Harrison et al., 2021). Similar techniques for predicting CH<sub>4</sub> diffusion from lake sediments have not been developed, yet there is evidence that some basic lake characteristics could be useful in predicting sediment diffusive flux. For example, a recent study successfully modeled sediment CH<sub>4</sub> production as a function of particulate organic matter supply and reactivity (Grasset et al., 2021). Moreover, a recent meta-analysis of over 60 lakes and reservoirs suggests sediment CH<sub>4</sub> production rates can be linked to trophic status (D'Ambrosio and Harrison, 2021), which can be readily measured on site with surface water sampling. Exploring the power of lake characteristics to predict CH<sub>4</sub> diffusion from sediments could elucidate how the supply of CH<sub>4</sub> to the lake water column potentially changes across seasons, latitudes, lake types, and other system characteristics, uninhibited by direct sampling effort.

### 4.4 Expanding Method Comparisons

Of the 163 studies included in this review, just 13% ( $n = 22$ ) used multiple methods to estimate CH<sub>4</sub> diffusion from sediments (Figure 5; Supplementary Table S1). Approximately half of the comparative studies in our dataset compare the most popular approaches (sediment incubations and sediment diffusion models; Figure 1; Supplementary Table S1). To our knowledge, less common methods such as water column models have fewer direct comparisons (Figure 5). Comparisons between approaches in one or multiple lakes are common in studies of CH<sub>4</sub> surface emission (Schubert et al., 2012; Podgrajsek et al., 2014; Deemer et al., 2016; Sanches et al., 2019), and oxidation in the water column or sediments (Bastviken et al., 2002; Su et al., 2019), but are uncommon in the study of CH<sub>4</sub> diffusion from

sediments. More method comparisons would benefit the field because observed agreement or deviation between approaches highlights methodological limitations and potential caveats when considering estimates between studies.

## 5 CONCLUSION

The diffusive flux of CH<sub>4</sub> from sediments is a critical source of CH<sub>4</sub> to lake and reservoir ecosystems, which collectively contribute significantly to global greenhouse gas emissions. Here, we critically assess the most popular methods for quantifying CH<sub>4</sub> diffusion from sediments, including incubations, diffusion and diffusion-reaction models applied in the sediment, and mass balance and advection-diffusion-reaction models applied in the water column. We also discuss lessons learned from the small body of studies that directly compare some of these methods, including 1) estimating flux across the SWI with sediment diffusion models is challenging because these models are quite sensitive to surface sediment CH<sub>4</sub> concentration gradients, which are difficult to measure at an appropriate spatial resolution; 2) incubation-based approaches can bias flux estimates by stimulating methanogenesis and/or inhibiting methanotrophy in sediments; 3) depth-integrating methanogenesis rates to estimate flux can lead to error if the sampling spatial resolution is not fine enough to resolve changes in CH<sub>4</sub> production with depth; and 4) most studies estimate flux based on sampling shallow sediments (<20 cm depth), and therefore may not consider the possibility of significant CH<sub>4</sub> production demonstrated deeper in the sediments of some systems. Furthermore, we explore how methodological limitations have shaped knowledge gaps regarding the rate and timing of CH<sub>4</sub> supply to lake interiors. Specifically, the coarse spatiotemporal resolution of most established methods contributes to a poor understanding of the short-term variability of diffusive flux from sediments and the potential control of boundary layer conditions. Furthermore, the spatiotemporal coverage of diffusive flux estimates from different systems is likely biased towards physically accessible lakes sampled during the summer months.

We also identify several important avenues for future methodological advancement. *In situ* approaches with sub-hourly temporal resolution are needed to address questions of short-term variability and the role of boundary layer conditions. Recent applications of flux gradient techniques and possible future adaptations of eddy correlation or relaxed eddy accumulation approaches could be useful tools to this end. Expanding CH<sub>4</sub> flux measurements using these techniques can help inform models that predict diffusive flux from sediments using basic lake characteristics, possibly improving the future spatiotemporal coverage of estimates. More quantitative comparisons between techniques at the finest and coarsest spatiotemporal resolution considered here (cm/min scales and whole lake/seasonal scales, respectively) would highlight additional strengths weaknesses of additional methods, point out additional knowledge gaps, and clarify the implications of methodological approach for flux estimation.

## AUTHOR CONTRIBUTIONS

SD performed the literature review and wrote the manuscript. JH provided scientific and editorial support.

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## SUPPLEMENTARY MATERIAL

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