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Basin-wide estimates of the input of methane from seeps and clathrates to the Black Sea

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Abstract

Numerous methane-emitting bottom features, such as seeps, methane clathrate hydrates (clathrates), and mud volcanoes, have been identified recently in the Black Sea. The fluxes of methane from these sources averaged over large spatial scales are unknown. Here we take advantage of the fact that the Black Sea is a semi-enclosed basin with restricted deep water circulation to establish first-order estimates of basin-wide fluxes of methane from these sources to the water column and atmosphere. First, we measured the natural radiocarbon content of methane (^{14}C–CH_4) dissolved in the water column and emitted from seeps. The ^{14}C–CH_4 results showed that the dominant source of methane to the water column is emitted from seeps and a smaller source is diagenetically produced in relatively modern sediments. The ^{14}C–CH_4 results were then used to partition a basin-wide total methane budget; this analysis estimated the basin-wide flux of methane from seeps and clathrates to the water column to be 3.60 to 4.28 Tg yr^{-1}. Second, a geochemical box model was used to calculate possible distributions of methane inputs from seeps and clathrates as well as provide additional estimates of the basin-wide flux of methane from seeps and clathrates to the water column (4.95 to 5.65 Tg yr^{-1}).

Keywords: methane; seeps; methane clathrate hydrates; Black Sea; methane radiocarbon; seep methane flux

1. Introduction

As the world's largest anoxic basin, the Black Sea has been the site of numerous studies on methane (CH_4) biogeochemistry (e.g. [1–14]). Concentration and oxidation rate measurements of CH_4 dissolved in the water column and sediments [1–6] have been used to assemble CH_4 geochemical budgets for the entire Black Sea [1] and the north-western shelf [5]. These studies indicate that the Black Sea is the largest surface water reservoir of dissolved CH_4 (96 Tg) of which 0.066 Tg yr^{-1} are emitted into the atmosphere [1].

During the last decade, numerous seeps and mud volcanoes, emitting or capable of emitting CH_4, have been identified on the shelf and slope of the northern Black Sea [7–11]. Methane clathrate hydrates (clathrates), an important global CH_4 reservoir estimated to contain over 10^3 times more CH_4 than the atmosphere [15], are also present in deep Black Sea sediments [11,12], and represent an unknown CH_4 source. The stability of clathrates is governed by pressure, temperature, and CH_4 concentration

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[16–19]. Even in a pressure–temperature zone where clathrates are stable, a clathrate will decompose if the water surrounding it contains a CH_4 concentration below what is necessary to form clathrates. This condition is not met for clathrates outcropping at the seafloor and in some sediments. While a few direct observations of individual seeps have led to a regional estimate of fluxes of CH_4 from seeps to the atmosphere [7], there are no estimates of the quantity of CH_4 contributed to the entire Black Sea by these sources. Recent discoveries of globally distributed seeps suggest that CH_4 released from seeps and clathrates may play a role in the global and oceanic CH_4 budget [10,20,21] and climate change [22–24]. One of the limitations to understanding the role of these reservoirs in global carbon cycles and climate change is that there have been few attempts to extend individual observations to larger spatial scales.

Here we present first-order estimates for basin-wide fluxes of CH_4 from seeps and clathrates to the water column and atmosphere in the Black Sea. To estimate these basin-wide fluxes, we conducted both measurement and modeling studies, which give similar results. The measurement studies involved two main investigations. First, the total source of CH_4 into the waters of the Black Sea was determined. If the concentration of CH_4 in the waters of the Black Sea is in steady-state, then the total source of CH_4 to water column is balanced by the total sink of CH_4 from the water column. Reeburgh et al. [1] quantified the magnitudes of the sinks of CH_4 from the waters of the Black Sea (Table 2) and we present $\delta^{13}C$–CH_4 data that suggests that the CH_4 concentration is in steady-state. Second, the total source of CH_4 into the waters of the Black Sea was partitioned between a) CH_4 that is released from seeps and decomposing clathrates and b) CH_4 that is produced diagenetically in relatively modern sediments and released to the water column. We measured the natural radiocarbon content of CH_4 (^{14}C–CH_4) in the Black Sea (Fig. 1, Table 1) and performed a ^{14}C–CH_4 isotope mass balance to determine the fraction of CH_4 emitted to the water column that is from seeps and decomposing clathrates. (Previous ^{14}C–CH_4 measurements from seeps and clathrates show that they are both devoid of natural radiocarbon [25–27], so radiocarbon measurements cannot distinguish between CH_4 released from seeps and clathrates; for brevity, we use the term "seep" to apply to both.) This fraction was multiplied by the total source of CH_4 to the Black Sea, resulting in an estimate of the flux of CH_4 from seeps to the water column (3.60 to 4.28 Tg CH_4 yr^{-1}) and atmosphere (0.05 to 0.21 Tg CH_4 yr^{-1}).

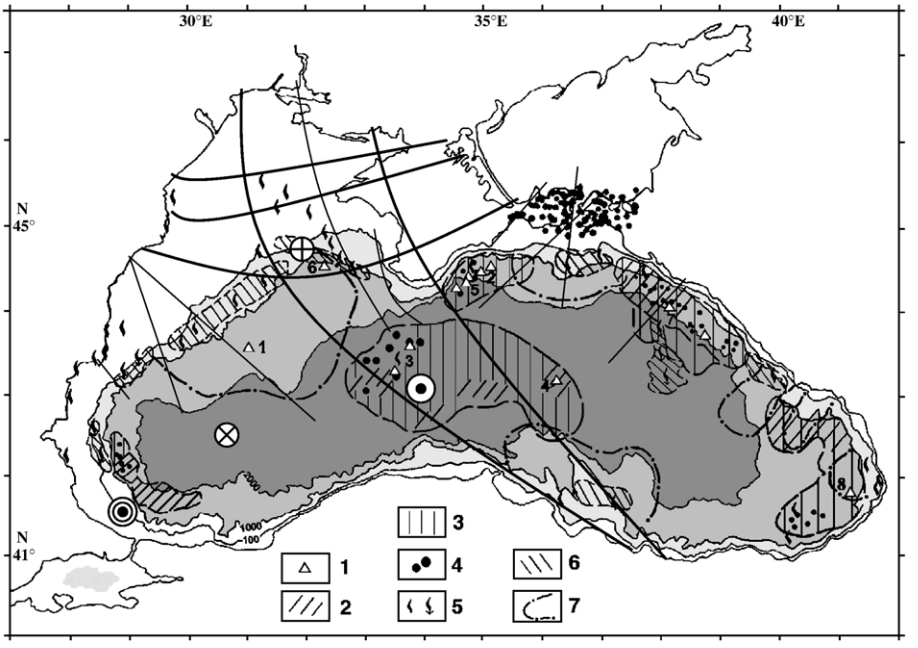

Fig. 1. Black Sea sampling locations and deep faults. (⊙) July 1988 sample site (CH_4 concentration, CH_4 oxidation rates, and $\delta^{13}C$–CH_4) [1,50]; (◎) July 1988 shelf sample site (CH_4 concentration in sediment); (⊗) May 2001 sample site (water column: CH_4 concentration, $\delta^{13}C$–CH_4, ^{14}C–CH_4); and (⊕) September 2004 sample site (seep gas collection). The map is from Vassilev and Dimitrov [12] with the following symbols: (1) Gas hydrate sampling (see Table 1 in Vassilev and Dimitrov [12] for numbering); (2) areas with seismic indications of gas hydrates; (3) areas of high gas hydrates prospect; (4) mud volcanoes; (5) areas of intensive fluid discharging; (6) gas seepage and seabed pockmarks; (7) mine submarine fans. The solid lines are deep faults interpolated after Kutas et al. [64].

Table 1
Sampling stations and measurements

Station	Location	Water depth (m)	Sampling date	Measurements	Purpose
Central basin	43°05′N, 34°00′E	2200	July, 1988 [1,50]	*Water column:* CH_4 concentration, AOM rates, and $\delta^{13}C$–CH_4 *Sediment:* CH_4 concentration and AOM rates	Estimating total Black Sea CH_4 budget
Shelf Station	41°35.5′N, 28°56.92′E	170	July, 1988 [1]	*Sediment:* CH_4 concentration	
Western basin	42°30.21′N, 30°45.21′E	2100	May–June, 2001	*Water column:* CH_4 concentration, $\delta^{13}C$–CH_4 and ^{14}C–CH_4	Determining the sources of CH_4 to the water column to partition the Black Sea total CH_4 budget
N.W. Shelf	44°46.48′N, 31°59.42′E	222	September, 2004	*Seep:* $\delta^{13}C$–CH_4 and ^{14}C–CH_4	

The modeling studies involved modifying a time-dependent geochemical box model [28] to include a source term for CH_4 emitted from seeps and adhere to the parameters of the Black Sea. The modeling results estimate depth distributions and magnitudes (4.95 to 5.65 Tg CH_4 yr^{-1}) of the input of CH_4 from seeps to the water column.

2. Results and discussion

2.1. Measuring the flux of methane from seeps

2.1.1. Total methane budget

The total Black Sea CH_4 budget was assembled from CH_4 concentration and anaerobic oxidation of CH_4 (AOM) rate measurements made during the 1988 U.S.-Turkey Black Sea Expedition [1] (Table 1). Measurements of CH_4 dissolved in the water column (concentration and AOM rates) were restricted to a central station (43°05′N, 34°00′E, 2200 m depth) well-removed from shelves, and were intended to represent a basin-wide integration of processes affecting the Black Sea CH_4 distribution and budget. Distributions of CH_4 concentration in sediment cores were measured at a shelf station (41°35.5′N, 28°56.92′E, 170 m depth) and a deep station (43°04.82′N, 33°58.88′E, 2212 m depth) (Fig. 1). Water column profiles of CH_4 concentration and AOM rates were assumed to represent average Black Sea values so that a first-order estimate of the Black Sea CH_4 budget could be established. This budget was based on the following sinks of CH_4: measured water column and sediment rates of AOM, calculated gas evasion rates to the atmosphere, and export by the Bosporus outflow (Table 2). Reeburgh et al. [1] determined that the dominant sink of CH_4, AOM in the water column, is about 70-fold larger than the next largest sink of CH_4, evasion at the air : sea interface.

This budget assumed that the CH_4 concentration in the waters of the Black Sea is in steady-state [1], so the total loss of CH_4 must be balanced with a CH_4 source of the same magnitude (Table 2). Only CH_4 produced diagenetically in sediments was considered a source in the original budget [1]. Thermodynamic arguments indicate that there can be no large-scale production of CH_4 in the water column so long as sulfate reduction is occurring [1,29,30]. Measurements by Albert et al. [31] show that sulfate reduction occurs in the water column of the Black Sea at nM day^{-1} rates, so we conclude that large-scale methanogenesis cannot occur in the anoxic Black Sea water column. A minor contribution of CH_4 to the water column may be from zooplankton guts and

Table 2
Black Sea total methane budget [1]

	Tg CH_4 yr^{-1}
Sinks	
Evasion at the air : sea interface	
Rate: 9.7 mmol m^{-2} yr^{-1}	0.066
Extent: 4.23×10^{11} m^2	
Water column oxidation	
Upper 100 m (aerobic/anaerobic)	
Rate: 0.36 nM yr^{-1}	3.0×10^{-4}
Extent: 5.3×10^{16} L	
Below 100 m (anaerobic)	
Rate: 0.6 μM yr^{-1}	4.65
Extent: 4.8×10^{17} L	
Oxidation by abyssal sediments	
Rate: 0.1 mmol m^{-2} yr^{-1}	3.7×10^{-4}
Extent: 2.3×10^{11} m^2	
Outflow at Bosporus	
Rate: 1.9×10^{14} L yr^{-1}	3.0×10^{-5}
Extent: 10 nM	
Sources	
Shelf/slope sediments (100–1500 m)	
Rate: 0.2 mol m^{-2} yr^{-1}	0.35
Extent: 1.1×10^{11} m^2	
Seeps and clathrates (from this study: combined measurement and modeling results)	3.60 to 5.65
Rate: 0.53 to 0.84 mol m^{-2} yr^{-1}	

fecal pellet microenvironments [32–34]. Globally, only nM water column CH_4 concentrations have been reported from these sources [35–42]. Given the relatively high Black Sea water column CH_4 concentrations (μM) (Fig. 2), zooplankton guts and fecal pellet microenvironments likely provide ≤1% of the total source of CH_4 to the water column.

At the shelf station, the CH_4 concentration measured in a sediment core displayed a concave up distribution which shows that AOM is occurring [43]. A small positive CH_4 concentration gradient between the surface sediments and the water column indicates that sediments on the shelf are a source of CH_4 to the water column. In contrast, CH_4 concentrations in sediments at the deep station are lower than in the adjacent overlying waters, indicating that these sediments are consuming CH_4 from the water column. This was confirmed by AOM rate measurements using ^{14}C-labelled CH_4 [1]. The Reeburgh et al. budget assumed that sediments below the anoxic: oxic interface (100 m) and above the continental slope-abyssal plane transition (1500 m) were the source of CH_4 to the water column [1]. Given this source interval, a flux of CH_4 from sediments of 1.5 mol m^{-2} yr^{-1} is needed to balance the sinks and maintain a steady-state CH_4 concentration in the water column. However, they determined the flux of CH_4 from the shelf core to be 0.2 mol m^{-2} yr^{-1} leaving 86.7% of the balancing source flux not quantified [1]. Subsequent measurements of CH_4 concentration profiles in sediment cores [5,6] indicate that the diffusive flux of CH_4 from sediments to the water

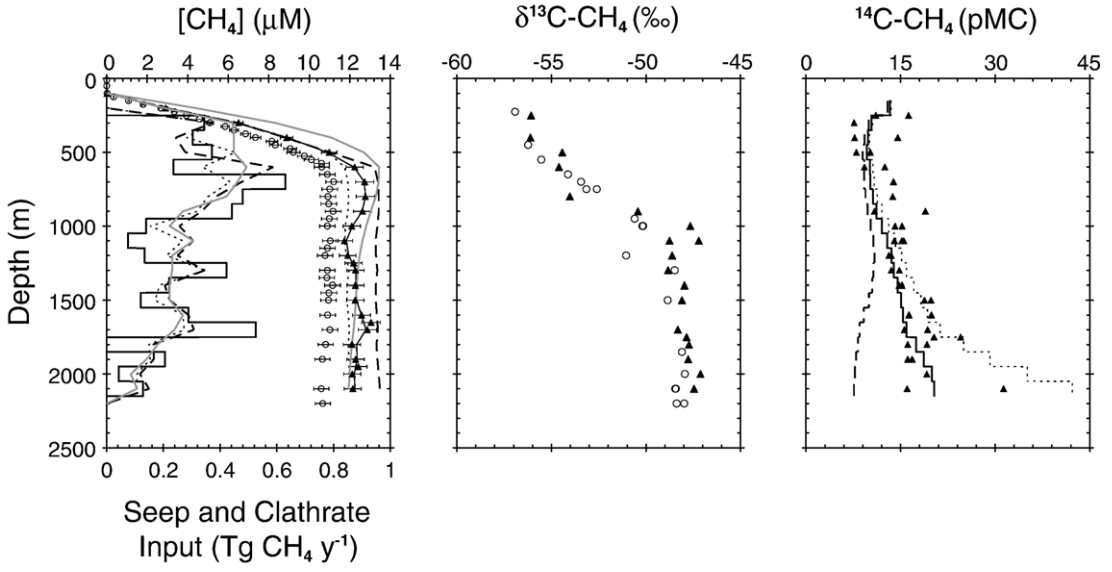

Fig. 2. Measured Black Sea CH_4 concentration (μM) and isotope ($\delta^{13}C$–CH_4 and ^{14}C–CH_4) data in the water column. The $\delta^{13}C$–CH_4 data is expressed vs. VPDB (Vienna Peedee belemnite) standard. The ^{14}C–CH_4 data is expressed as percent Modern Carbon (pMC) [47]. By convention [47], all radiocarbon results are normalized to ^{13}C. Samples were collected in the (○) central Black Sea water column in July 1988 [1,50] and (▲) western Black Sea water column in May 2001. Precision of ±1σ for the: 1) CH_4 concentration measurements is 3–4% based on replicate analyses of samples, 2) $\delta^{13}C$–CH_4 measurements is 0.3‰ based on replicate analyses of standard samples, and 3) ^{14}C–CH_4 measurements is 0.1 pMC. Error bars for the $\delta^{13}C$–CH_4 and ^{14}C–CH_4 measurements are less than the width of the data points. A previously published multi-box model [28] was used to quantify the depth distributions of the inputs of $CH_{4[S]}$ and to provide additional estimates of the basin-wide flux of $CH_{4[S]}$. This model was modified to have box thicknesses of 100 m, to not consider depths less than 150 m due to low water column CH_4 concentrations and oxic conditions in the shallow surface waters, and to match the parameters of the Black Sea (bathymetry and eddy diffusion coefficients). The model was initiated with no CH_4 in the basin and was run for 200 yr to reach steady-state. The inputs of $CH_{4[S]}$ were varied until the modeled CH_4 concentration profile matched the measurements made in year 2001. LEFT PANEL: The model was assigned inputs of $CH_{4[D]}$ (150–1550 m: 0.2 mol m^{-2} yr^{-1}, 1550–2050 m: 0.1 mol m^{-2} yr^{-1}, 2050–2150 m: 0.02 mol m^{-2} yr^{-1}). The following model results are displayed for CH_4 concentration and inputs of $CH_{4[S]}$: (solid black line) model dependent upon the CH_4 concentration data represented by (▲), (dashed line) model dependent upon a uniform CH_4 concentration profile of 13.32 μM below 700 m depth, (dotted line) model dependent upon a uniform CH_4 concentration profile of 11.82 μM below 700 m depth, (solid gray line) model dependent upon average values of CH_4 concentration. The inputs of seep and clathrate CH_4 represented by the dashed, dotted, and solid gray lines are not plotted in histogram style only to increase legibility. RIGHT PANEL: The model was dependent upon the CH_4 concentration data represented by (▲) in the left panel. The solid black line represents the model results with the assigned inputs of $CH_{4[D]}$ used in the left panel. The dashed line represents the model results with the assigned inputs of $CH_{4[D]}$ as suggested by Reeburgh et al. [1]. The dotted line represents the model results with the assigned inputs of $CH_{4[D]}$ as suggested by Reeburgh et al. [1] and with an additional input of 0.2 mol CH_4 m^{-2} yr^{-1} from 2050 to 2150 m.

column may be even smaller. How the CH_4 concentration and AOM rate distributions in the water column are maintained with this small diffusive source of CH_4 from sediments is a major puzzle. The recently reported seeps [7–14] appear to provide the balancing flux of CH_4.

2.1.2. Methane concentration, $\delta^{13}C$, and radiocarbon measurements

Water samples were collected from May 26 to June 3, 2001, on board the *R/V Knorr* within a 4.24 km radius of a station located in the western section of the Black Sea (42°30.21′N, 30°45.21′E, 2100 m) (Table 1, Fig. 1). Concentrations of CH_4 (μM) were measured with a headspace equilibration technique based on Henry's Law. Samples were prepared for seawater CH_4 concentration analyses by filling 120 cc serum vials directly from Niskin bottles. After the seawater vials were sealed with stoppers and crimp caps, a 10 cc headspace of ultrahigh-purity helium was introduced by displacing an equivalent volume of sample. The vials were vigorously shaken and allowed to equilibrate for 12 h. Shipboard CH_4 concentration analyses were performed by analyzing two 5 cc aliquots of the headspace with gas chromatography and flame ionization detection (GC-Mini 2; Shimadzu Corp). The results have been corrected for the amount of CH_4 still dissolved in solution using Bunsen solubility coefficients established by Yamamoto et al. [44] (Fig. 2).

Lamont radon stripping boards [45,46] were modified to quantitatively extract and trap the CH_4 dissolved in seawater for natural isotopic analysis. For each sample, an evacuated 20 L glass carboy was filled with 19 L of seawater directly from Niskin bottles. The carboy was connected to a stripping board which circulated helium through the seawater sample to extract the dissolved CH_4. The extracted CH_4 was trapped at liquid nitrogen temperature in a stainless steel U-trap, filled with a molecular sieve. (Due to low water column concentrations of CH_4 at and above 300 m water depth, CH_4 was extracted from two carboys (38 L) for the shallowest samples.) The traps were returned to UC Irvine where the CH_4 was extracted, purified, and analyzed for the natural content of ^{13}C and radiocarbon. The entire CH_4 collection, extraction, and analysis procedures are quantitative and the backgrounds are small ($0.52_8 \pm 0.39$ μmol of CH_4 with radiocarbon content $^{14}C/C = 96.1 \pm 0.3$ pMC (percent Modern Carbon) [47]) relative to the average sample size (228 μmol). Details of the isotope procedures (apparatus, techniques, blank determinations, precision, and the lack of isotope fractionation) are presented in Kessler and Reeburgh [48].

Gas emitted from seeps was collected from September 10 to 26, 2004, on board the *F/S Poseidon* with the submersible *JAGO*. Gas from five seeps located around 44°46.48′N, 31°59.42′E (average depth of 222 m) was sampled (Table 1, Fig. 1) and the isotope procedures were adapted to analyze the seep gas for $\delta^{13}C$–CH_4 and ^{14}C–CH_4 [48].

Since there are no time-series data for the concentrations of CH_4 at a single station in the Black Sea, we use the $\delta^{13}C$–CH_4 data to test the steady-state assumption in three separate investigations. First, a stable isotope equation, derived to describe an "open-system" where CH_4 is continually added from seeps while simultaneously being removed by reaction, predicts that the Black Sea is in steady-state. When the measured values of $\delta^{13}C$–CH_4 emitted from seeps and dissolved in the water column are input into this equation, along with the isotopic fractionation factors for AOM, this equation predicts that the rate at which CH_4 is input from seeps equals the rate at which CH_4 is removed by reaction [49]. Second, the concentration of CH_4 dissolved in the water column is on average 11.5% higher is the western Black Sea (measured in 2001) than in the central Black Sea (measured in 1988) (Fig. 2). If we assume that the CH_4 concentration values measured in 1988 and 2001 represent average values for the entire basin and not spatial heterogeneities in CH_4 concentration, then the CH_4 concentration has increased by 11.5% over a 13 yr period. This increase in CH_4 inventory would cause the $\delta^{13}C$ of CH_4 dissolved in the water column to decrease by 1.4±0.7‰ over this 13 yr period [49]. While this difference is small, our measurements of $\delta^{13}C$–CH_4 are indistinguishable from those conducted 13 yr ago [50] (Fig. 2). This suggests that the Black Sea is in steady-state with regard to CH_4 and the 11.5% difference between the CH_4 concentration profiles possibly displays the spatial heterogeneities of CH_4 concentration (Figs. 1 and 2). Third, Tans [51] showed that the timescales for changes in the isotope ratio and the large-scale spatial isotopic gradients of a reservoir are often longer than they are for changes in total CH_4 concentration (i.e. isotopic steady-state is reached after concentration steady-state). Since our $\delta^{13}C$-CH_4 results show no temporal (1988 to 2001) or spatial (central to western Black Sea) variation, the steady-state assumption in the Black Sea CH_4 budget [1] may be appropriate. The possibility exists of non-steady-state conditions above the shallow shelves (0–500 m depth) where episodic intrusions of CH_4 from seeps influence the water column CH_4 concentration. However, this region of possible non-steady-state accounts for only 3% of the total volume of the Black Sea [52].

The source of CH_4 dissolved in the Black Sea water column is dominated by CH_4 that is radiocarbon-free (fossil; pMC=0), but also contains a smaller source of CH_4 with relatively modern contents of radiocarbon (Fig. 2). The concentration weighted average of the ^{14}C–CH_4 data in the water column is $15.7_2 \pm 6.7_5$ pMC (Eq. 1).

$$pMC_{Ave} = \frac{\sum([CH_4]_i \times V_i \times pMC_i)}{\sum([CH_4]_i \times V_i)} \quad (1)$$

Here, $[CH_4]_i$, V_i, and pMC_i are the CH_4 concentration, percent volume [52], and ^{14}C–CH_4, respectively, in the depth interval i.

The results of our ^{14}C–CH_4 measurements on gas emitted from seeps were unexpected; all samples of CH_4 emitted from seeps ($CH_{4[S]}$) contain measurable amounts of radiocarbon ($5.0_2 \pm 0.4$ pMC; 24 kA ^{14}C BP (thousand radiocarbon years Before Present)). We have no explanation for this finding; a possible reason why this $CH_{4[S]}$ is not radiocarbon-free is that CH_4, generated from late Eocene source rock [53], acquires CH_4 with modern radiocarbon contents during transit through recently deposited sediments. Gulin et al. [8] indirectly estimated the radiocarbon content of Black Sea $CH_{4[S]}$ assuming that carbonate in structures formed around CH_4 seeps [10] is formed from a mixture of seawater bicarbonate and the product of AOM. Their results (8.5 to 10.6 kA ^{14}C BP or 34.7 to 26.7 pMC) were calculated from measurements of CH_4 ($\delta^{13}C$), seawater bicarbonate ($\delta^{13}C$ and radiocarbon), and the carbonate structures formed around 230 m deep CH_4 seeps ($\delta^{13}C$ and radiocarbon) located ca. 26 km south-east of our seep site. The process of anaerobically oxidizing CH_4 to total CO_2 causes significant isotopic fractionation in both the reactant and the product. Equations describing the isotopic content of the reactant and product were established by Bigeleisen and Wolfsberg [54] and the isotopic fraction factors specific to AOM have been previously quantified [49,55,56]. Gulin et al. [8] did not account for isotopic fractionation caused by AOM and their range of $\delta^{13}C$ values of Black Sea carbonate structures did not include other reports of values up to 10‰ heavier [10,13]. These two factors cause the upper range reported by Gulin et al. [8] to increase to 18.2 kA ^{14}C BP (or 10.4 pMC), and show how sensitive their indirect analysis is to parameter changes.

There are no ^{14}C–CH_4 measurements in the Black Sea of CH_4 produced diagenetically in sediments ($CH_{4[D]}$). However, CH_4 formed at relatively shallow depths in sediments can diffuse into the water column and should contain measurable amounts of radiocarbon (pMC>0) and possibly a radiocarbon content influenced by atmospheric nuclear weapons testing (pMC>100). Recent ^{14}C–CH_4 measurements in the sediments of the Cariaco Basin [57] and Skan Bay, AK [27] show that near-modern radiocarbon values are found in near-surface sediments and the ^{14}C content decreases with depth; this indicates that CH_4 is produced locally and is not dominated by CH_4 diffusing up from deep sediments [55,58]. Previous radiocarbon measurements aimed at determining the Black Sea sediment chronology show that in the interval of 0 to 50 cm depth, the total organic carbon and total carbonate carbon ranges from 105 to 63 pMC [59,60]. Decadal turnover times for $CH_{4[D]}$, determined from concentration and oxidation rate measurements of CH_4 [1,5,6], indicate that $CH_{4[D]}$ likely has a similar radiocarbon signature to its substrates, the total carbon material. Since CH_4 dissolved in the Black Sea water column also has decadal turnover times [1], the ^{14}C–CH_4 results indicate that the source of CH_4 to the water column is a mixture of $CH_{4[S]}$ and $CH_{4[D]}$.

2.1.3. Partitioning the total flux of methane to the water column

To estimate the magnitude of the flux of $CH_{4[S]}$ to the water column, first we determine the fraction of the total source of CH_4 to the water column that is emitted from seeps and then we multiply that fraction by the total flux of Black Sea CH_4 to the water column (4.72 Tg yr^{-1} = sum of the sinks in Table 2). We used a radiocarbon isotopic mass balance to determine the fraction of the total CH_4 source this is emitted from seeps (Eq. 2).

$$pMC_S \times F + pMC_D \times (1-F) = pMC_W \quad (2)$$

Here, F is the fraction of the source of CH_4 that is emitted from seeps and pMC_S, pMC_D, and pMC_W are the ^{14}C–CH_4 contents of $CH_{4[S]}$ ($5.0_2 \pm 0.4$ pMC), $CH_{4[D]}$, and CH_4 dissolved in the water column ($15.7 \pm 6.7_5$ pMC), respectively. We have no direct measurements of the ^{14}C–CH_4 content of $CH_{4[D]}$. Based on radiocarbon measurements of total organic and carbonate carbon in the sediment [59,60], the most likely radiocarbon content of $CH_{4[D]}$ is between 63 and 105 pMC. We have placed conservative bounds on the radiocarbon signature of $CH_{4[D]}$ in the four cases presented in Table 3. This analysis indicates that the basin-wide flux of $CH_{4[S]}$ to the water column is likely between 3.60 and 4.28 Tg CH_4 yr^{-1} (Table 3).

For CH_4 dissolved in the near surface waters of the Black Sea, 0.066 Tg yr^{-1} evade into the atmosphere (Table 2) [1]. The average ^{14}C–CH_4 content in the

Table 3
Estimates of inputs of $CH_{4[S]}$ in the Black Sea based on radiocarbon measurements

Methane Input (Tg yr^{-1})	Assumed $CH_{4[D]}$ percent Modern Carbon (pMC)			
	120	100	75	50
To water column	4.28±0.27	4.19±0.32	4.00±0.42	3.60±0.64
To atmosphere	0.061±0.002	0.060±0.002	0.058±0.003	0.053±0.005

surface 250 m of the water column is 13.7±3.7 pMC. We estimate a range of fluxes of $CH_{4[S]}$ to the atmosphere in the Black Sea (Table 3) for CH_4 dissolved in the near surface waters that evades to the atmosphere (0.05 to 0.06 Tg yr^{-1}); bubbles that enter the atmosphere are not considered in this estimate. Dimitrov [7] found this to be a substantial flux (0.03 to 0.15 Tg CH_4 yr^{-1}) compared with our flux of dissolved CH_4, so to account for the shallow water bubble flux, we adjust the total flux of $CH_{4[S]}$ to the atmosphere in the Black Sea to 0.05 to 0.21 Tg yr^{-1}.

2.2. Modeling the flux of methane from seeps

We apply a time-dependent geochemical box model [28] to the anoxic region (150–2150 m depth) of the Black Sea to quantify the depth distribution of inputs of $CH_{4[S]}$ as well as to provide an additional estimate of the basin-wide input of $CH_{4[S]}$. The model includes a source term for $CH_{4[S]}$, assumes the concentration of CH_4 dissolved in the water column is in steady-state, uses the Black Sea bathymetry [52], and assigns each box a thickness of 100 m. The model incorporates the specific rate of AOM in the water column (0.06 yr^{-1}) [1]. (Rates of AOM in the water column have been shown to increase linearly with CH_4 concentration [61]. Specific rates of AOM are normalized to CH_4 concentration, so that they may be accurately applied to different concentration regions.) Also, the model includes a term for the consumption of CH_4 from the water column by abyssal sediments (0.1 mmol m^{-2} yr^{-1}) (Table 2) [1]. Our multi-box model is one-dimensional (vertical), so the possibility exists that there are regions in the area defined by each box where CH_4 is being inputted to the water column from sediments and separate regions where CH_4 is being consumed from the water column by the sediments. Initially, we assigned inputs of $CH_{4[D]}$ to the water column over the depth interval of 150 to 1550 m, at a rate of 0.2 mol m^{-2} yr^{-1}, as suggested by Reeburgh et al. [1] (Table 2).

The model was initiated with no CH_4 in the Black Sea water column and was run for 200 yr (time step = 0.1 yr), significantly longer than the model predicts is necessary to reach steady-state. The inputs of $CH_{4[S]}$ were varied until the modeled concentrations of CH_4 dissolved in the water column agreed with the year 2001 western Black Sea measurements to less than 0.6% on average. No isotopic data is input into the model, so the newly predicted inputs of $CH_{4[S]}$ and the assigned values of $CH_{4[D]}$ can be used to model a ^{14}C–CH_4 profile in the water column (Fig. 2). This model predicts a ^{14}C–CH_4 profile containing significantly less radiocarbon than our measurements in the deep Black Sea. We conclude that the deep waters of the Black Sea must have an additional source of CH_4 with relatively modern radiocarbon contents. To account for this additional source of relatively "modern" CH_4, we conducted two modeling experiments where we manually increased the deep basin sources of $CH_{4[D]}$ beyond what was suggested by Reeburgh et al. [1] (Fig. 2.).

Inputs of $CH_{4[S]}$ are predicted at most depths between 250 and 2150 m (Fig. 2), consistent with the distribution of known seeps, clathrates, mud volcanoes, and seabed pockmarks (Fig. 1) [8,12,14]. The model-predicted input profile of $CH_{4[S]}$ shows local maxima or minima at 700, 1100, and 1700 m depth consistent with congruent fluctuations in the mean values of CH_4 concentration at similar depths. However, the uncertainty in our concentration measurements is such that a uniform CH_4 concentration profile below 700 m depth is possible. To account for this possibility, we have conducted two additional modeling experiments dependent upon uniform CH_4 concentration values (below 700 m depth) at either the lower end (11.82 μM) or the upper end (13.32 μM) of the standard deviations of our CH_4 concentration measurements. These "uniform CH_4 concentration" models predict more uniform distributions for the inputs of $CH_{4[S]}$ (Fig. 2).

Due to the large predicted inputs of $CH_{4[S]}$, this model is relatively insensitive to the water column eddy diffusion coefficients. Changing the eddy diffusion coefficients from 1 to 4 cm^2 s^{-1} in the anoxic region of the Black Sea only changes the final results by 3.7% on average. Also, $CH_{4[S]}$ released below the clathrate stability zone (700 m) will partially resist dissolution due to the formation of a clathrate mantle around the bubbles [62]. If $CH_{4[S]}$ only dissolved in waters above 700 m depth, eddy diffusion in the water column could not

maintain CH_4 concentration and radiocarbon profiles, so bubbles must dissolve in deep waters or CH_4 must be added in solution.

Averaged over the entire basin, our results indicate that 4.95 to 5.65 Tg yr^{-1} (0.73 to 0.84 mol m^{-2} yr^{-1}) of $CH_{4[S]}$ are being added to the water column. Since this multi-box model is one-dimensional (vertical), it assumes that the CH_4 concentration profile measured in the western Black Sea water column is representative of average values for the entire basin. In *Section 2.1. Measuring the flux of methane from seeps*, we assumed that the CH_4 concentration profile measured in the central Black Sea water column is representative of average values for the entire basin, again to estimate the basin-wide inputs of $CH_{4[S]}$. Since the CH_4 concentration profile measured in the western Black Sea water column is on average 11.5% greater than in the central Black Sea, these separate estimates of the basin-wide inputs of $CH_{4[S]}$ likely bound the true value.

3. Conclusions

The contribution of decomposing clathrates to the global CH_4 budget remains a major uncertainty [63]. Substantial microbial oxidation in adjacent sediments and overlying waters precludes the use of stable isotopes of CH_4 to identify the fraction of CH_4 dissolved in the water column or sediment that is released from clathrates. Rehder et al. [19] measured the rate of dissolution of synthetic CH_4 clathrate in the clathrate stability zone (P, T) in an advecting field of seawater that was undersaturated with respect to CH_4 concentration. Since natural clathrates are usually located within a sediment matrix surrounded by CH_4-rich or CH_4-saturated fluids, the Rehder et al. rates place an upper bound on the decomposing clathrate contribution (11670 ± 950 mol CH_4 m^{-2} yr^{-1}). Presuming the fluxes of $CH_{4[S]}$ estimated in this study are all of clathrate origin, the Black Sea clathrate decomposition rate is 0.53 to 0.84 mol CH_4 m^{-2} yr^{-1}, or 10^5-fold smaller.

In conclusion, we have estimated the basin-wide flux of CH_4 emitted from seeps and decomposing clathrates to the water column and atmosphere in the Black Sea. The radiocarbon results indicate that the flux of CH_4 to the water column is dominated by emissions from seeps and decomposing clathrates. Our measurements and modeling studies indicate that between 3.60 to 5.65 Tg yr^{-1} of CH_4 emitted from seeps and decomposing clathrates enter the Black Sea water column and 0.05 to 0.21 Tg yr^{-1} escape to the atmosphere. These estimates of the fluxes of CH_4 emitted from seeps and decomposing clathrates to the Black Sea may be refined with long term sampling programs; multiple sites can be established characterizing the entire Black Sea where high precision measurements of CH_4 concentration, rates of AOM, and natural isotopes of CH_4 are routinely made.

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