

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

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**Abstract.** Mixing diagrams of methane ( $\text{CH}_4$ ) concentration and stable isotopic ratio ( $\delta^{13}\text{C}-\text{CH}_4$ ) were used to examine the fate of river-borne  $\text{CH}_4$  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  $\text{CH}_4$  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,  $\text{CH}_4$  concentration and  $\delta^{13}\text{C}-\text{CH}_4$  displayed near-conservative behavior. In the Columbia River estuary, there was loss of riverine  $\text{CH}_4$  coupled with shifts to heavier isotopic values, apparently the result of in situ  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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 ( $\text{CH}_4$ ) in riverine and estuarine waters or on the effects of this  $\text{CH}_4$  on the  $\text{CH}_4$  cycle of the open ocean. This is somewhat surprising in light of the importance of atmospheric  $\text{CH}_4$  on global radiative heat budgets [e.g., Rasmussen and Khalil, 1981; Cicerone and Oremland, 1988; Lelieveld et al., 1993] the ongoing increase in atmospheric  $\text{CH}_4$  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  $\text{CH}_4$  budget [e.g., Ehhalt, 1974; Quay et al., 1988]. In particular, existing information is unsatisfactory in explaining why atmospheric  $\text{CH}_4$  is increasing because of significant uncertainties in the estimated rates of production and consumption of  $\text{CH}_4$  in many natural environments. For example, wetlands and the oceans have long been known to be sources of  $\text{CH}_4$  to the atmosphere [e.g., Ehhalt, 1974] but processes controlling the origins and distribution of  $\text{CH}_4$  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  $\text{CH}_4$  cycle.

The presence of elevated dissolved  $\text{CH}_4$  concentrations in rivers and bays has been noted ever since the first  $\text{CH}_4$  measurements were made in aquatic systems [e.g., Lamontagne et al., 1973]. It has been established that even rivers without anthropogenic sources of  $\text{CH}_4$  have dissolved  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  ( $\delta^{13}\text{C}-\text{CH}_4$ ) in a system is dependent on the mechanisms and rates of  $\text{CH}_4$  production and consumption and thus can be useful in efforts to elucidate  $\text{CH}_4$  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  $\text{CH}_4$  sources are important parameters in constraining global atmospheric  $\text{CH}_4$

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Paper number 1999GB900012.

0886-6236/99/1999GB900012\$12.00

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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$ , 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  $\text{CH}_4$  oxidation. Ultimately, such research will allow determination of the mean isotopic signature of  $\text{CH}_4$  released directly to the atmosphere from rivers and estuaries and should aid understanding of the importance of these systems to the oceanic and atmospheric  $\text{CH}_4$  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  $\sim 2.4$  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  $\sim 2.7$  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  $\sim 2.9$  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  $\sim 2.8$  m.

### 2.5. Kaneohe Bay (Figure 1d)

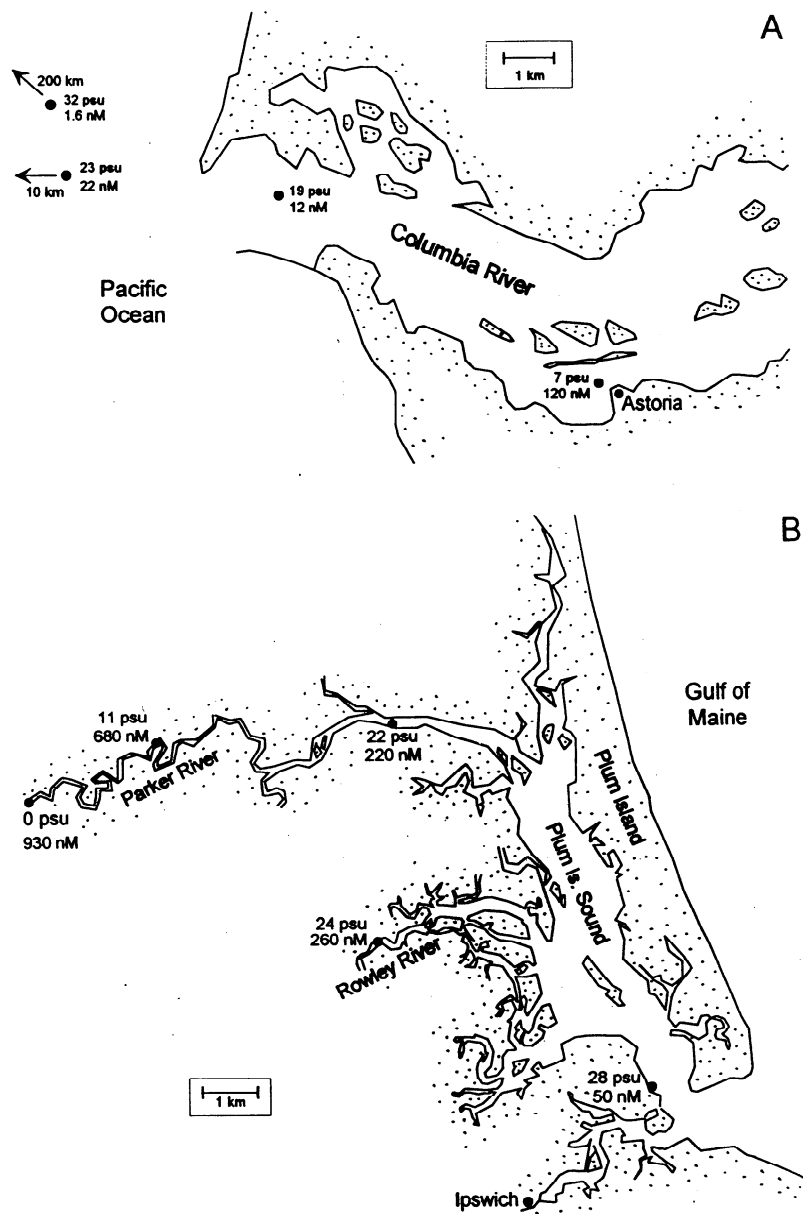
Samples were collected on July 5, 1996, from a stream feeding the bay, two sites from within the south bay, and from the main channel into the bay from the open ocean. The stream drains a suburban watershed and the nearby Koolau mountains. The tidal range in the bay is  $\sim 0.6$  m. The oceanic end-member was collected on July 8, 1997, at Station ALOHA [*Karl and Lukas*, 1996], located in the open ocean  $\sim 125$  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  $\sim 1.8$  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) Kancock Bay, and (e) Elkhorn Slough.

rubber septa. Samples were preserved with saturated  $\text{HgCl}_2$  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 ( $\pm 0.5$  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

Kancock Bay samples was measured ( $\pm 0.05$  psu) using an AGE model 2100 induction salinometer; the salinity of other samples was determined ( $\pm 0.35$  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  $\text{CH}_4$  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  $\text{CH}_4$  mixing ratio of 1.7 ppm

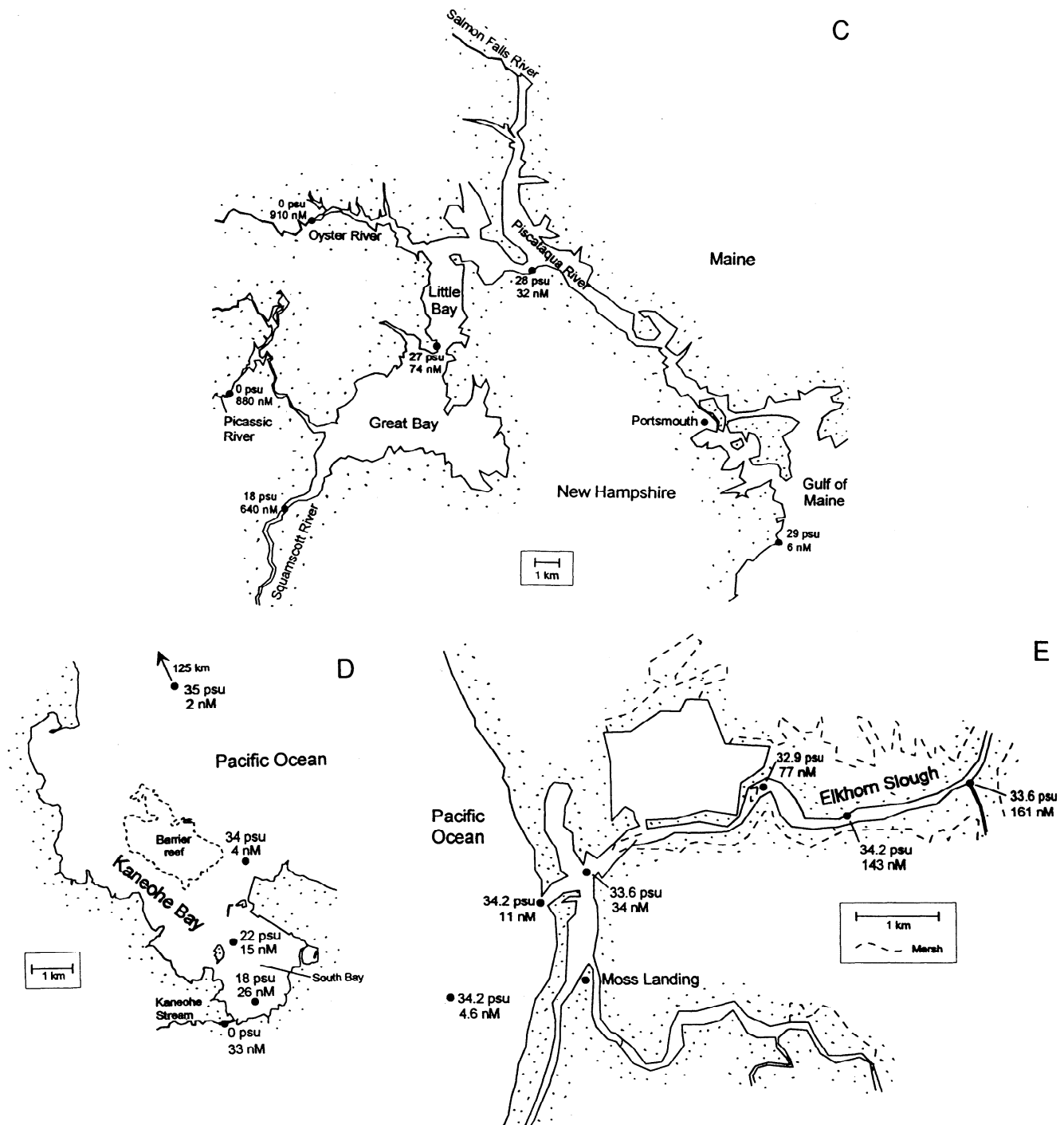


Figure 1. (continued)

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

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

where  $R_{\text{mix}}$  is the isotopic ratio of a river-ocean mixture,  $C_{\text{mix}}$  is the  $\text{CH}_4$  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  $\text{CH}_4$  input to the water column at a given salinity in an estuary, the isotopic composition of the added  $\text{CH}_4$  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  $C_{\text{input}}$ , the  $\text{CH}_4$  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  $C_{\text{conserv}}$  is the conservative  $\text{CH}_4$  concentration and  $R_{\text{conserv}}$  is the conservative isotopic ratio.

### 4.4. Isotopic Fractionation During Oxidation

In cases in which there was net  $\text{CH}_4$  removal from the water column at a given salinity in an estuary, the apparent biological kinetic isotopic fractionation factor ( $\alpha$ ) for in situ  $\text{CH}_4$  oxidation was calculated assuming first-order kinetics [Coleman *et al.*, 1981]:

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

## 5. Results and Discussion

### 5.1. Estuarine Mixing Diagrams

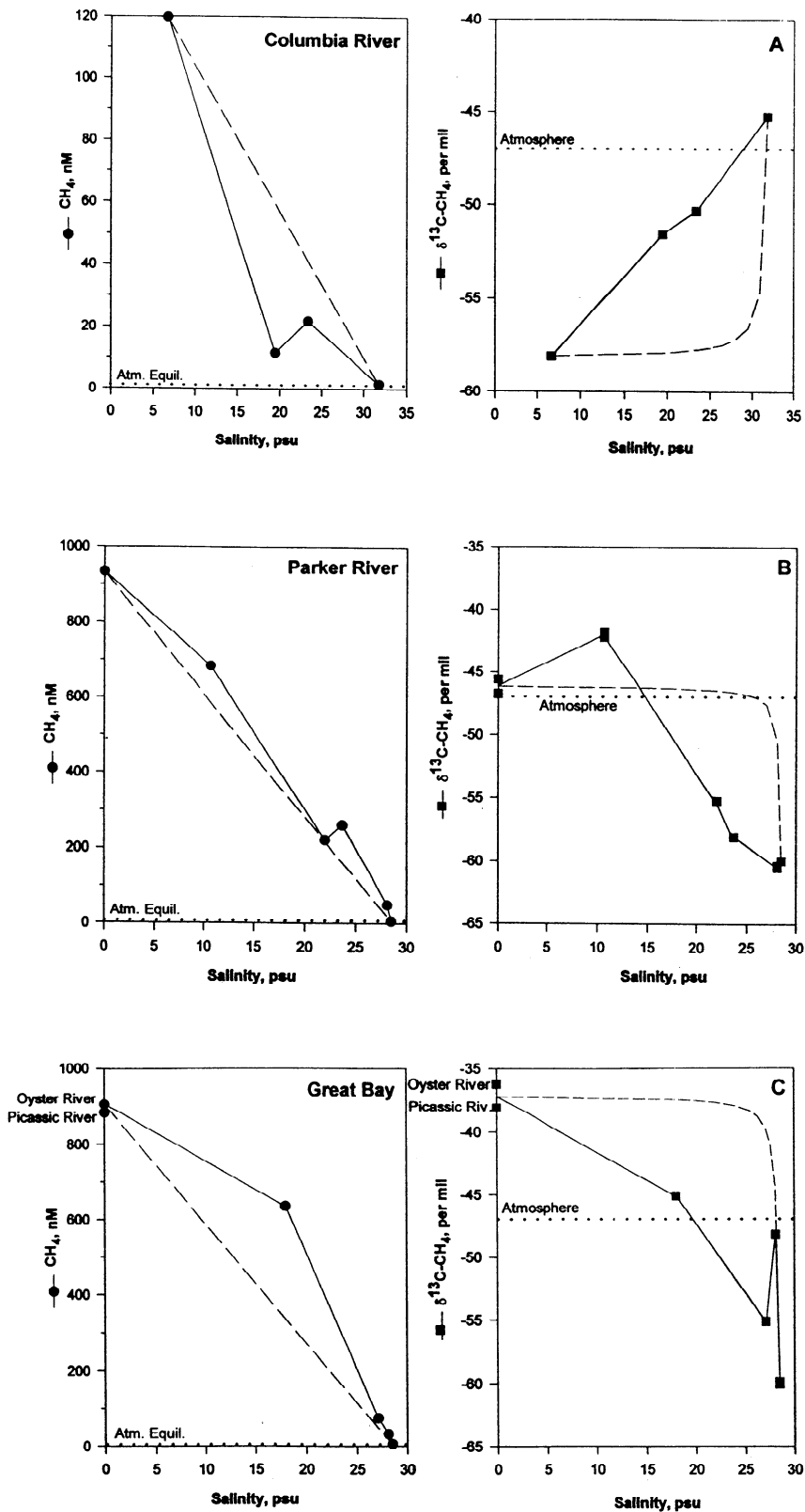
Of the six estuaries discussed here, the Columbia River (Figure 1a) is the most advective, with its large river flow dominating the estuary's hydrodynamics. At the other extreme are the Parker River (Figure 1b) and Elkhorn Slough (Figure 1e), both of which have relatively small, disperse freshwater inputs. 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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$ , 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  $\text{CH}_4$  concentration below the conservative mixing line between salinities of 7 and 23 psu suggests that  $\text{CH}_4$  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<sup>-1</sup> and calculated a water-to-air flux of 6-20 mg m<sup>-2</sup>d<sup>-1</sup> (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,  $\text{CH}_4$  in the Columbia River does not exhibit conservative isotopic behavior: The two midestuary samples are enriched in <sup>13</sup>C relative to corresponding points on the conservative mixing curve. Methane oxidation is likely to be the cause of this nonconservative behavior because (1) the  $\text{CH}_4$  concentrations in these samples are less than expected from conservative mixing and (2) oxidation would result in residual  $\text{CH}_4$  with  $\delta^{13}\text{C}-\text{CH}_4$  values less negative than the source  $\text{CH}_4$  [e.g., Barker and Fritz, 1981]. To test this hypothesis, apparent  $\text{CH}_4$  oxidation kinetic isotopic fractionation factors ( $\alpha$ , 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  $\text{CH}_4$  oxidation within this reach of the river.

The lack of net  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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 CH<sub>4</sub> concentration and δ<sup>13</sup>C-CH<sub>4</sub> versus salinity: (a) Columbia River, (b) Parker River (1996 data), (c) Great Bay (1996 data), (d) Kanoche Bay, and (e) Elkhorn Slough. The dotted lines indicate the air-equilibrated CH<sub>4</sub> concentrations at the in situ concentration and salinity (see text) and the approximate δ<sup>13</sup>C-CH<sub>4</sub> value for the atmosphere [Quay *et al.*, 1991]. The dashed lines indicate the computed conservative mixing lines for CH<sub>4</sub> concentration and δ<sup>13</sup>C-CH<sub>4</sub> (see text).

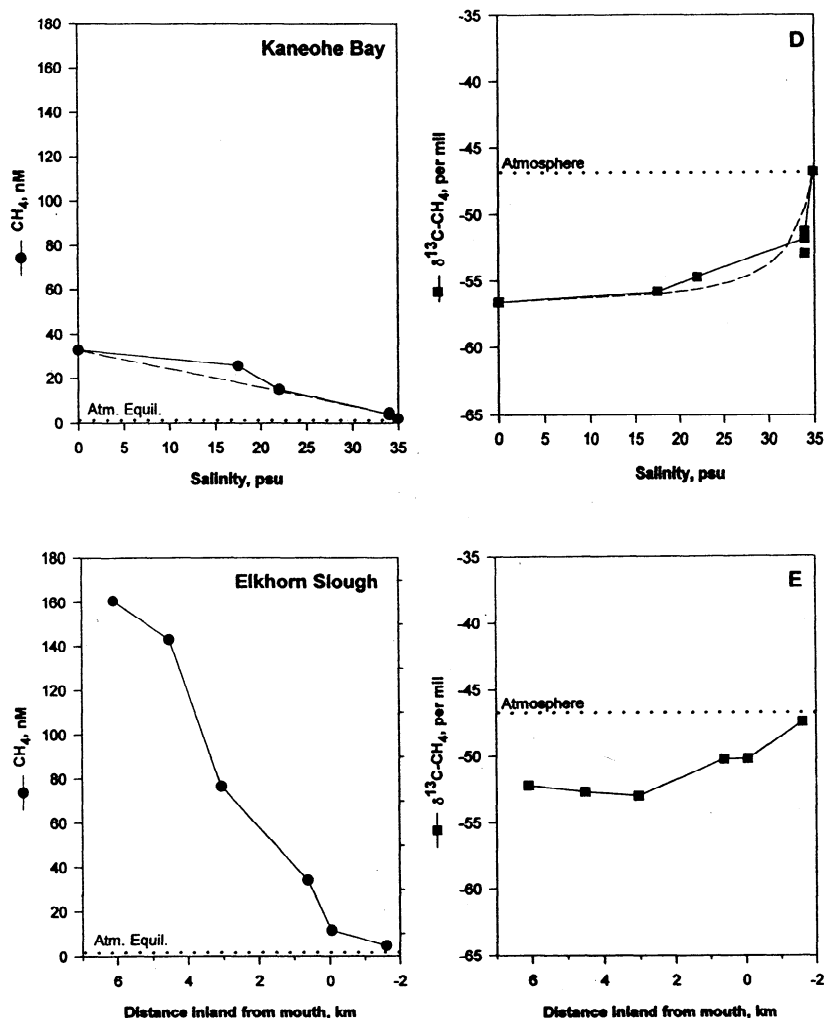


Figure 2. (continued)

**5.1.2. Parker River.** The Parker River (Figure 2b) is a marked contrast to the Columbia River in several respects. First, the CH<sub>4</sub> concentration in the Parker's freshwater end-member is much higher (930 nM, the highest measured in this study), and its δ<sup>13</sup>C-CH<sub>4</sub> 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 CH<sub>4</sub> is subject to oxidation, and consequent isotopic fractionation, before reaching the pond. Alternatively, the methanogens in this system may be using a <sup>13</sup>C-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 CH<sub>4</sub> within the Gulf to significantly influence the Gulf's CH<sub>4</sub> pool.

Although the nearly linear concentration relationship in the mixing diagram indicates apparent conservative mixing of CH<sub>4</sub> across the estuary, this interpretation is not consistent with the isotopic mixing curve. The observed upper-estuary (11 psu)

maximum in δ<sup>13</sup>C-CH<sub>4</sub> indicates the presence of an input of isotopically heavy CH<sub>4</sub>. If this was due to an input with a salinity of 11 psu, equation (2) would predict the δ<sup>13</sup>C-CH<sub>4</sub> 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 CH<sub>4</sub> that is evident from the deviation of the isotopic mixing diagram from conservative behavior at a salinity of 24 psu. The calculated δ<sup>13</sup>C-CH<sub>4</sub> value of the added CH<sub>4</sub> 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 CH<sub>4</sub> [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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  inputs. The calculated  $\delta^{13}\text{C}-\text{CH}_4$  values of the added  $\text{CH}_4$  are -53.6 and -86.3 per mil for the 18 and 27 psu samples, respectively; the latter may be from direct  $\text{CH}_4$  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  $\text{CH}_4$  input.

**5.1.4. Kaneohe Bay.** Kaneohe Bay shows the most conservative behavior of the systems studied, both with respect to  $\text{CH}_4$  concentration and isotopic signature (Figure 2d). This estuary also has the smallest  $\text{CH}_4$  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  $\text{CH}_4$  concentration of the Kaneohe end-member is only a quarter of that in the Columbia River. In both estuaries, the  $\text{CH}_4$  signatures of the freshwater end-members presumably reflect the effects of  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  concentration and location along the estuary.

The oceanic end-member is in near-equilibrium with atmospheric  $\text{CH}_4$  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  $\text{CH}_4$  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 $\text{CH}_4$ Released to the Atmosphere

All of the estuaries examined in this study showed large supersaturations in  $\text{CH}_4$ ; it is therefore not surprising that the release of  $\text{CH}_4$  to the atmosphere from rivers and estuaries is considered potentially important to global  $\text{CH}_4$  budgets [e.g., Quay *et al.*, 1988, Lilley *et al.*, 1996]. Thus a knowledge of the stable carbon isotopic signature of this global  $\text{CH}_4$  flux would be of use in attempts to constrain global  $\text{CH}_4$  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  $\text{CH}_4$  concentrations and isotopic values observed suggests that accurately estimating the global flux using an isotopic balance will be difficult.

The  $\text{CH}_4$  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  $\text{CH}_4$  and occurred at relatively low concentrations. In contrast,  $\text{CH}_4$  in the Parker River and Great Bay freshwater end-members (-36 to -46 per mil) was much heavier than atmospheric  $\text{CH}_4$  and occurred at quite high concentrations. Finally, the Merrimack displayed properties between these two extremes, with a  $\text{CH}_4$  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  $\text{CH}_4$  production.

These differences likely reflect differences in the fate of  $\text{CH}_4$  from its source to the sampling site. Lilley *et al.* [1996] hypothesized that the bulk of the  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  oxidation, although even after this removal there are high levels of  $\text{CH}_4$  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  $\text{CH}_4$  production within the reservoir's sediments would contribute light  $\text{CH}_4$  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  $\text{CH}_4$  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 <sub>4</sub> , nM	δ <sup>13</sup> C-CH <sub>4</sub> , per mil	Salinity, psu	CH <sub>4</sub> , nM	δ <sup>13</sup> C-CH <sub>4</sub> , 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 CH<sub>4</sub>, with δ<sup>13</sup>C-CH<sub>4</sub> 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 CH<sub>4</sub>. The very heavy riverine δ<sup>13</sup>C-CH<sub>4</sub> values in the Parker River, Great Bay, and the Salmon Falls River, however, indicate that the source of CH<sub>4</sub> in the offshore water (which is much lighter than the CH<sub>4</sub> 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 CH<sub>4</sub>. 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> concentration/isotope approach to understanding estuarine CH<sub>4</sub> dynamics. This approach is a useful technique for understanding CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> concentration and δ<sup>13</sup>C-CH<sub>4</sub>. In the Columbia River estuary, there was loss of riverine CH<sub>4</sub> coupled with shifts to more positive isotopic values, apparently the result of in situ CH<sub>4</sub> oxidation; this oxidation exhibited an apparent kinetic isotopic fractionation factor of 1.0042-1.012.

Water at the mouths of the estuaries had CH<sub>4</sub> 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 CH<sub>4</sub> to the ocean. However, as for the freshwater end-members, the isotopic composition of this CH<sub>4</sub> will vary between systems. The effect of estuarine CH<sub>4</sub> on the isotopic composition of the nearshore ocean will likewise be site specific, as there is wide variability in the δ<sup>13</sup>C-CH<sub>4</sub> 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 CH<sub>4</sub> 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, CH<sub>4</sub> in the surface of shallow shelf waters can become isotopically depleted in <sup>13</sup>C, 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 CH<sub>4</sub> 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 CH<sub>4</sub> in these highly dynamic systems

**Acknowledgments.** We thank Steve Smith and Xiyuan Wen for discussions on data interpretation. Sample collections would have been impossible without the assistance of Linda Deegans and Chuck Hopkinson (Marine Biological Laboratory), Mike Prince (Moss Landing Marine Laboratory), and the crew of the R/V *Atlantis II*. This research was supported by the U.S. Office of Naval Research (grant N00014-94-1-0631) and the U.S. National Science Foundation (grant OCE-9504251). University of Hawaii, School of Ocean and Earth Science and Technology contribution no. 4756.

## References

- Barker, J.F., and P. Fritz, Carbon isotope fractionation during microbial methane oxidation, *Nature*, 293, 289-291, 1981.
- Bartlett, K.B., R.C. Hariss, and D.I. Sebacher, Methane flux from coastal salt marshes, *J. Geophys. Res.*, 90, 5710-5720, 1985.
- Bathen, K.H., A descriptive study of the physical oceanography of Kaneohe Bay, Oahu, Hawaii, *Tech. Rep. 14*, 353 pp. Univ. of Hawaii, Hawaii Inst. Mar. Biol., 1968.
- Burke, R.A., Jr., and W.M. Sackett, Stable hydrogen and carbon isotopic compositions of biogenic methanes from several shallow aquatic environments, in *Symposium on Organic Marine Geochemistry*, edited by M.L. Sohn, pp. 297-313, Am. Chem. Soc., Washington, D.C., 1986.
- Chanton, J.P., and C.S. Martens, Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary, *Global Biogeochem. Cycles*, 2, 289-298, 1988.
- Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, 2, 299-327, 1988.
- Coleman, D.D., J.B. Risatti, and M. Schoell, Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria, *Geochim. Cosmochim. Acta*, 45, 1033-1037, 1981.
- Craig, H., Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, 12, 133-149, 1957.
- de Angelis, M.A., and M.D. Lilley, Methane in surface waters of Oregon estuaries and rivers, *Limnol. Oceanogr.*, 32, 716-722, 1987.
- Devol, A.H., J.E. Richey, S.L. King, J. Lansdown, and L.A. Martinelli, Seasonal variation in the <sup>13</sup>C-CH<sub>4</sub> of Amazon floodplain waters, *Mitt. Internat. Verein. Limnol.*, 25, 173-178, 1996.
- Dlugokencky, E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L.P. Steele, and E.G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the Northern Hemisphere during 1992, *Geophys. Res. Lett.*, 21, 45-48, 1994.
- Ehhalt, D. H. The atmospheric cycle of methane, *Tellus*, 26, 58-70, 1974.
- Etheridge, D.M., G.I. Pearman, and P.J. Fraser, Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, *Tellus, Ser. B.*, 282-294, 1992.
- Fuex, A.N., Experimental evidence against an appreciable isotopic fractionation of methane during migration, *Phys. Chem. Earth*, 12, 725-732, 1980.
- Games, L.M., and J.M. Hayes, On the mechanisms of CO<sub>2</sub> and CH<sub>4</sub> production in natural anaerobic environments, in *Environmental Biogeochemistry: Proceedings of the 2nd International Symposium on Environmental Geochemistry*, edited by J.O. Nriagu, pp. 51-73, Ann Arbor Sci., Ann Arbor, Mich., 1975.
- Happell, J.D., J.P. Chanton, G.J. Whiting, and W.J. Showers, Stable isotopes as tracers of methane dynamics in Everglades marshes with and without active populations of methane oxidizing bacteria, *J. Geophys. Res.*, 98, 14,771-14,782, 1993.
- Harriss, R.C., D.I. Sebacher, and F.P. Day, Methane flux in the Great Dismal Swamp, *Nature*, 297, 673-674, 1982.
- Hein, R., P.J. Crutzen, and M. Heimann, An inverse modeling approach to investigate the global atmospheric methane cycle, *Global Biogeochem. Cycles*, 11, 43-76, 1997.
- Jones, R.D., and J.A. Amador, Methane and carbon monoxide production, oxidation, and turnover times in the Caribbean Sea as influenced by the Orinoco River, *J. Geophys. Res.*, 98, 2353-2359, 1993.
- Karl, D.M., and R. Lukas, The Hawaii Ocean Time-series (HOT) program: Background, rationale and field implementation, *Deep Sea Res.*, 43, 129-156, 1996.
- Khalil, M.A., R.A. Rasmussen, and M.J. Shearer, Trends of atmospheric methane during the 1960s and 1970s, *J. Geophys. Res.*, 94, 18,279-18,288, 1989.
- King, G.M., and W.J. Wiebe, Methane release from soils of a Georgia salt marsh, *Geochim. Cosmochim. Acta*, 42, 343-348, 1978.
- Lamontagne, R.A., J.W. Swinnerton, V.J. Linnenbom, and W.D. Smith, Methane concentrations in various marine environments, *J. Geophys. Res.*, 78, 5317-5324, 1973.
- Lansdown, J.M., P.D. Quay, and S.L. King, CH<sub>4</sub> production via CO<sub>2</sub> reduction in a temperate bog: A source of <sup>13</sup>C-depleted CH<sub>4</sub>, *Geochim. Cosmochim. Acta*, 56, 3493-3503, 1992.
- Lelieveld, J., P.J. Crutzen, and C. Brühl, Climate effects of atmospheric methane, *Chemosphere*, 26, 739-768, 1993.
- Lilley, M.D., M.A. de Angelis, and E.J. Olson, Methane concentrations and estimated fluxes from Pacific Northwest rivers, *Mitt. Internat. Verein. Limnol.*, 25, 187-196, 1996.
- Lyons, W.B., and H. E. Gaudette, Sulfate reduction and the nature of organic matter in estuarine sediments, *Org. Geochem.*, 1, 151-155, 1979.
- Martens, C.S., N.E. Blair, C.D. Green, and D.J. Des Marais, Seasonal variations in the carbon isotopic composition of biogenic methane in a coastal sediment, *Science*, 233, 1300-1302, 1986.
- Officer, C.B., and D.R. Lynch, Dynamics of mixing in estuaries, *Estuarine Coastal Shelf Sci.*, 12, 525-533, 1981.
- Popp, B.N., F.J. Sansone, T.M. Rust, and D.A. Merritt, Rapid method for determining abundance and carbon isotopic composition of dissolved methane in sediments and nearshore waters, *Anal. Chem.*, 67, 405-411, 1995.

- M. Prather, R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1994: Relative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios.*, edited by J.T. Houghton et al., pp. 73-126, Cambridge Univ. Press, New York, 1995.
- Quay, P.D., S.L. King, J.M. Lansdown, and D.O. Wilbur, Isotopic composition of methane released from wetlands: Implications for the increase in atmospheric methane, *Global Biogeochem. Cycles.*, 2, 385-397, 1988.
- Quay, P.D., et. al., Carbon isotopic composition of atmospheric CH<sub>4</sub>: fossil and biomass burning strengths. *Global Biogeochem. Cycles.*, 5, 25-47, 1991.
- Rasmussen, R. A. and M. A. K. Khalil, Atmospheric methane (CH<sub>4</sub>): Trends and seasonal cycles, *J. Geophys. Res.*, 86, 9826-9832, 1981.
- Reeburgh, W.S., A.I. Hirsch, F.J. Sansone, B.N. Popp, and T.M. Rust, Carbon isotope effect accompanying microbial oxidation of methane in boreal forest soils, *Geochim. Cosmochim. Acta.*, 61, 4761-4767, 1997.
- Sansone, F.J., and C.S. Martens, Methane oxidation in Cape Lookout Bight, N.C., *Limnol. Oceanogr.*, 23, 349-355, 1978.
- Sansone, F.J., and C.S. Martens, Volatile fatty acid cycling in organic-rich marine sediments, *Geochim. Cosmochim. Acta.*, 46, 1575-1589, 1982.
- Sansone, F.J., B.N. Popp, and T.M. Rust, Stable carbon isotopic analysis of low-level methane in water and gas, *Anal. Chem.*, 69, 40-44, 1997.
- Sansone, F.J., T.R. Rust, and S.V. Smith, Methane distribution and cycling in Tomales Bay, California, *Estuaries*, 21, 66-77, 1998.
- Sass, R.L., F.M. Fisher, F.T. Turner, and M.F. Jund, Methane emission from rice fields as influenced by solar radiation, temperature, and straw incorporation, *Global Biogeochem. Cycles.*, 5, 335-350, 1991.
- Schoell, M., The hydrogen and carbon isotopic composition of methane from natural gases of various origins, *Geochim. Cosmochim. Acta.*, 44, 649-661, 1980.
- Sieburth, J.M., Methane and hydrogen sulfide in the pycnocline: A result of tight coupling of photosynthetic and "benthic" processes in stratified waters, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes*, edited by J.E. Rogers and W.B. Whitman, pp. 147-174, Amer. Soc. Microbiol., Washington, D.C., 1991.
- Spiker, E.C., The behavior of <sup>14</sup>C and <sup>13</sup>C in estuarine water: Effects of *in situ* CO<sub>2</sub> production and atmospheric exchange, *Radiocarbon*, 22, 647-654, 1980.
- Tans, B.P., A note on isotopic ratios and the global atmospheric methane budget, *Global Biogeochem. Cycles.*, 11, 77-81, 1997.
- Tsurushima, N., S. Watanabe, and S. Tsunogai, Methane in the East China Sea water, *J. Oceanogr.*, 52, 221-233, 1996.
- Watanabe, S., N. Higashitani, N. Tsurushima, and S. Tsunogai, Annual variation of methane in seawater in Funka Bay, Japan, *J. Oceanogr.*, 50, 415-421, 1994.
- Watson, R.T., L.G. Meira Filho, E. Sanhueza, and A. Janetos, Greenhouse gases: sources and sinks, in *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, edited by J.T. Houghton, B.A. Callander, and S.K. Varney, pp. 25-46, Cambridge Univ. Press, Washington D.C., 1992.
- Wen, X., J.P. Cowen, R. Thompson, B. Popp, and F. Sansone, Methane carbon isotopic fractionation and composition at the Endeavor Segment hydrothermal system in the northeastern Pacific Ocean, *Eos Trans. AGU* 77(46), Fall Meet. Suppl., F404-F405, 1996.
- Whiticar, M.J., E. Farber, and M. Schoell, Biogenic methane formation in marine and freshwater environments: CO<sub>2</sub> reduction vs. acetate fermentation: Isotopic evidence, *Geochim. Cosmochim. Acta.*, 50, 693-709, 1986.
- Wilkness, P.E., R.A. Lamontagne, R.E. Larson, and J.W. Swinnerton, Atmospheric trace gases and land and sea breezes at the Sepik River coast of Papua New Guinea, *J. Geophys. Res.*, 83, 3672-3674, 1978.
- Yamamoto, S., J. B. Alcauskas, and T.E. Crozier, Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data.*, 21, 78-80, 1976.

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(Received May 18, 1998; revised January 7, 1999; accepted February 8, 1999)