

Methane stable isotopic ratios and concentrations as indicators of methane dynamics in estuaries

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Abstract. Mixing diagrams of methane (CH_4) concentration and stable isotopic ratio ($\delta^{13}\text{C}-\text{CH}_4$) were used to examine the fate of river-borne CH_4 as it crosses a variety of estuaries: Columbia River (Oregon/Washington), Parker River (Massachusetts), Great Bay (New Hampshire), Kaneohe Bay (Hawaii), and Elkhorn Slough (California). Unlike the surface of the open ocean, these systems are not in near atmospheric equilibrium with respect to concentration or $\delta^{13}\text{C}-\text{CH}_4$ value. The range of observed CH_4 concentrations and $\delta^{13}\text{C}-\text{CH}_4$ values were 33-440 nM and -36 to -58 per mil, respectively, for the freshwater end-members for these systems, 12-330 nM and -48 to -60 per mil for water at the mouths of the estuaries, and 1.6-6 nM and -45 to -60 per mil for the seawater end-members. In the Kaneohe Bay estuary, CH_4 concentration and $\delta^{13}\text{C}-\text{CH}_4$ displayed near-conservative behavior. In the Columbia River estuary, there was loss of riverine CH_4 coupled with shifts to heavier isotopic values, apparently the result of in situ CH_4 oxidation; this oxidation exhibited an apparent kinetic isotopic fractionation factor of 1.0042-1.012. In contrast, the other estuaries showed elevated concentrations and more negative $\delta^{13}\text{C}-\text{CH}_4$ values apparently resulting from inputs of biogenic CH_4 from midestuary marshes and sediments. The upper reaches of all these systems were well out of equilibrium with the atmosphere on a concentration basis, indicating that they are atmospheric CH_4 sources. However, these first $\delta^{13}\text{C}-\text{CH}_4$ measurements show that there is a wide range of isotopic variation in these waters, which indicates that it will be difficult to estimate the collective isotopic contribution of estuaries to the global methane budget.

1. Introduction

There is currently only a limited knowledge of the details of the cycling of dissolved methane (CH_4) in riverine and estuarine waters or on the effects of this CH_4 on the CH_4 cycle of the open ocean. This is somewhat surprising in light of the importance of atmospheric CH_4 on global radiative heat budgets [e.g., Rasmussen and Khalil, 1981; Cicerone and Oremland, 1988; Lelieveld et al., 1993] the ongoing increase in atmospheric CH_4 levels [e.g., Khalil et al., 1989; Etheridge et al., 1992], and the potential for estuarine and oceanic systems to be significant factors in the global CH_4 budget [e.g., Ehhalt, 1974; Quay et al., 1988]. In particular, existing information is unsatisfactory in explaining why atmospheric CH_4 is increasing because of significant uncertainties in the estimated rates of production and consumption of CH_4 in many natural environments. For example, wetlands and the oceans have long been known to be sources of CH_4 to the atmosphere [e.g., Ehhalt, 1974] but processes controlling the origins and distribution of CH_4 in marine and estuarine environments are not presently well understood. This limitation has significantly restricted our understanding of the role of the ocean, bays, and estuaries on the global CH_4 cycle.

The presence of elevated dissolved CH_4 concentrations in rivers and bays has been noted ever since the first CH_4 measurements were made in aquatic systems [e.g., Lamontagne et al., 1973]. It has been established that even rivers without anthropogenic sources of CH_4 have dissolved CH_4 concentrations 1-2 orders of magnitude higher than typical open ocean seawater [e.g., Lamontagne et al., 1973; Wilkness et al., 1978; de Angelis and Lilley, 1987; Lilley et al., 1996]. As a result, natural riverine CH_4 has been tracked for distances of 750 km into the open ocean [Jones and Amador, 1993]. However, published estimates of global atmospheric methane fluxes have not considered the specific contributions of rivers or estuaries [e.g., Watson et al., 1992; Prather et al., 1995].

In general, it appears that CH_4 in advectively dominated estuaries is largely from riverine input, while in more stagnant systems there can be significant inputs from estuarine sediments and wetlands [e.g., King and Wiebe, 1978; de Angelis and Lilley, 1987; Harriss et al., 1982; Sansone et al., 1998]. However, the source of CH_4 in river water is not well established, although it is possible that groundwater from organic rich forest soils may be important [Lilley et al., 1996].

The stable carbon isotopic composition of CH_4 ($\delta^{13}\text{C}-\text{CH}_4$) in a system is dependent on the mechanisms and rates of CH_4 production and consumption and thus can be useful in efforts to elucidate CH_4 cycling [e.g., Whiticar et al., 1986; Martens et al., 1986; Burke and Sackett, 1986; Lansdown et al., 1992]. In addition, the isotopic signature of atmospheric CH_4 sources are important parameters in constraining global atmospheric CH_4

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models [e.g., *Hein et al.*, 1997; *Tans*, 1997]. Unfortunately, stable isotopic measurement techniques have not until recently been sufficiently sensitive for accurate determination of $\delta^{13}\text{C}-\text{CH}_4$ in surface waters, that typically have CH_4 concentrations in the nanomolar range. This limitation has prevented the use of $\delta^{13}\text{C}-\text{CH}_4$ measurements as a tool for studies of surface water CH_4 cycling; to our knowledge, there have been no published measurements of $\delta^{13}\text{C}-\text{CH}_4$ for riverine or estuarine surface waters. However, recent analytical advances [*Popp et al.*, 1995; *Sansone et al.*, 1997] have made possible the measurement of $\delta^{13}\text{C}-\text{CH}_4$ in fresh and marine surface waters using sample volumes <250 mL, thereby allowing the use of samples collected using conventional techniques.

The purpose of this paper is to present the first $\delta^{13}\text{C}-\text{CH}_4$ data collected along transects in a variety of rivers, estuaries, and adjacent nearshore marine environments. There have been previous studies of $\delta^{13}\text{C}-\text{CH}_4$ in estuarine sediments, sediment gas bubbles, and the adjacent atmosphere [e.g., *Happell et al.*, 1993; *Devol et al.*, 1996], but the present study is the first to examine the isotopic signatures of estuarine waters themselves. This initial survey was used to determine if $\delta^{13}\text{C}-\text{CH}_4$ data could be used to better understand CH_4 dynamics in estuarine systems, particularly those with complicated mixing regimes. We show that $\delta^{13}\text{C}-\text{CH}_4$ deviates considerably from conservative mixing in both positive and negative directions, reflecting consumption and production, respectively. Although our limited data set does not resolve temporal variations or the specific mechanisms of production and consumption of dissolved CH_4 , our approach allows identification of situations in which there is mixing of waters with either identical concentrations or isotopic compositions and allows estimation of the kinetic isotopic fractionation associated with in-situ CH_4 oxidation. Ultimately, such research will allow determination of the mean isotopic signature of CH_4 released directly to the atmosphere from rivers and estuaries and should aid understanding of the importance of these systems to the oceanic and atmospheric CH_4 pools.

2. Sampling Sites

Five estuarine systems were examined for this study: Columbia River (Oregon/Washington), Parker River (Massachusetts), Great Bay (New Hampshire), Kaneohe Bay (Hawaii), and Elkhorn Slough (California). The locations of the sampling sites within each estuary are shown in Figures 1a-e.

2.1. Columbia River (Figure 1a)

Samples were collected on August 22, 1995. Two samples were collected within the river; one was collected outside the river mouth but within the river's discharge plume; and an offshore sample was collected 200 km to the northwest of the river mouth. The Columbia is the second-largest river in the United States, with a mean discharge of $\sim 7280 \text{ m}^3 \text{ s}^{-1}$, and drains a largely forested watershed [*Lilley et al.*, 1996]. The tidal range at the river inlet is ~ 2.4 m.

2.2. Parker River (Figure 1b)

Samples were collected on August 23, 1996, and August 19-20, 1997. The freshwater end-member for this system is a pond

that is fed by swamp and forest drainage, and is isolated from tidal influences by a small dam. The estuary downstream of the dam is surrounded by extensive freshwater and saltwater marshes. The most saline samples were collected at a site adjacent to the estuary mouth on an ebb tide in 1996 and on a flood tide in 1997. The tidal range at the river mouth is ~ 2.7 m.

2.3. Great Bay (Figure 1c)

Samples were collected on August 20, 1996, and August 15-16, 1997, from several sites along this relatively complicated estuary system. Three freshwater end-members were sampled: (1) a dammed pond draining a forested watershed (Oyster River), (2) a small, slow-flowing forest stream (Picassic River), and (3) a moderate-sized, free-flowing river draining a mixed-forested/agricultural watershed (Salmon Falls River). The saltwater end-member was collected during a flood tide from a rocky promontory along the coastline adjacent to the mouth of the estuary. The tidal range at the river mouth is ~ 2.9 m.

2.4. Merrimack River

The Merrimack River is located between the Parker River and Great Bay and is the main drainage for much of southern New Hampshire. Samples were collected from two points along the Merrimack: (1) in Newburyport, Massachusetts, 4 km upstream of the river mouth (August 23, 1996, and August 16, 1997) and (2) in Methuen, Massachusetts, 150 km upstream of the river mouth (August 20, 1997). The tidal range at the river mouth is ~ 2.8 m.

2.5. Kaneohe Bay (Figure 1d)

Samples were collected on July 5, 1996, from a stream feeding the bay, two sites from within the south bay, and from the main channel into the bay from the open ocean. The stream drains a suburban watershed and the nearby Koolau mountains. The tidal range in the bay is ~ 0.6 m. The oceanic end-member was collected on July 8, 1997, at Station ALOHA [*Karl and Lukas*, 1996], located in the open ocean ~ 125 km NNW of Kaneohe Bay.

2.6. Elkhorn Slough (Figure 1e)

Samples were collected on May 15, 1996. Six samples were collected: an offshore sample collected 1.6 km from the mouth of the estuary, a sample from the inlet, two samples from the main stream of the slough, a sample of a tributary draining a dairy ranch, and a sample from a marsh drainage channel. The slough meanders through an area of extensive saltmarsh and receives only a limited amount of freshwater runoff. The tidal range at the mouth of the slough is ~ 1.8 m.

3. Analytical Methods

Surface water samples were collected using a 10-20 L bucket gently lowered into the surface of the water. The water was then transferred without aeration to sample bottles using a heavy wall Tygon-tube siphon. Samples were collected without headspace in 200 mL or 60 mL glass serum bottles with butyl

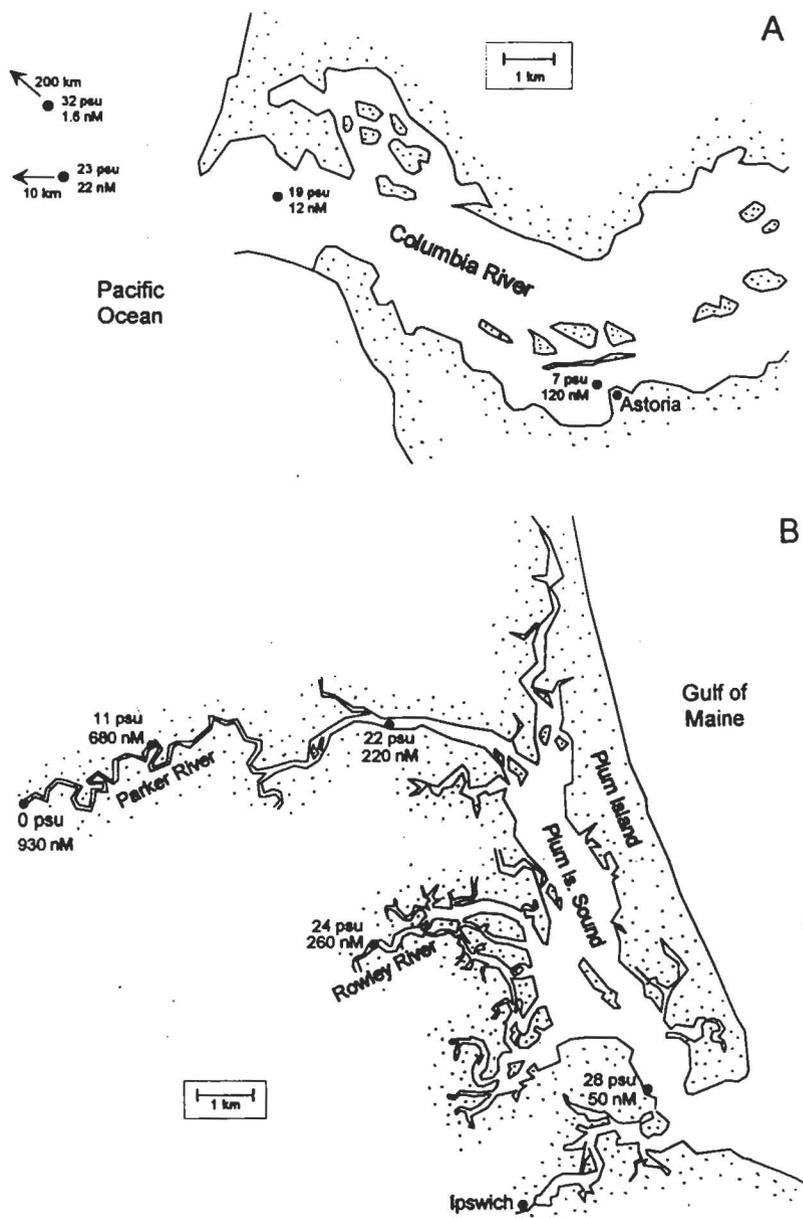


Figure 1. Locations of sampling sites within the estuaries studied, along with the measured salinities (psu) and methane concentrations (nM): (a) Columbia River, (b) Parker River, 1996 data, (c) Great Bay, 1996 data, (d) Kaneohe Bay, and (e) Elkhorn Slough.

rubber septa. Samples were preserved with saturated HgCl_2 solution (1 mL per 200 mL sample and 0.5 mL per 60 mL sample). Replicate analyses were performed for some stations; these were performed on separate samples, and their variability thus reflects all the steps from sample collection to analysis.

Methane carbon stable isotopic ratios ($\delta^{13}\text{C-CH}_4$) were measured (± 0.5 per mil) using the methods of Popp *et al.* [1995] and Sansone *et al.* [1997]. Isotopic ratios are reported here versus the Pee Dee belemnite (PDB) standard using conventional delta notation [Craig, 1957]. Methane concentrations were determined ($\pm 1\%$) by purge-and-trap techniques in combination with gas chromatography and flame ionization detection. The salinity of the Columbia River and

Kaneohe Bay samples was measured (± 0.05 psu) using an AGE model 2100 induction salinometer; the salinity of other samples was determined (± 0.35 psu) using a Oakton WD-35607-10 conductivity meter calibrated with seawater that had been previously analyzed by the induction salinometer.

4. Calculations

4.1. Air-Seawater Equilibration

Air-equilibrated seawater CH_4 concentrations were calculated for in-situ temperatures and salinities using the solubility data of Yamamoto *et al.* [1976]; we have assumed for these calculations an atmospheric CH_4 mixing ratio of 1.7 ppm

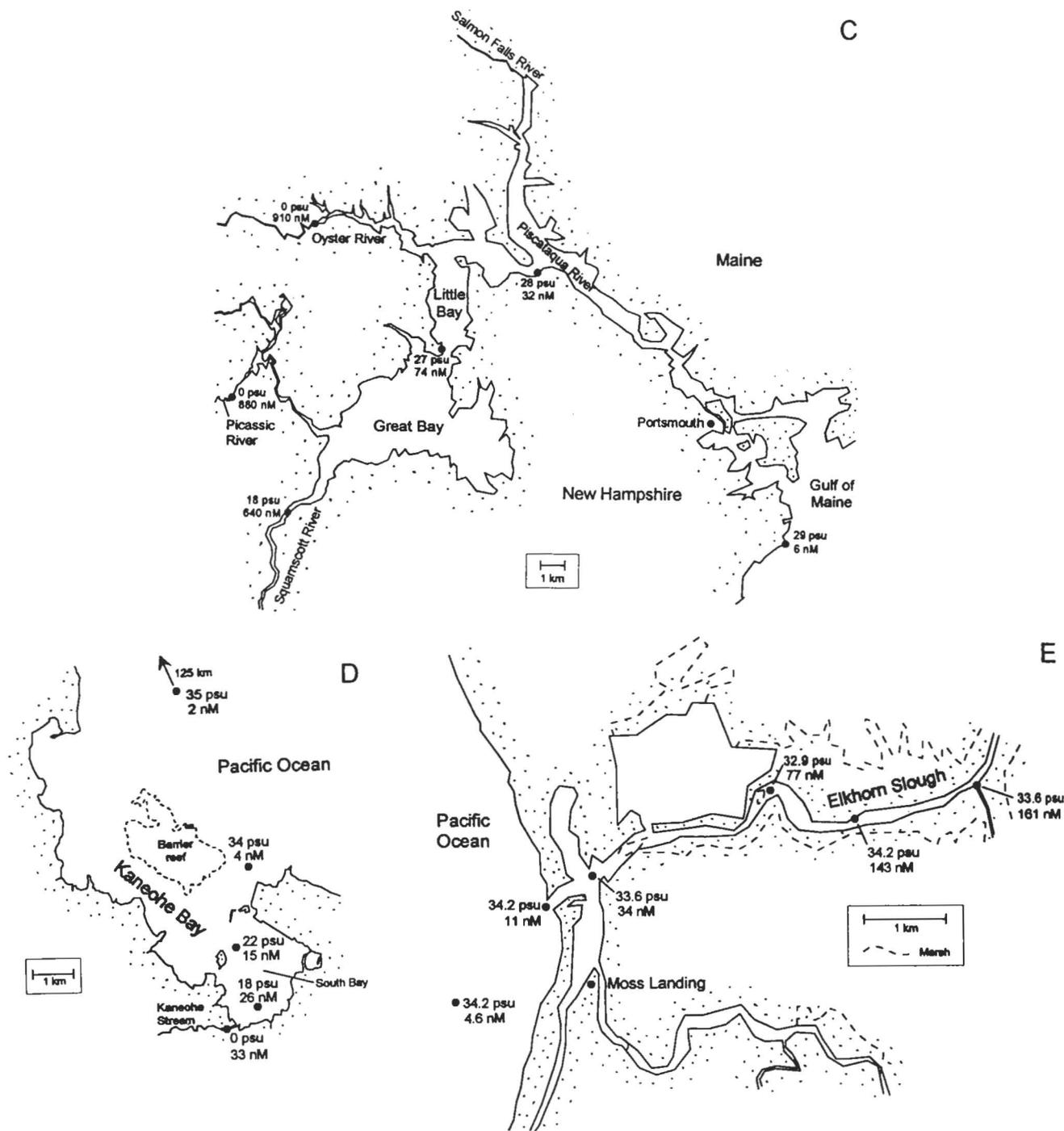


Figure 1. (continued)

[Dlugokencky et al., 1994]. The data presented by Quay et al. [1991] were used to estimate the $\delta^{13}\text{C}-\text{CH}_4$ of the atmosphere over the estuaries studied. However, dissolved CH_4 in air-equilibrated water will be somewhat enriched in ^{13}C relative to atmospheric CH_4 . For example, Fuex [1980] measured equilibrium carbon isotope fractionation of ~ 0.3 per mil during the dissolution of gaseous CH_4 in freshwater at 20°C , with enhanced ^{13}C levels in the aqueous phase.

4.2. Mixing Diagrams

Whereas salinity versus concentration mixing curves under steady state conditions are straight lines drawn between the freshwater and saltwater end-members, isotopic-ratio versus salinity mixing curves are nonlinear [e.g., Spiker, 1980]. The latter were calculated using

$$R_{\text{mix}} = [fR_f C_f + (1-f)R_o C_o] / C_{\text{mix}} \quad (1)$$

where R_{mix} is the isotopic ratio of a river-ocean mixture, C_{mix} is the CH_4 concentration of the mixture, R_r is the isotopic ratio of the river end-member, C_r is the concentration of the river end-member, R_o is the isotopic ratio of the ocean end-member, C_o is the concentration of the ocean end-member, and f is the freshwater fraction [Spiker, 1980]. Salinity was used to calculate f .

4.3. Isotopic Composition of Methane Inputs

In cases in which there was net CH_4 input to the water column at a given salinity in an estuary, the isotopic composition of the added CH_4 was estimated as follows:

$$R_{\text{input}} = [(C_{\text{mix}} R_{\text{mix}}) - (C_{\text{conserv}} R_{\text{conserv}})] / (C_{\text{input}}) \quad (2)$$

where C_{input} , the CH_4 concentration added to the estuary at the point in question, is defined as

$$C_{\text{input}} = C_{\text{mix}} - C_{\text{conserv}} \quad (3)$$

and where C_{conserv} is the conservative CH_4 concentration and R_{conserv} is the conservative isotopic ratio.

4.4. Isotopic Fractionation During Oxidation

In cases in which there was net CH_4 removal from the water column at a given salinity in an estuary, the apparent biological kinetic isotopic fractionation factor (α) for in situ CH_4 oxidation was calculated assuming first-order kinetics [Coleman *et al.*, 1981]:

$$\alpha = \frac{\ln\left(\frac{C_{\text{mix}}}{C_{\text{conserv}}}\right)}{\ln\left(\frac{R_{\text{mix}} + 1000}{R_{\text{conserv}} + 1000}\right)} + 1 \quad (4)$$

5. Results and Discussion

5.1. Estuarine Mixing Diagrams

Of the six estuaries discussed here, the Columbia River (Figure 1a) is the most advective, with its large river flow dominating the estuary's hydrodynamics. At the other extreme are the Parker River (Figure 1b) and Elkhorn Slough (Figure 1e), both of which have relatively small, disperse freshwater inputs. An interesting hybrid is the Great Bay estuary (Figure 1c), which features a diffusively dominated upper estuary, coupled with an advectively driven lower estuary; the latter is the result of the confluence of the Piscataqua River with the lower estuary, combined with the system's relatively large tidal range. Finally, Kaneohe Bay (Figure 1d) includes both the terrestrially influenced South Bay and a central bay that is well mixed with relatively pristine offshore ocean water [Bathen, 1968]. We have found that the type of estuary is reflected in the CH_4 concentration and $\delta^{13}\text{C}\text{-CH}_4$ value distributions; the differences and similarities of each system studied is discussed below.

5.1.1 Columbia River. The highly advective Columbia River estuary is dominated by the rapid discharge of the Columbia River, which leads to appreciable riverine influence well offshore. For example, the sample we collected ~10 km offshore had a salinity of 23 psu. As shown by the dotted lines in Figure 2a, the far offshore end-member had a CH_4 concentration (1.6 nM) close to the 2.2 nM value that would be in equilibrium with the atmosphere (~1.7 ppmv). Similarly, this sample had a $\delta^{13}\text{C}\text{-CH}_4$ value (-45.3 per mil) close to that of the atmosphere at this latitude (-47.2 per mil) [Quay *et al.*, 1991]. The observed riverine endmember had a CH_4 concentration of 120 nM, similar to the 185-279 nM values reported by Lilley *et al.* [1996]. This end-member's $\delta^{13}\text{C}\text{-CH}_4$ value (-58.1 per mil) presumably reflects upstream inputs of biogenic CH_4 , which typically have isotopic ratios of approximately -50 to -80 per mil [e.g., Games and Hayes, 1975; Schoell, 1980; Burke and Sackett, 1986].

The drop in the CH_4 concentration below the conservative mixing line between salinities of 7 and 23 psu suggests that CH_4 oxidation and/or loss to the atmosphere may be important in the outer estuary and in the nearshore waters. This is consistent with the results of Lilley *et al.* [1996] for the Columbia; they measured an average oxidation rate of 10 nM d⁻¹ and calculated a water-to-air flux of 6-20 mg m⁻²d⁻¹ (approximately 4 times the depth-integrated oxidation rate). Our results suggest there is less oxidation far offshore, perhaps owing to the lower levels of suspended particulate matter; suspended particles are known to stimulate oxidation activity in seawater [e.g., Sansone and Martens, 1978].

As seen in Figure 2a, CH_4 in the Columbia River does not exhibit conservative isotopic behavior: The two midestuary samples are enriched in ¹³C relative to corresponding points on the conservative mixing curve. Methane oxidation is likely to be the cause of this nonconservative behavior because (1) the CH_4 concentrations in these samples are less than expected from conservative mixing and (2) oxidation would result in residual CH_4 with $\delta^{13}\text{C}\text{-CH}_4$ values less negative than the source CH_4 [e.g., Barker and Fritz, 1981]. To test this hypothesis, apparent CH_4 oxidation kinetic isotopic fractionation factors (α , Equation (4)) were calculated for the samples with salinities of 19.4 and 23.4 psu. The resulting values, 1.0042 and 1.012, respectively, are similar to the 1.008-1.025 range of values obtained from oxidation experiments in other environments [Coleman *et al.*, 1981; Wen *et al.*, 1996; Reeburgh *et al.*, 1997], thus supporting the hypothesis of significant CH_4 oxidation within this reach of the river.

The lack of net CH_4 input to the water in the Columbia estuary is in contrast to the behavior seen in the other systems we studied. However, the Columbia does not have significant shoreline marsh development, particularly given the substantial area of the estuary and high flow rate of the river. It has been suggested by de Angelis and Lilley [1987] and Lilley *et al.* [1996] that runoff and groundwater from organic rich forest and agricultural soils may be the dominant sources of CH_4 to temperate rivers and that sediments are responsible for only minor inputs. Finally, it is possible that the relatively low temperature of the Columbia may limit in situ CH_4 production, as methanogens are known to be quite temperature sensitive [e.g., Sansone and Martens, 1982; Sass *et al.*, 1991].

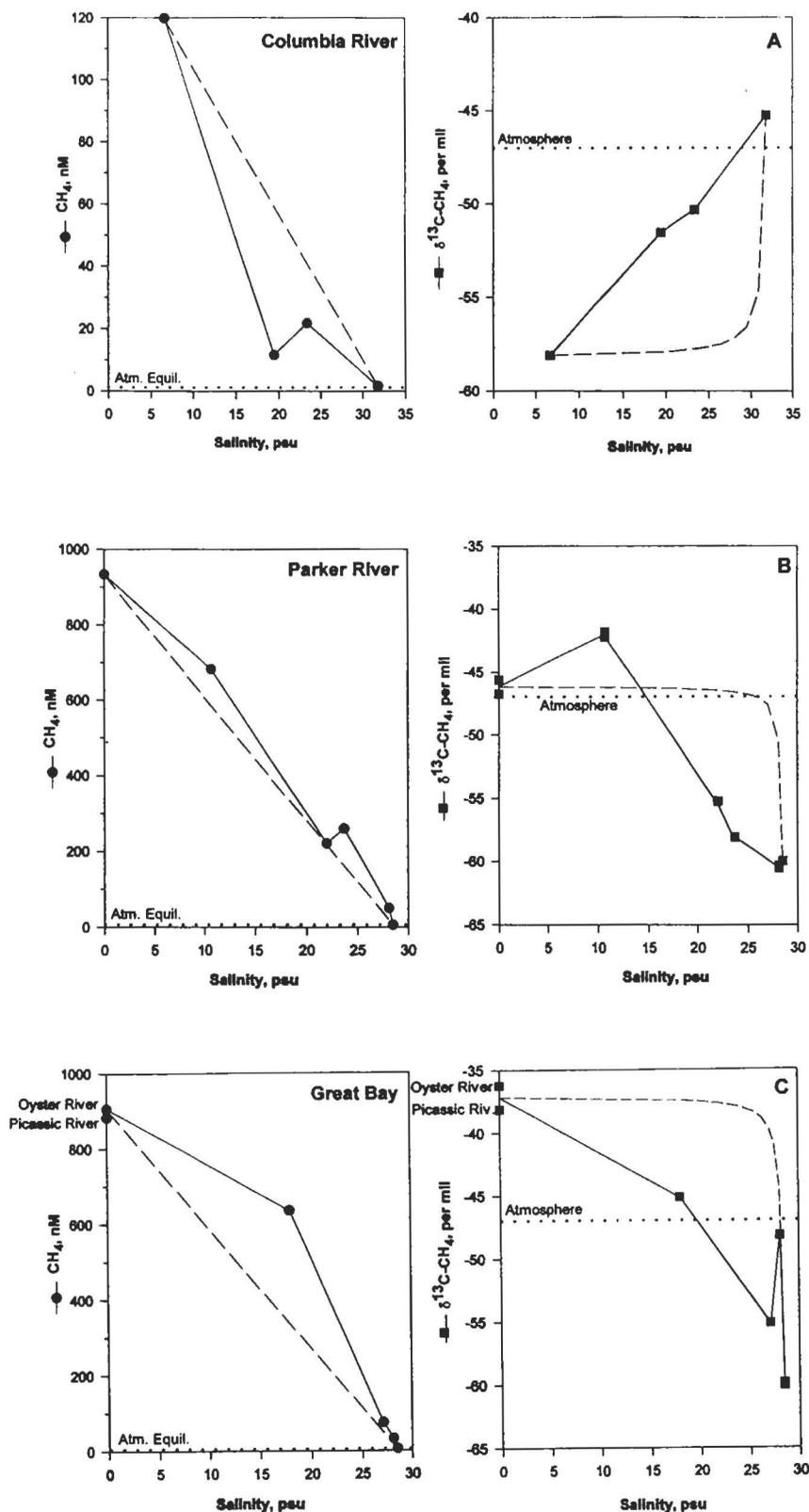


Figure 2. Mixing diagrams for CH₄ concentration and δ¹³C-CH₄ versus salinity: (a) Columbia River, (b) Parker River (1996 data), (c) Great Bay (1996 data), (d) Kaneohe Bay, and (e) Elkhorn Slough. The dotted lines indicate the air-equilibrated CH₄ concentrations at the in situ concentration and salinity (see text) and the approximate δ¹³C-CH₄ value for the atmosphere [Quay *et al.*, 1991]. The dashed lines indicate the computed conservative mixing lines for CH₄ concentration and δ¹³C-CH₄ (see text).

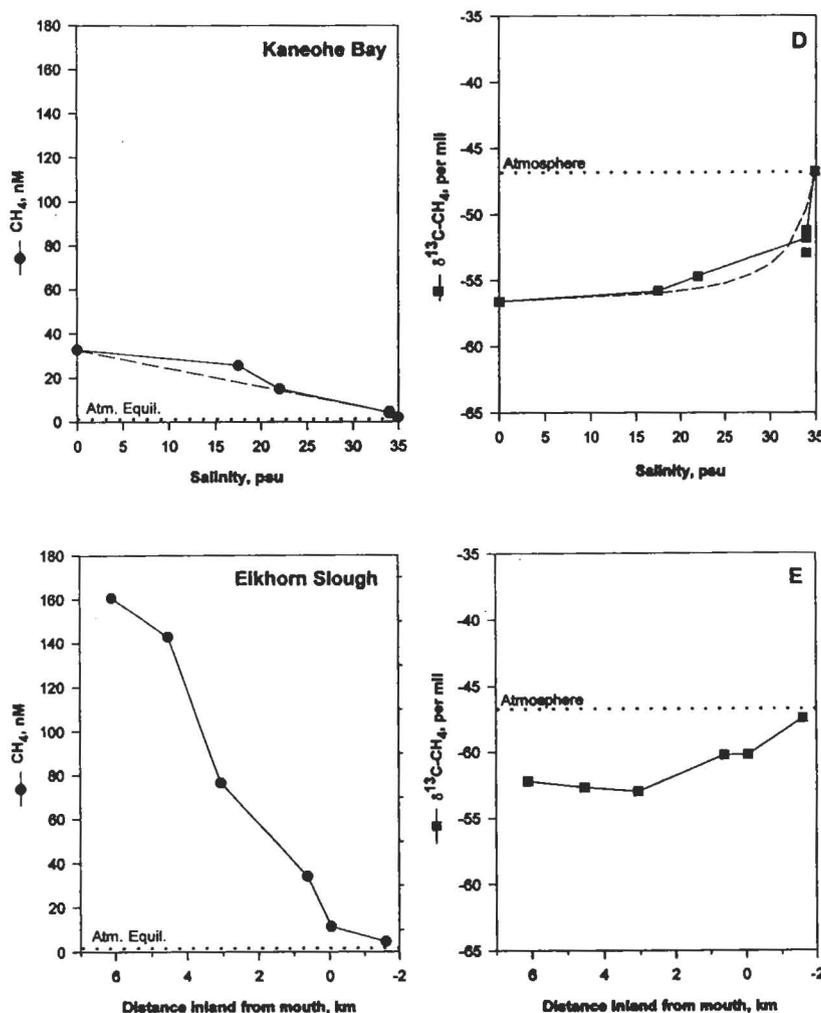


Figure 2. (continued)

5.1.2. Parker River. The Parker River (Figure 2b) is a marked contrast to the Columbia River in several respects. First, the CH₄ concentration in the Parker's freshwater end-member is much higher (930 nM, the highest measured in this study), and its δ¹³C-CH₄ value is essentially atmospheric (-46.7 per mil). This suggests that the methanogenic environments upstream of the dammed pond defining the end-member have even higher concentrations and that this CH₄ is subject to oxidation, and consequent isotopic fractionation, before reaching the pond. Alternatively, the methanogens in this system may be using a ¹³C-enriched source of carbon. Second, the Parker River seawater end-member is well out of isotopic equilibrium with the atmosphere. This may be due to relatively poor flushing of the nearshore regions of the Gulf of Maine by water from the open Atlantic; such conditions could allow benthic sources of biogenic CH₄ within the Gulf to significantly influence the Gulf's CH₄ pool.

Although the nearly linear concentration relationship in the mixing diagram indicates apparent conservative mixing of CH₄ across the estuary, this interpretation is not consistent with the isotopic mixing curve. The observed upper-estuary (11 psu)

maximum in δ¹³C-CH₄ indicates the presence of an input of isotopically heavy CH₄. If this was due to an input with a salinity of 11 psu, equation (2) would predict the δ¹³C-CH₄ value of the input to be -5.8 per mil, an unrealistic value. Instead, it is likely that there is more than one freshwater end-member in this system. For example, an additional freshwater end-member with a concentration and isotopic signature similar to that observed in the nearby Great Bay system (Figure 2c, discussed in section 5.1.3) and with a flow rate similar to the one plotted for Parker River would make both the concentration and isotopic mixing curves conservative at a salinity of 11 psu.

At midestuary (24 psu), there is a net input of isotopically light CH₄ that is evident from the deviation of the isotopic mixing diagram from conservative behavior at a salinity of 24 psu. The calculated δ¹³C-CH₄ value of the added CH₄ is -81.0 per mil; this is consistent with the observation in this reach of the river of saltmarsh pore water, which presumably contains elevated levels of biogenic CH₄ [e.g., Bartlett *et al.*, 1985], directly flowing into the river from river banks.

5.1.3. Great Bay. The Great Bay estuary (Figure 2c) illustrates several similarities to the Parker River system,

although the former is somewhat more hydrographically complex owing to its confluence with the Piscataqua River. The Oyster River freshwater end-member is a dammed pond similar to that on the Parker River and which has a nearly identical CH_4 concentration (Figure 1b). However, the $\delta^{13}\text{C}-\text{CH}_4$ value of the Oyster River pond is less negative, perhaps reflecting even greater levels of oxidation during transport of the CH_4 from its source environments to the pond. This may reflect the differences between marshy and forested watersheds in the Parker and Oyster Rivers, respectively, although data are not available to test this hypothesis. This hypothesis is supported by the fact that the CH_4 concentration and isotopic ratio of the Picassic River end-member, which is a small stream running through a forest, are nearly identical to those of the Oyster River end-member.

The two samples collected at the ends of Great Bay proper (18 psu and 27 psu) show clearly the effects of isotopically light CH_4 inputs. The calculated $\delta^{13}\text{C}-\text{CH}_4$ values of the added CH_4 are -53.6 and -86.3 per mil for the 18 and 27 psu samples, respectively; the latter may be from direct CH_4 inputs from sedimentary production within the anoxic sediments of Great Bay [Lyons and Gaudette, 1979] or the adjacent marshes. The utility of using an isotopic mixing diagram can be seen in the case of the 27 psu sample: Its concentration does not lie far from the conservative mixing line, but its isotopic ratio falls far off the conservative line, providing a clear indication of CH_4 input.

5.1.4. Kaneohe Bay. Kaneohe Bay shows the most conservative behavior of the systems studied, both with respect to CH_4 concentration and isotopic signature (Figure 2d). This estuary also has the smallest CH_4 concentration range, reflecting the relatively small extent of methane-generating environments such as marshes along the shoreline and the general lack of methane-releasing sediments. The isotopic ratios of the freshwater Kaneohe and Columbia end-members are very similar, although the CH_4 concentration of the Kaneohe end-member is only a quarter of that in the Columbia River. In both estuaries, the CH_4 signatures of the freshwater end-members presumably reflect the effects of CH_4 oxidation in the watershed between the source environments and the receiving stream, and it is likely fortuitous that the resulting isotopic ratios in the two systems are so similar.

The concentration mixing diagram indicates CH_4 input to the inner bay (salinity = 18 psu), most likely from streams and shoreline marshes as the surface sediments in South Bay are generally aerobic and highly bioturbated (data not shown). Using equation (2), a $\delta^{13}\text{C}-\text{CH}_4$ value of -55.3 per mil can be calculated for this added methane, which, probably fortuitously, is not far off the isotopic mixing line (Figure 2d).

5.1.5. Elkhorn Slough. In contrast to the other estuaries, Elkhorn Slough receives only small amounts of freshwater input, as evidenced by the narrow salinity range (32.9-34.2 psu) measured across the estuary (Figure 1e). This restricted salinity signal makes salinity-property mixing diagrams difficult to use, so the data are plotted instead versus distance from the mouth of the estuary (Figure 2e). There is a surprisingly linear relationship between CH_4 concentration and location along the estuary.

The oceanic end-member is in near-equilibrium with atmospheric CH_4 on both a concentration and isotopic basis,

despite its being collected <2 km offshore of the mouth of the estuary; the latter is a reflection of the low runoff rates in this system. The elevated CH_4 concentrations and light isotopic ratios of the estuarine samples reflect the influence of adjacent tidally drained marshes and dairy farm drainage.

5.2. Isotopic Signature of CH_4 Released to the Atmosphere

All of the estuaries examined in this study showed large supersaturations in CH_4 ; it is therefore not surprising that the release of CH_4 to the atmosphere from rivers and estuaries is considered potentially important to global CH_4 budgets [e.g., Quay *et al.*, 1988, Lilley *et al.*, 1996]. Thus a knowledge of the stable carbon isotopic signature of this global CH_4 flux would be of use in attempts to constrain global CH_4 budgets. In particular, the systems studied here are very different from the surface of the open ocean, which has both concentration and $\delta^{13}\text{C}-\text{CH}_4$ values very close to equilibrium with the atmosphere (M.E. Holmes *et al.*, manuscript in preparation, 1999). However, the range of CH_4 concentrations and isotopic values observed suggests that accurately estimating the global flux using an isotopic balance will be difficult.

The CH_4 concentrations and isotopic ratios of the freshwater end-members varied considerably at the different sites (Table 1), although they clustered into three groups. Methane in the Columbia and Kaneohe Bay end-members (-58 and -57 per mil, respectively) was lighter than atmospheric CH_4 and occurred at relatively low concentrations. In contrast, CH_4 in the Parker River and Great Bay freshwater end-members (-36 to -46 per mil) was much heavier than atmospheric CH_4 and occurred at quite high concentrations. Finally, the Merrimack displayed properties between these two extremes, with a CH_4 concentration similar to that of the Parker River and Great Bay but with a $\delta^{13}\text{C}-\text{CH}_4$ value (-49.3 per mil) showing greater evidence for active biogenic CH_4 production.

These differences likely reflect differences in the fate of CH_4 from its source to the sampling site. Lilley *et al.* [1996] hypothesized that the bulk of the CH_4 in the Columbia River comes from forest soil groundwater, a mechanism that would also seem likely to be important for the Kaneohe and Merrimack watersheds; apparently this CH_4 is not greatly oxidized within these rivers. In contrast, the Parker and Great Bay systems have freshwater end-members which have evidently undergone significant amounts of CH_4 oxidation, although even after this removal there are high levels of CH_4 remaining. In the cases with a dammed reservoir (Oyster and Parker Rivers) this might be explained by oxidation within the water column of the reservoir, although it would also be expected that CH_4 production within the reservoir's sediments would contribute light CH_4 to the water column. Clearly there is likely to be a wide range of processes responsible for the observed variability between these systems; this suggests that, although isotopic measurements will be helpful in identifying the mechanisms controlling CH_4 distributions in these systems, it will be difficult to establish a global mean isotopic value for atmospheric fluxes from them.

The saltwater end-members were all in near-equilibrium with the atmosphere on a concentration basis, but they again clustered into two groups isotopically. The Columbia, Kaneohe,

Table 1. Methane Concentrations and Stable Isotopic Ratios of Rivers and Streams Sampled in This Study and in Water at the Mouths of Their Respective Estuaries.

River	Date	Observed Freshwater End-Member			Mouth of Estuary		
		Salinity, psu	CH ₄ , nM	δ ¹³ C-CH ₄ , per mil	Salinity, psu	CH ₄ , nM	δ ¹³ C-CH ₄ , per mil
Columbia	Aug. 1995	6.6	120	-58.1	19	12	-51.5
Kaneohe Stream	July 1996	0	33	-56.6	34	4	-52.0
Merrimack	Aug. 1996					330	-49.2
	Aug. 1997	0	740	-49.3	11	290	-53.1
Parker	Aug. 1996	0	930	-46.2	28	50	-60.4
	Aug. 1997	0	580	-38.1			
Oyster	Aug. 1996	0	910	-36.2	28	32	-48.2
	Aug. 1997	0	870	-40.5			
Picassic	Aug. 1996	0	880	-38.1	28	32	-48.2
	Aug. 1997	0	2440	-38.9			
Salmon Falls	Aug. 1997	0	630	-41.4	28	32	-48.2

Note that the Oyster, Picassic, and Salmon Falls Rivers all feed the Great Bay estuary.

and Elkhorn Slough end-members were approximately in equilibrium with atmospheric CH₄, with δ¹³C-CH₄ values of -45 to -47 per mil. In contrast, the Parker River and Great Bay saltwater end-members were -60 per mil, indicating significant inputs of relatively fresh biogenic CH₄. The very heavy riverine δ¹³C-CH₄ values in the Parker River, Great Bay, and the Salmon Falls River, however, indicate that the source of CH₄ in the offshore water (which is much lighter than the CH₄ in the rivers) is not predominantly terrestrial. Instead, the signal may reflect in situ inputs, such as from shelf sediments or in situ production [e.g., Sieburth, 1991; Tsurushima et al., 1996].

5.3. Temporal Variability

One limitation of the data set is the lack of time series sampling, particularly for the mixing diagram end-members; this prevents resolution of temporal variability which occurs on timescales shorter than the estuary mixing time [e.g., Officer and Lynch, 1981]. However, the compositional consistency of the different Great Bay freshwater end-members argues that, for at least this system, short-term variability is not a dominating effect. In addition, effort was made to collect samples only during stable meteorological conditions, thus minimizing the effects of transient runoff events and wind-induced mixing and currents within the estuaries.

At longer timescales, it is possible that there is seasonal variation in the concentration and isotopic signature of the surface water CH₄. Previous work has shown significant seasonal variability in estuarine concentrations [e.g., de Angelis and Lilley, 1987; Watanabe et al., 1994] and in the isotopic signature of CH₄ produced in aquatic sediments [e.g., Chanton and Martens, 1988; Devol et al., 1996]. This suggests that considerable additional work will be required to accurately estimate the amplitude and isotopic signature of the global CH₄ flux to the atmosphere from rivers, estuaries, and coastal waters.

6. Conclusions

An examination of a wide variety of estuaries was used to determine the utility of the CH₄ concentration/isotope approach to understanding estuarine CH₄ dynamics. This approach is a useful technique for understanding CH₄ dynamics in estuarine systems, particularly those with complicated mixing regimes. Specifically, the combination of concentration and isotopic ratio data allows mixing of waters with similar concentrations or isotopic ratios to be resolved. In addition, it enables identification of regions of CH₄ production or oxidation. The initial data presented here should provide a useful groundwork for more detailed studies.

Methane concentration generally decreased across the estuaries studied, reflecting the dominant role of upstream terrestrial sources, particularly in systems with large river flows. The upper reaches of all these systems were well out of equilibrium with the atmosphere on a concentration basis, indicating that they are atmospheric CH₄ sources. However, there was a wide range of isotopic variation in these waters, which indicates that it will be difficult to estimate the collective isotopic contribution of estuaries to the global methane budget. This difficulty is related to the still unresolved issue of the source of CH₄ to rivers, particularly in rivers that do not have significant shoreline marsh development. It has been suggested by de Angelis and Lilley [1987] and Lilley et al. [1996] that runoff and groundwater from organic rich forest and agricultural soils may be the dominant sources of CH₄ to temperate rivers and that sediments are responsible for only minor inputs. However, this important issue remains to be rigorously investigated in a range of systems.

Midestuary CH₄ sources were also observed to be significant in the Parker River and Great Bay, low discharge-rate systems with extensive marshes and anoxic sediments. In contrast, the Kaneohe Bay estuary displayed near-conservative

behavior for both CH₄ concentration and δ¹³C-CH₄. In the Columbia River estuary, there was loss of riverine CH₄ coupled with shifts to more positive isotopic values, apparently the result of in situ CH₄ oxidation; this oxidation exhibited an apparent kinetic isotopic fractionation factor of 1.0042-1.012.

Water at the mouths of the estuaries had CH₄ concentrations of 12-330 nM, whereas the seawater end-members had concentrations of 1.6-6 nM. Thus it can be expected that estuaries will generally be sources of CH₄ to the ocean. However, as for the freshwater end-members, the isotopic composition of this CH₄ will vary between systems. The effect of estuarine CH₄ on the isotopic composition of the nearshore ocean will likewise be site specific, as there is wide variability in the δ¹³C-CH₄ values of both estuarine and nearshore seawater. For example, the surface waters of the open Pacific Ocean are typically in near-equilibrium with the atmosphere with respect to CH₄ concentration and isotopic ratio (Figures 2a, 2d, and 2e) [Sansone et al., 1997] (M.E. Holmes et al., manuscript in preparation, 1999). In contrast, as seen in the east coast data, CH₄ in the surface of shallow shelf waters can become isotopically depleted in ¹³C, presumably owing to shelf-derived inputs. This is likely to be particularly true along the inshore margin of wide continental shelves and in regions with restricted mixing with the open ocean.

Finally, there is a need for studies of other estuarine systems, particularly in nontemperate systems, to enable CH₄ cycling to be fully understood generically in estuaries. The present study demonstrates the utility of stable isotopic measurements in efforts to evaluate the role of estuaries in the cycling of this important trace gas. However, there is a need for more intensive sampling in order to allow better resolution of the temporal and spatial variation in CH₄ in these highly dynamic systems

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