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DETECTION OF METHANE SOURCES ALONG THE CALIFORNIA CONTINENTAL MARGIN USING WATER COLUMN ANOMALIES

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ABSTRACT

Water column methane measurements have been used to understand both the global distribution of methane in the oceans and the local flux of methane from geologic sources on the continental margins, including methane vents and gas-hydrate-bearing sites. We have measured methane concentrations in 1607 water samples collected along the central California continental margin. Methane supersaturation of the surface mixed layer (0-50 msbsl) is widespread and above a well-defined subsurface particle maximum (~50 mbsl) that generally corresponds with the pycnocline. Local production of methane appears to be occurring in the surface mixed layer above the particle maximum and may not be particle-associated. Methane concentrations in water column CTD cast profiles and ROV-collected bottom waters obtained in Partington, Hueneme, Santa Monica, and Redondo submarine canyons increase towards the seafloor and are distinctly higher (up to 186 nM) compared to open-slope and shelf waters at similar depths. These values are in excess of measured surface water methane concentrations and could not be generated by mixing with surface water. Elevated methane concentrations in these submarine canyons and persistent mid-water methane anomalies in Ascension and Ano Nuevo Canyons could result from restricted circulation and/or proximity to gas vents, seafloor exposure of methane gas hydrates, recently-eroded methane-rich sediment, submarine discharge of methane-rich groundwater, or particle-associated methane production. On the Santa Barbara shelf water column methane profiles near known gas vents also increase in concentration with increasing depth. Thus, elevated bottom water methane concentrations observed in submarine canyons may not be diagnostic of proximity to methane vents and may be caused by other processes.

Keywords: methane, water column, submarine canyons, gas vents, turbidity, organic detritus

NOMENCLATURE

AUV Autonomous Underwater Vehicle
cc cubic centimeters
CTD Conductivity Temperature Depth
GC Gas Chromatograph
HOV Human Occupied Vehicle
mbsl meters below sea level
mL milliliters
OD Outside Diameter
nM nanomolar (nanomoles/liter)
ppm parts per million
PTFE Polytetrafluoroethylene (Teflon®)
ROV Remotely Operated Vehicle
SGD Submarine Groundwater Discharge

INTRODUCTION

In the past few decades the existence of widespread methane venting from the seafloor along continental margins around the world has become well established. Methane venting is now considered to be a process capable of rapidly transferring large amounts of methane carbon from geologic to oceanographic and atmospheric reservoirs [1]. Methods for detection of methane venting include acoustic imaging of bubble plumes [2], acoustic identification of seafloor vent sites [3], direct observation by HOV/ROV [4], and water column sampling [5]. Except for a few efforts to measure bubble flux at small clusters of gas vents [6], measurement of water column methane concentration is the only practical means for estimating the amount of methane emanating from

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seafloor sources [7] and determining its vertical distribution in the water column.

Methane concentration profiles in the ocean

Methane concentration profiles in the oligotrophic open ocean [9, 18, 19] provide an end-member for the spectrum of profiles obtained throughout the worlds's oceans where the influence of riverine methane input [12, 20], and benthic sources (such as methane-supported chemosynthetic communities [23], methane bubble plumes [7, 22], or hydrothermal vents [17]) are of little importance. The few published deep-water open ocean water column methane profiles [9, 18, 19] combined with the more numerous surface ocean methane measurements [11, 24, 25, 40] indicate that the surface oceans are nearly always supersaturated with respect to equilibrium with the overlying atmosphere and this is most likely caused by *in situ* biological production (e.g., mixed layer production at the base of the pycnocline [14, 16]). Open ocean methane concentrations decrease with depth from supersaturation at the surface to values close to the detection limits of the analytical methods employed (typically <0.5 nM). Aerobic methane oxidation is the primary biogeochemical process that removes methane from the deep ocean water column [14, 21, 48].

In contrast with the oligotrophic ocean, methane concentration profiles from the water column over continental margins show enrichment from a variety of sources, including rivers entering the coastal ocean [12, 29], production in the mixed layer (see [43] for a review), apparent intrusion of methane-enriched bottom waters along isopycnal surfaces [7], and benthic fluxes from microbial (Jamaica Ridge [15]), gas hydrate (Hydrate Ridge [22]; South China Sea [44]), and thermogenic sources [5].

Sources of water column methane anomalies

Supersaturated conditions in the upper water column are not easily explained by physical mixing of undetected lateral sources containing elevated methane concentrations or deep entrainment of methane-enriched bottom waters. Biological production in either anaerobic particle-associated microcosms [28], digestive tracts of plankton and nekton [30, 31], by methylotrophic methanogens [33], or possibly aerobic production of methane via cleavage of the C-P methylphosphonate bond [27, 32, Dave Karl, personal comm.] are likely explanations for elevated methane in the upper water column. Unless local production is rapid and widespread, intense mixing and aerobic oxidation [48] will attenuate the methane concentration signal.

Benthic sources of methane have generally been discovered during acoustic surveys of the continental margins [34-36], by HOV/ROV diving [23], by observing oil slicks and gas bubbles breaking the ocean surface (Santa Barbara Channel [7]; Bush Hill [39]), and by chance detection of water column acoustic anomalies in the mid-water (Guaymas Basin [2]; Blake Ridge Diapir [37]). These sources

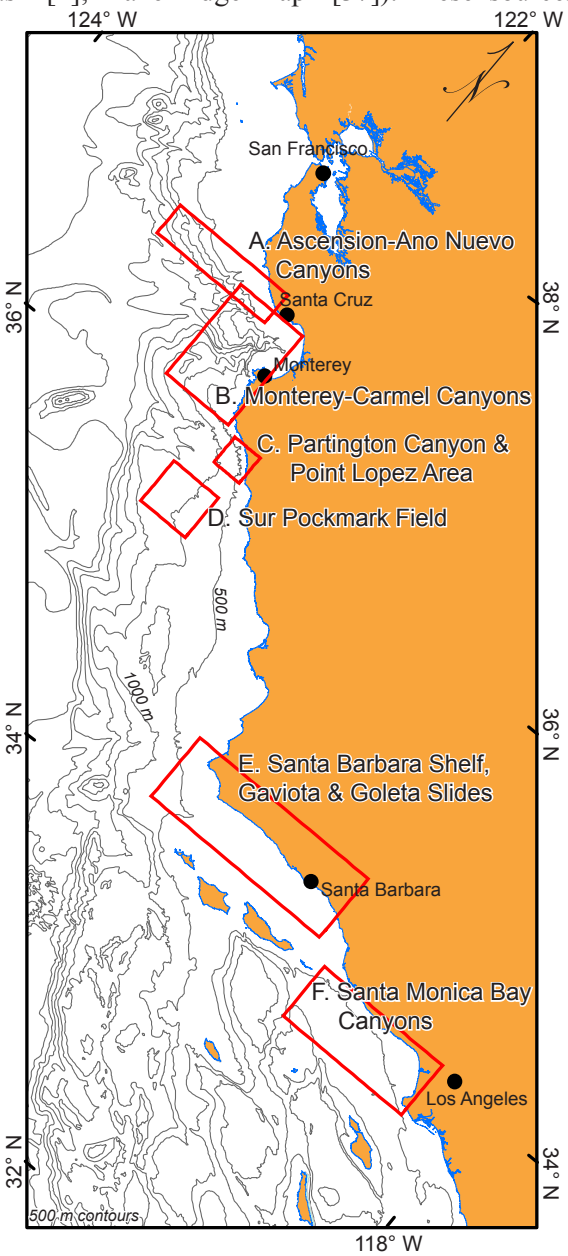

Figure 1: Water column study areas (shown in more detail in Figures 2A-2F) are outlined in red boxes.

of methane gas bubbles create vertical plumes of bubbles and methane-enriched water that rise many 100's meters into the water column and dissipate by dissolution, diffusion, and aerobic oxidation.

Water column methane concentration anomalies may occur: (1) in proximity to water column methane bubble plumes; (2) in areas where steep, rugged topography could be releasing methane by diffusion from erosionally exhumed, methane-bearing anoxic sediments; or (3) in submarine canyons where restricted circulation may trap water allowing methane released by diffusion from sediments, release from bubble vents, or biological production to accumulate in the water column. The rate of methane addition to the water column must exceed the total methane loss rate in order to produce net methane accumulation. The most important mechanisms that attenuate methane anomalies include loss by oxidation by aerobic bacteria and dilution by eddy diffusive mixing.

Detection of water column methane anomalies

Relative to the enormous area of the continental margins, methane bubble plumes can be viewed as tightly-constrained point sources that would be difficult to detect, much like the proverbial needle in a haystack. In some cases, methane bubble plumes disperse along isopycnal surfaces [7] creating thin, sub-horizontal layers that may be difficult to detect, if vertical sampling is insufficient. Obtaining sufficient numbers of discrete, vertically-spaced samples during a CTD/Niskin bottle profile, and then analyzing methane concentrations at nanomolar levels is analytically challenging and time consuming. Thus, the continental margins, where substantial amounts of methane production and release from a variety of sources are occurring, are vastly undersampled.

Systematic 3-dimensional surveys of methane distribution ("sniffer surveys") have been conducted for the oil and gas industry decades ago. These surveys were primarily conducted far shallower (<200 mbsl) than the occurrence of gas hydrate (<520 mbsl), and the data has generally remained proprietary. To our knowledge there are no known or published systematic analyses of this data from the point-of-view of locating discrete methane vents on the seafloor. More recently, AUV "sniffer surveys" conducted using a METS® methane sensor [49] have targeted areas of the seafloor purported to contain vent sites. Results have been ambiguous, primarily because there was no context as to what would happen up and down the margin, where there isn't any significant venting of methane from the seafloor.

Motivation for this study

Previous investigations of methane distribution in the water column along the continental margin of California [5,9] and Baja California Sur [26] have shown that water column methane concentrations increase with proximity to known or putative benthic sources, which may include gas vents, diffusion out of methane-rich sediments and proximity to methane gas hydrates. In the case of the Santa Barbara Basin [5, 50], the association of gas venting and elevated water column methane concentrations is clear. However, few, if any, systematic surveys of methane concentration in the water column over the continental margins have been conducted where methane gas vents are not known to occur.

In order to further explore the connection between water column methane anomalies and gas venting and to better determine how these methane anomalies are generated, we have accumulated more than 1600 methane concentration measurements from portions of the central and southern California continental margin over the past eight years (Figures 1 & 2). Some of these samples were taken in areas known to have methane vents, but others were purely for exploratory purposes. Here we address the question as to whether we can detect seafloor methane venting sites using the water column profiling technique, and whether we are able to associate water column methane anomalies with specific morphological or geologic factors.

METHODS

Water samples were obtained from 12 10-L Niskin bottles mounted on a CTD rosette (Seabird Electronics 911plus profiling CTD) or a pair of 5-L Niskin bottles mounted on MBARI's ROV *Tiburon*. ROV samples were collected ~2 m above the seafloor. Great care was exercised so as not to disturb the seafloor and cause sample bias by releasing potentially methane-enriched porewater trapped in surface sediments. Video observations made during sample collection confirmed the lack of obvious contamination of these water samples.

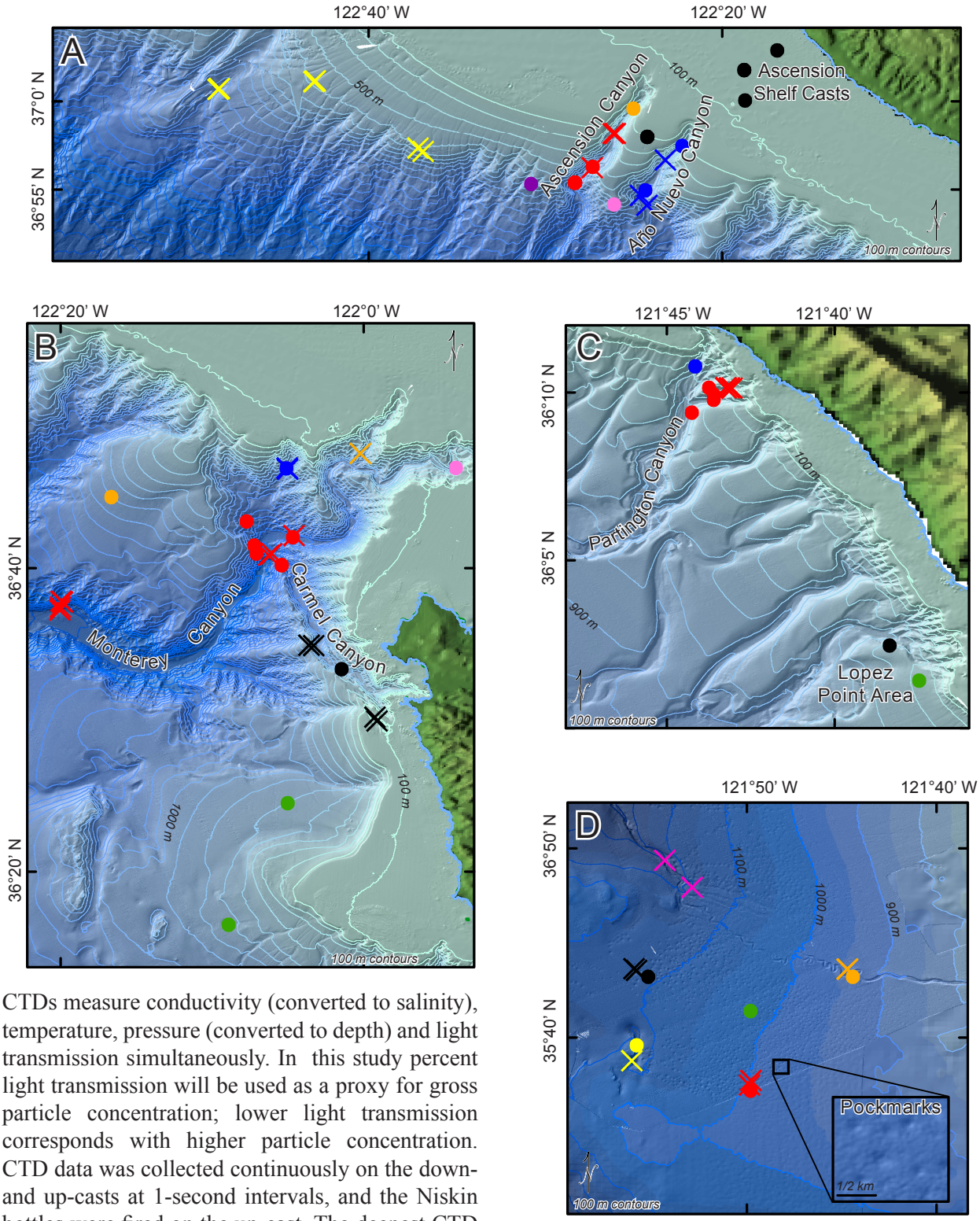

Figure 2A-2D: Locations for CTD casts (filled colored circles) and ROV (colored X's) water column methane samples are indicated for each study area as identified in Figure 1. Symbol colors are keyed to methane and light transmission data shown in Figure 3.

CTDs measure conductivity (converted to salinity), temperature, pressure (converted to depth) and light transmission simultaneously. In this study percent light transmission will be used as a proxy for gross particle concentration; lower light transmission corresponds with higher particle concentration. CTD data was collected continuously on the down- and up-casts at 1-second intervals, and the Niskin bottles were fired on the up-cast. The deepest CTD sample from a cast was obtained ~1 m above the seafloor. The CTD was equipped with a bottom sensor (lead weight hanging on a 1-m cable connected to a trip-switch) that indicated contact with the bottom, to avoid bottom impact by the CTD rosette during ship heave. Once the CTD was on

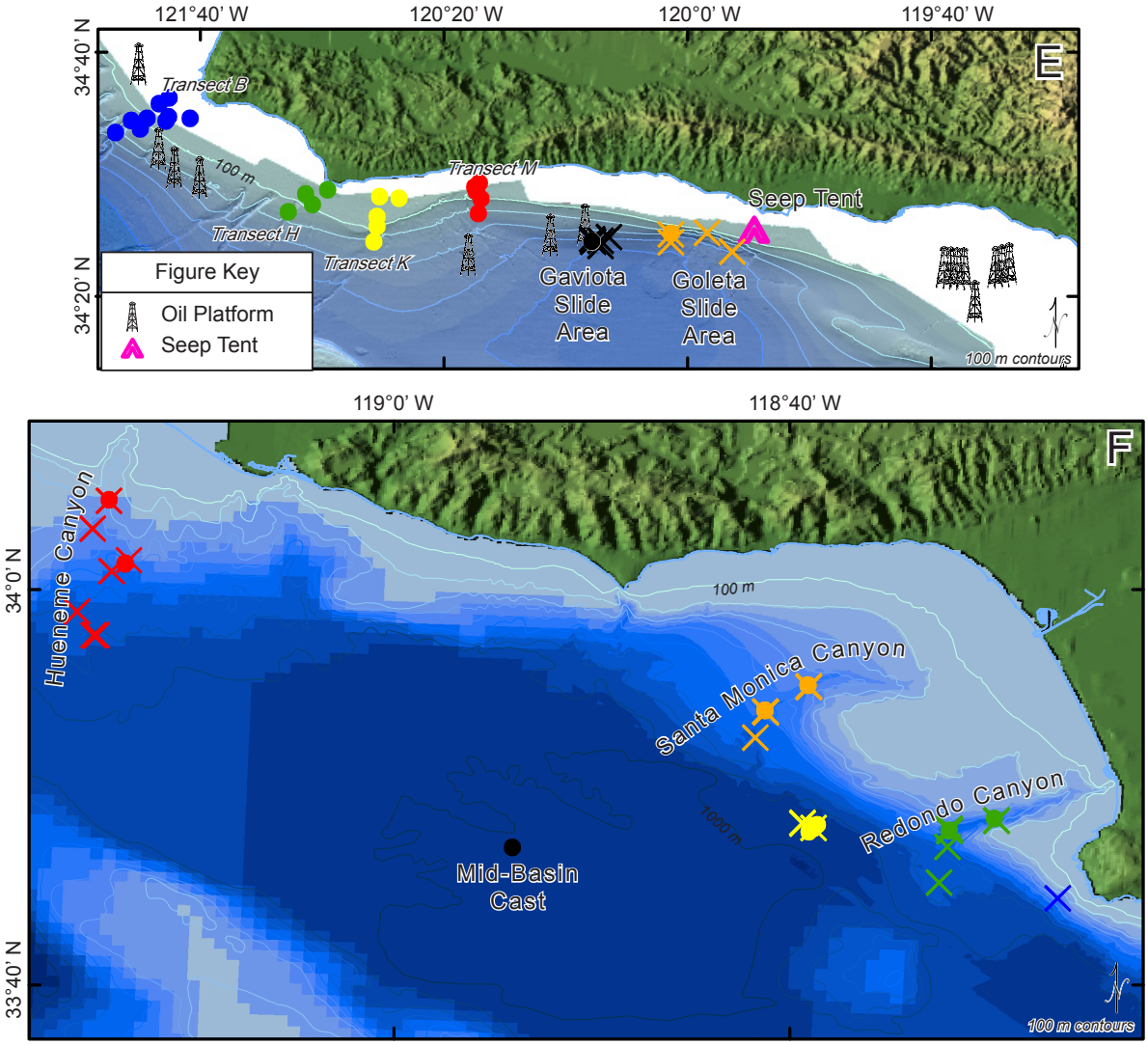

Figure 2 continued: Panels E and F indicate CTD casts and ROV water column methane sample locations.

deck, water was transferred immediately from each Niskin bottle via clear plastic tubing to a previously seawater rinsed 240-mL amber glass bottle. The end of the tubing was placed at the bottom of the bottle to prevent formation of bubbles. The bottle was filled to overflowing and sealed with a PTFE-silicon septum and screw cap without trapping a gas bubble under the septum. A 10-mL high-purity nitrogen gas headspace was added to the 240-mL bottle and equilibrated for 15 minutes using a commercial paint shaker. Methane concentration in this headspace was obtained shipboard using a Shimadzu mini-2 gas chromatograph equipped with a flame ionization detector. Methane was separated isothermally from other gases in a high-purity nitrogen carrier gas stream (Whatman nitrogen gas generator) using either a 5' x 1/8" OD stainless steel chromatographic column packed with 60/80 mesh Carbosieve G (Supelco, Bellefonte, PA) or a 6' x 1/8" OD stainless steel chromatograph column packed with 80/100 mesh Poropak-Q (Alltech Associates, Deerfield, IL). Oven temperature was typically 100°C and detector temperature was 125°C. Gas samples were injected into the gas chromatograph via a small volume magnesium perchlorate drying-trap in series with a 2-mL stainless steel sample loop. A primary methane standard (9.93 ppm in nitrogen) was run approximately every 10th sample. A 60-cc aliquot of nitrogen carrier gas was used to flush residual methane from the gas chromatograph sample loop between every sample. This method has a detection limit of ~0.5 nM.

RESULTS

Since initiation of our efforts in 2000 to survey the distribution of methane in the water column along the California continental margin (Figure 1), 1607

individual water column samples have been analyzed for methane concentration. Sample locations of the CTD profiles and ROV dives are plotted for each study area in Figure 2. Selected concentration profiles and ROV samples are plotted in Figure 3, organized by the study areas illustrated in Figure 2. Data from only 4 of the 13 cross-shelf transects for the Santa Barbara area are shown in Figures 3E & 3K; the complete methane concentration dataset for the Santa Barbara shelf is reported in Lorensen et al. [10]. Light transmission data obtained by the profiling CTD during collection of the methane samples are also plotted in Figure 3.

Except for three of the four profiles from the Sur Pockmark area (Figure 3D), near surface methane concentrations (0-50 mbsl) are saturated or supersaturated with respect to equilibrium with the overlying atmosphere (2-2.5 nM). Excluding Santa Barbara shelf surface waters, which are highly oversaturated because of widespread seafloor methane venting, 75% of the methane measurements in the surface layer (67 out of 89) exceed atmospheric saturation (2-2.5 nM). Profiles from the Ascension Shelf (black lines; Figure 3A) have some of the steepest gradients, increasing towards the ocean surface from 4.2 nM to 9 nM over less than 55 m.

All methane concentration profiles, except for those from Ascension and Ano Nuevo Canyons (Figure 3A) and the Goleta Slide (orange line; Figure 3E), can be grouped on the basis of either decreasing or increasing concentration with depth. Profiles from Monterey and Carmel Canyons (Figure 3B), the Lopez Point area (black and green lines; Figure 3C), the Sur Pockmarks (Figure 3D), the upper slope 350-mbsl cast at Point Conception (blue line; Figure 3E), the Gaviota Slide (black line; Figure 3E), and the mid-basin cast in the Santa Monica Basin (black line; Figure 3F) decrease with depth; whereas, profiles from Partington Canyon (Figure 3C), the Santa Barbara shelf (Figure 3E), and the Santa Monica Canyons (Hueneme, Santa Monica, and Redondo; Figure 3F) increase with depth. In general, profiles with methane increasing with depth are more erratic compared to those with methane decreasing with depth.

Persistent mid-water methane anomalies between 400-700 mbsl were observed in Ascension Canyon (3 casts, each collected 24 hours apart in October 2000, red lines; Figure 3A) and upper Ano Neuvo Canyon (6 years after the Ascension Canyon casts, blue line; Figure 3A). Upper slope casts from near the mouth of Ascension Canyon (also from the October 2000 cruise, purple and pink lines; Figure 3A) have mid-water methane anomalies similar to those in Ascension Canyon.

Methane profiles from the Santa Barbara shelf display a rapid increase in concentration with depth. The four transects presented in Figure 3E show a general trend in steeper methane gradients occurring closer to shore, and going from west (Transect B; Point Conception area) to east (Transect M).

The four water column methane profiles for the Sur Pockmark area (data originally published in [38]) are closely coincident with each other (Figure 3D) starting at approximately atmospheric saturation near the ocean surface and decreasing with depth, approaching the detection limit (~0.5 nM) below 800 mbsl. These profiles are comparable to 'open ocean' methane profiles obtained further offshore of the central California margin [9] and the equatorial Atlantic [8]. The mid-basin cast in Santa Monica Basin (black line, Figure 3F) and methane profiles in Ascension Canyon (below 700 mbsl) and Monterey Canyon (below 600 mbsl) also display characteristics of 'open ocean' methane profiles.

ROV water samples were collected within 2 m of the seafloor and often show higher methane concentrations than the deepest CTD profile sample collected nearby (e.g., Santa Monica Canyons, Figure 3F). The highest measured value in this dataset is 184 nM, collected by ROV from the head of Partington Canyon.

Percent light transmission data obtained during each CTD/Niskin bottle cast are displayed in Figures 3G through 3L. These CTD profiles were collected irrespective of the season, thus, a number of factors may influence the size of an anomaly or its depth. A well-defined subsurface light transmission minimum (as low as ~80%) occurs at the base of the mixed layer (~50 mbsl) below where methane is commonly supersaturated. Except for four profiles, {one in upper Monterey Canyon (UM; Figure 3H), two from the Goleta/Gaviota Slides (orange and black lines; Figure 3K), and one in upper Hueneme Canyon (UH; Figure 3L)}, the lowest values of light transmission

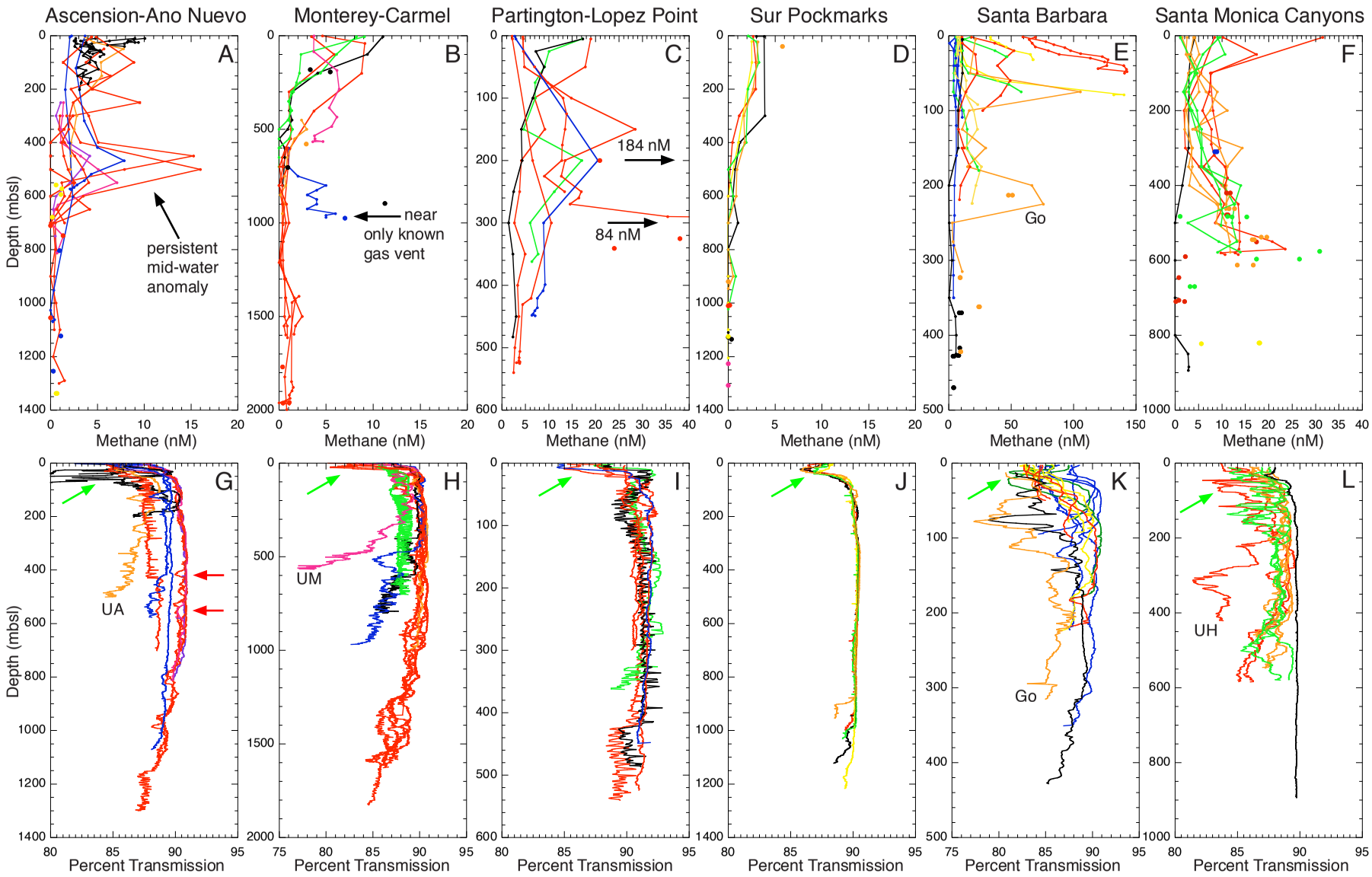

Figure 3: Methane concentration profiles (lines) and ROV-collected methane concentrations (filled circles) for each of the six study areas (Figure 2) are plotted versus depth in panels A-F and corresponding percent light transmission data are plotted in panels G-L (note different scales). Line color correlates between paired panels, i.e., panel A and G, B and H, etc. Green arrows indicate the light transmission minimum in the surface mixed layer. The red arrows in panel G indicate small light transmission anomalies. Data are available upon request. Line colors explained in the text. UA=upper Ascension Canyon; UM=upper Monterey Canyon; Go=Goleta Slide; and UH=upper Hueneme Canyon.

in any particular profile are found in the upper 50 m of the water column. In most submarine canyon profiles (Ascension, Monterey, Partington, and the Santa Monica canyons; Figures 3G-3I, & 3L) and outer shelf/upper slope profiles from Santa Barbara, light transmission remains constant with depth (~90%) below the light transmission minimum and decreases slowly below the mid-point of most CTD casts towards the seafloor, reaching values between 85% and 90%. Light transmission is nearly constant with depth below the light transmission minimum for the Sur Pockmark and mid-basin Santa Monica casts (Figures 3J & 3L). CTD data also reveal that there are no salinity anomalies (data not shown) indicative of freshwater input to the surface ocean where water column methane measurements were obtained. Thus, there is no obvious methane input to the surface ocean from terrestrial sources at the sites surveyed.

DISCUSSION

Open ocean methane profiles provide a context in which to evaluate the effects of geologic, terrestrial, and biological sources of methane to the coastal oceans. Studies of open ocean methane profiles [9, 18] and surface ocean methane concentrations [8, 12] have shown that the open ocean mixed layer (0-200 mbsl) is slightly supersaturated (3-6 nM) with respect to equilibrium with methane in the atmosphere (2-2.5 nM), which results in a net flux of methane to the atmosphere. Supersaturation of the mixed layer in the open ocean most likely has a biological origin because it is isolated from the influence of the continental margins. Karl and Tilbrook [28] have shown that supersaturation of the open ocean mixed layer is easily achieved. Particle-associated methane released into the mixed layer by sinking particles can produce methane supersaturation in less than a month [28] and methane concentrations increase towards the base of the mixed layer [18, 28]. Below the mixed layer, methane concentrations decrease with depth to values that reach the detection limits of the methods employed (<1 nM), which indicates net loss of methane from the water column. Thus, by comparing profiles obtained in this study with what would be expected for open ocean methane profiles, geologic and terrestrial sources, and enhanced biological production of methane can be inferred.

Open Ocean-like Methane Profiles

A small number of methane profiles and their corresponding light transmission profiles obtained along the California margin resemble open ocean methane profiles (Big Sur Pockmark field, Figure 3D; and the mid-basin cast in Santa Monica Basin, black line, Figure 3F). An ROV survey of the Big Sur Pockmark field [38] showed no evidence for methane venting or seepage from selected pockmarks in this giant deep-water (900-1200 mbsl) pockmark field. Methane profiles were collected over the same pockmarks within days of the visit by the ROV.

Methane in the Surface Mixed Layer

Light transmission profiles (Figures 3G-3L) obtained along the central California continental margin commonly have a pronounced subsurface minimum at approximately 50 mbsl that in most cases corresponds with the pycnocline (data not shown). Methane in the surface mixed layer (0-50 mbsl) above the pycnocline is commonly supersaturated, with concentrations as high as 32 nM (upper Hueneme Canyon; Figure 3F). In many profiles undersaturated values begin to appear below the particle maximum and methane concentrations continue to decrease with depth, reaching values at or below detection limit (Figures 3A-3D). This profile data indicate that local production of methane is occurring in the surface mixed layer above the particle maximum and may not be particle-associated as suggested by Karl and Tilbrook [28], or Sansone et al. [42]. Except for nearly every profile from the Santa Barbara shelf (Figure 3E), the majority of methane profiles increase in concentration from the particle maximum *towards the ocean surface,* not the base of the mixed layer. Methane concentration profiles that increase towards the ocean surface cannot be produced by vertical mixing of methane from greater depths as observed in open ocean methane profiles [18].

Although little is known about the capacity of local rivers to transport methane into the coastal ocean along the California continental margin, their ephemeral nature and low total discharge, and the absence of salinity anomalies in the surface mixed layer indicative of freshwater input, makes it unlikely that rivers entering the coastal ocean are important sources for methane found in the mixed layer, including those on the Ascension Shelf. These observations suggest that methane supersaturation in the surface mixed layer along the central California margin is not related to fluvial export nor

is it particle-associated, but may be biologically-mediated through other processes, such as cleavage of methylphosphonate [27, 32] or production by methylotrophic methanogens [33].

Methane in Submarine Canyon Systems

Within most of the submarine canyon systems surveyed, elevated methane concentrations commonly occur in the benthic bottom water (Partington Canyon, red lines, Figure 3C; Hueneme, Santa Monica, and Redondo Canyons in Santa Monica Bay, Figure 3F) or appear as persistent anomalies in the mid-water (Ascension and Ano Nuevo Canyons, red and blue lines, respectively, Figure 3A). Monterey Canyon (red lines, Figure 3B) is a notable exception to this observation.

The steady rise in methane concentration with depth in the three canyons from Santa Monica Bay and the highly elevated methane concentrations near the seafloor in upper Partington Canyon (184 nM at 200 mbsl; 84 nM at 298 mbsl) may result from restricted circulation in these canyon systems. Restricted circulation would increase the residence time of methane and other constituents, such as ocean-margin derived organic-rich particles, which might serve as a methane source. Restricted circulation would also allow the accumulation of methane in the bottom waters released by local geologic sources (vents, methane gas hydrates, and/or eroded anoxic seafloor sediments).

Ascension and Ano Neuvo Canyon profiles display mid-water methane anomalies between approximately 400-700 mbsf of varying intensity, that persist over a few days to perhaps years, superimposed on methane profiles that decrease with depth. These anomalies may also result from increased methane residence time and/or lateral proximity to geologic sources of methane. Although there are no data that indicate the occurrence of methane gas hydrates along this portion of the California continental margin (gas hydrates have only been reported from the Eel River [45] and an authigenic carbonate mound in the Santa Monica Basin [23]), the depth interval for the mid-water methane anomalies corresponds with the upper depth limit for methane hydrates (~520 mbsl). Slowly decomposing methane gas hydrates could provide a sustained source of methane to the water column that would maintain water column methane anomalies over annual time-scales.

Submarine groundwater discharge (SGD) has been shown to export methane-rich (200+ nM levels) freshwater to the continental shelves [41]. Although salinity anomalies indicative of freshwater input to benthic bottom waters along the California margin have not been identified, SGD may contribute a yet undetected contribution of methane to the coastal ocean. Submarine canyons may intersect off-shore aquifers and provide exit points for fluid discharge, much like that seen in box canyons on land and the base of the West Florida Escarpment [46].

Many of the light transmission profiles in the submarine canyons surveyed trend toward lower values near the seafloor indicating higher suspended particle concentrations. Distinctly larger increases in suspended particle concentrations occur in the upper reaches (<500 mbsl) of three canyons (UA, UM, and UH, Figure 3). Although particle concentrations are similar to those obtained in the surface mixed layer, and the upper canyons are closer to higher productivity zones of the coastal ocean, there is not a corresponding increase in methane concentration in the water. This observation suggests that either particle-associated methane production is not important or particle-type is different in the mixed layer compared to the benthic boundary layer in submarine canyons.

Proximity to Known Methane Gas Vents

Methane concentrations in Ascension (up to 16 nM), Partington (up to 184 nM), and Santa Monica canyons (up to 24 nM) are comparable to values obtained over or near known methane gas vents on the Santa Barbara shelf (up to 143 nM; Figure 3E), yet, there are no known methane gas vents in these canyon systems. In Monterey Canyon, elevated near-bottom methane concentrations occur adjacent to a known fluid vent at Extravert Cliff (Figure 3B). However, the Extravert Cliff anomalies are modest (up to 6 nM) compared to methane concentrations measured in the other canyon systems. CTD casts taken on the Ascension Shelf (Figure 3A), were located as close as possible to reported water column acoustic anomalies once interpreted to be methane bubble plumes [47]. These profiles show no indication of gas venting from the seafloor; the methane gradients are opposite what would be expected for a seafloor source.

Methane concentration profiles from the Santa Barbara shelf increase with increasing depth (Figure 3E), consistent with a benthic source for the methane. The entire water column is methane-enriched, with only 12 of the 480 methane measurements made in the surface layer (0-100 mbsl, or less) at or below atmospheric saturation. Although gas vents are numerous and widespread along the Santa Barbara shelf [5, 7], it would be difficult to find an individual gas vent using water column methane profiles alone.

Water vapor plumes from power plants (Figure 4) provide a physical analogy for the problem of identifying a methane source. A single vertical profile through the dispersed vapor plume downwind of the stack would provide evidence that a source of water vapor is nearby, but there would be little directional information. Samples a few meters away from the vapor plume would not indicate its nearby existence! A dense 3-dimensional grid of directed-sampling would be necessary to pinpoint the source.

Figure 4: Water vapor plume emanating from the Moss Landing, CA power plant illustrates the sharply-defined nature of plumes. Photo courtesy of Todd Walsh, MBARI.

CONCLUSIONS

As a result of prospecting for new seafloor sources for methane using water column methane profiling, several classes of methane anomalies have been identified. Supersaturation of the surface mixed layer (0-50 mbsl) is widespread and is above a well-defined subsurface particle maximum (~50 mbsl). Particle-associated methane production appears not to be an important process along the central California margin. Persistent mid-water methane anomalies that occur in the Ascension and Ano Nuevo Canyon systems may be the combined result of restricted circulation and a proximal geologic source for methane, potentially methane gas hydrate or methane-rich, recently eroded sediments on the canyon walls. In some of the upper canyon systems, near-seafloor particle concentrations are comparable to those found at the particle maximum below the mixed layer, but do not correlate with a methane increase. In the Santa Barbara Basin, we know there are numerous gas vents, but based on the results we have obtained, it would be hard to find one using water column methane profiles alone.

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