Re: Pooling Expert Assessments

ira leifer to: Franklin.Shaffer 06/08/2010 11:41 AM

Cc: pdy, pmbommer, savas, antonio.possolo, pedro.espina, Bill.Lehr, Wereley, aaliseda, rileyj, lasheras, mark_sogge, mcnutt

History: This message has been replied to.

Antonio,

I have 20 years of hourly data from the hydrocarbon seeps, which we submitted for publication in Atm Environments - a seep field which is migration through a complex fractured, faulted reservoir system to the seabed and seasurface and thus represents the subsurface migration processes to the pipe (also just published a study relating spatial variability to structural geology, and working on on on the a manuscript on the relationship between geologic structure and temporal emission variability).

I am happy to share that data, it illustrates how these type of systems (hc migration) behave, which has greater similarity to a geyser system than a river flow. To use the analogy.

I have attached the manuscript for anyone who is interested, however, for those who are very busy (everyone!!) there are a number of very pretty and highly meaningful figures.

warmest regards,
Ira

PS Helpful comments always welcome - its at the submitted stage now.

On Jun 8, 2010, at 7:29 AM, Franklin Shaffer wrote:

> Antonio,
> Welcome to the Plume Team!
> The issue is raised relates to the length of the data sample we
> have. Since you're an expert on statistical analysis and
> uncertainty, would you please comment on whether a data sample taken
> over a continuous sample period of about 30 minutes is long enough
> for us to state an average total flow rate over a period of more
> than one month? Is it possible to set bounds on the uncertainty due

> to such a short sample period?
> Thanks,
> Frank
>
>>>> "Possolo, Antonio" < antonio.possolo@nist.gov> 6/8/2010 10:12 AM >>>
> Colleagues,
>
> I attach a note that describes the results of pooling the
> assessments that six of the experts shared during the telecon
> yesterday: think of it as a consensus assessment (produced using a
> formal, established statistical method).
>
> Director McNutt may like to use this as a support item in her
> conversations with Secretary Chu.
>
> In the meantime I'll work on the issue that Frank raised - maximum
> versus expected volume - within the same general framework. I'm also
> ready to handle a similar collection of revised assessments that
> each of you may produce based on the new video.
>
> Bill: please add Dr. Blaza Toman (Statistical Engineering Division,
> NIST) to the list of people in the acknowledgments section of the
> final report.
>
>
> - Antonio
>
> - Antonio Possolo, PhD -- Chief
> Statistical Engineering Division
> Information Technology Laboratory
> National Institute of Standards & Technology
> Telephone: 301-975-2853
>
>
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Title: Long-term Monitoring of a Marine Geologic Methane Source by a Coastal Air Pollution Station in Southern California

Article Type: Research Paper

Keywords: Methane emissions; CH4; Coal Oil Point seep field; marine seeps; wind sector analysis

Corresponding Author: Ms. Eliza Bradley,

Corresponding Author's Institution: University of California, Santa Barbara

First Author: Eliza Bradley

Order of Authors: Eliza Bradley; Ira Leifer, PhD; Dar Roberts, PhD; Marc Moritsch

Abstract: Hourly total hydrocarbon (THC) data spanning 1990 to 2008 from a California air pollution station located near the Coal Oil Point (COP) seep field, were analyzed and clearly showed geologic CH4 emissions as the dominant local source. Annual COP emissions are conservatively estimated as 0.015 Tg CH4 year-1, relative to 2 - 8% of Los Angeles basin emissions. THC showed a strong wind dependency with elevated levels closely correlated with a sonar-derived spatial distribution of seep field emissions. THC varied seasonally, with a maximum in January and minimum in July and a peak-to-peak amplitude of 0.24 ppm. The seasonal signal was more readily apparent midday (R2=0.69 harmonic fit), compared to nighttime and morning (R2<0.45). The bimodal diel THC pattern consisted of seasonally-modulated peaks in the morning and evening.

THC temporal and spatial trends were consistent with both transport and source emission variations. Long-term, annual seep field emissions consistently decreased on a field-wide basis until the late 1990s, before increasing consistently, most likely as a function of underlying geologic processes. This study demonstrates the value of municipal air quality monitoring stations for insight into local GHG sources and highlights the non-negligible and variable influence of marine seeps.

*Cover Letter

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10 December 2009

RE: Long-term Monitoring of a Marine Geologic Methane Source by a Coastal Air Pollution Station in Southern California, by Eliza Bradley, Ira Leifer, Marc Moritsch, and Dar Roberts

Dear Editor Dr. Hanwant Singh,

Please consider our paper, "Long-term Monitoring of a Marine Geologic Methane Source by a Coastal Air Pollution Station in Southern California", for publication in *Atmospheric Environment*. This manuscript presents first analysis of an extensive hourly total hydrocarbon time-series, 1990-2008, proximal to the Coal Oil Point (COP) seep field. Our results indicate that COP is the dominant local source of methane emissions and is temporally variant, with geologically-driven long-term trends. These findings have implications for methane emission inventories and are a novel example of leveraging extant air quality data for greenhouse gas research.

I am under the impression that the text (not including references) should be under 6,500 words (current word count: 6146, total: 7310). Please let me know if I am mistaken and I will submit a further condensed version.

The manuscript has not been published or simultaneously submitted for publication elsewhere. If you have any further questions about the submission, please feel free to contact me at ebradley@geog.ucsb.edu.

Thank you for your consideration.

Eliza S. Bradley

Eliza Bradley

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Long-term Monitoring of a Marine Geologic Methane Source by a Coastal Air Pollution Station in Southern California

Eliza Bradley[a*], Ira Leifer[b], Marc Moritsch[c], Dar Roberts[a]

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Abstract

Hourly total hydrocarbon (THC) data spanning 1990 to 2008 from a California air pollution station located near the Coal Oil Point (COP) seep field, were analyzed and clearly showed geologic CH_4 emissions as the dominant local source. Annual COP emissions are conservatively estimated as 0.015 Tg CH_4 year^{-1}, relative to 2 – 8% of Los Angeles basin emissions. THC showed a strong wind dependency with elevated levels closely correlated with a sonar-derived spatial distribution of seep field emissions. THC varied seasonally, with a maximum in January and minimum in July and a peak-to-peak amplitude of 0.24 ppm. The seasonal signal was more readily apparent midday (R^2=0.69 harmonic fit), compared to nighttime and morning (R^2<0.45). The bimodal diel THC pattern consisted of seasonally-modulated peaks in the morning and evening.

THC temporal and spatial trends were consistent with both transport and source emission variations. Long-term, annual seep field emissions consistently decreased on a field-wide basis until the late 1990s, before increasing consistently, most likely as a function of underlying geologic processes. This study demonstrates the value of municipal air quality monitoring

stations for insight into local GHG sources and highlights the non-negligible and variable influence of marine seeps.

Keywords: Methane emissions, CH_4, Coal Oil Point seep field, marine seeps, wind sector analysis

1. Introduction

Marine seeps emit to the hydrosphere and atmosphere the important greenhouse gas (GHG), methane (CH_4). Radiative forcing from methane emissions has been estimated to be as high as 61% of the forcing from CO_2 (Shindell et al., 2005). Due to its decadal time scale, high GWP, and relatively inexpensive abatement opportunities, CH_4 is more amenable to regulatory approaches than CO_2 and reduction treaty negotiations may proceed more quickly (Reilly et al., 2006).

Although the global CH_4 budget is relatively well understood, source appropriation (essential for CH_4 regulation) remains at best, poorly quantified. For example, geological sources were not included in global inventories prior to IPCC 2007, yet geo-seepage was estimated to contribute ~39% of European natural CH_4 emissions (Etiope et al., 2009). Total geological emissions are estimated at 53 ± 11 Tg yr^{-1} (Etiope et al., 2008) and are a source of ancient carbon. Of the total global CH_4 source of ~582 Tg yr^{-1} (IPCC, 2007), the estimated fossil fraction is 30± 5% (Etiope et al. 2008). Marine seeps are estimated to contribute annually ~20 Tg (Kvenvolden et al., 2005). Uncertainties are large because few marine seep emissions have been quantified.

Fluxes for single vents have been reported for the Gulf of Mexico (Leifer and MacDonald, 2003), offshore Norway (Sauter et al., 2006), and a few other areas, while basin

estimates have been extrapolated for the Black Sea (Wallmann et al., 2006) and for seeps globally (Milkov et al., 2003). Repeat sonar surveys have quantified the spatial distribution of emissions for the Coal Oil Point (COP) seep field (Hornafius et al., 1999, Leifer et al., 2009 *in prep*). Nevertheless, these data are "snapshots" of a phenomenon that varies on a range of time scales (Leifer and MacDonald, 2003; Boles et al., 2001; Fischer, 1978). Thus, considerable uncertainty arises in extrapolating to annual emissions and to larger scales. A general lack of long-term emission data, which would allow evaluation of spatial and temporal variability, is a problem.

Although surface-station CH_4 monitoring provides such local source information, the primary objective has been to characterize ambient conditions at remote sites for global estimates (Cunnold et al., 2002). However, recent work has leveraged such datasets to investigate temporal variability of proximal sources, e.g., Mace Head station for monitoring nearby peat bogs (Derwent et al., 2009). Further, new programs have been established, such as the Mt. Wilson station in Los Angeles County, California, for measuring CH_4 and creating local "top-down" emission inventories (Hsu et al., 2009) in support of the California Global Warming Solutions Act of 2006, which mandates statewide, GHG emission inventories.

Herein, we present long-term (1990-2008), hourly total hydrocarbon (THC) mixing ratio data from the Santa Barbara County Air Pollution Control District (SBCAPCD) West Campus Station (WCS) near the COP marine seep field in southern California. This dataset has particular relevance because (1) analysis of concurrent wind speed and direction data can be used to assess local transport processes and identify sector emission sources, (2) the proximity to COP allows investigation into the dynamics of marine geologic seeps at numerous time scales, and (3) comparison to in-situ data at other locations in Southern California, namely Los Angeles (Hsu et

al., 2009, Wunch et al., 2009), helps provide a more complete understanding of regional CH_4 sources and their variability.

1.1 Overview of the Coal Oil Point seep field

The COP seep field (Fig. 1) is among the largest and best-studied areas of active marine seepage in the world. These perennial and continuous oil and gas seeps have been active on the northern edge of the Santa Barbara Channel for at least 500,000 years (Boles et al., 2004). Seepage occurs from the reservoir layer (Monterey Formation) through faults, fractures, and outcroppings in the overlying, capping Sisquoc Formation (Leifer et al., 2009 *submitted*). Atmospheric gas flux estimates, 1.0×10^5 m^3 day^{-1} from 1994-1995 sonar mapping surveys (Hornafius et al., 1999), coupled with direct gas capture (bubble 60% CH_4 mole fraction), suggest emissions of ~ 0.015 Tg CH_4 $year^{-1}$ (Clark et al., 2009). A roughly equal amount dissolves into the coastal ocean (Clark et al., 2000). Comparison with estimated emissions for the SBCAPCD using the approach of Zhao et al. (2009) and CARB (2008) data suggest the COP seep field contributes 46–69% of Santa Barbara County CH_4 emissions. Evasion of dissolved CH_4 occurs downcurrent of the seeps and forms a diffuse atmospheric plume. At low wind speeds, the diffuse flux is small with most of the CH_4 remaining in the water column for tens of kilometers, reaching Pt. Conception and beyond (Mau et al., 2007); however, at higher wind speeds the sea-air gas flux would increase significantly. Associated oil seepage is estimated at over 100 barrels day^{-1} (1.6×10^4 L day^{-1}) (Hornafius et al., 1999).

Infrequent sonar surveys since 1995 show significant changes in the seepage spatial distribution (Leifer et al., 2009 *in prep*), while comparison with surveys in the 1940s and 1950s show a significant decrease in seep extent (Fischer, 1978). Data from the Seep Tents (two 30 x

30 m capture tents on the seafloor) show a consistent trend of decreasing emissions from the mid 1980s to the mid 1990s (Boles et al., 2001); however, data interpretation is unreliable regarding natural processes because they are strongly affected by production-related activities (Boles, 2009). Thus, emission changes captured by the tents may or may not be mirrored by changes from the overall seep area. Finally, environmental parameters affect seepage on timescales from swell (Leifer and Boles, 2005), to tidal (Boles et al., 2001), to seasonal (Del Sontro et al., 2007).

At the seabed, COP seep bubbles primarily are CH_4 (Clark et al., 2009), which partitions into the water column and atmosphere. Although WCS measures total hydrocarbons (THC), field gas chromatograph measurements at the site observed CH_4 concentrations up to 10 ppm for south winds, while n-alkanes were below the detection limit – 20 to 50 ppb (Leifer, unpublished data, 2009). Analysis of an atmospheric sample from immediately above Shane Seep (34° 23.070'N, 119° 53.425'W) showed 19,100 ppm with combined non-methane hydrocarbons (NMHC) less than 0.02%.

2. Experimental study site and monitoring program

The SBCAPCD has been monitoring THC at the WCS (34°24.897'N, 119°52.770'W) since before 1991. The WCS is situated along a south-facing coastline at 11-m elevation in a coastal grassland/scrub region ~0.5 km from the shoreline (Fig 1). The seep field lies within an 8 km arc of WCS from 130 to 240°, with inshore seeps, such as Horseshoe Seep, located less than 2 km distant (Fig. 1B). To the east of the station lies Devereux Slough and to the west-northwest are the Ellwood Marine Terminal (EMT) oil storage tanks and facility (owned and operated by Venoco, Inc.) (Fig. 1C).

< Insert Figure 1 about here>

Coastal southern California has a Mediterranean climate influenced by the subtropical high pressure cell of the North Pacific with dry summers and wet winters. Atmospheric conditions in the Santa Barbara Channel result from coupled interactions between the lower troposphere, ocean, and coastal mountain ranges (i.e. the ~1300 m E-W trending Santa Ynez Mountains lie directly to the north of WCS) (Dorman and Winant, 2000). Winds tend to be strongest in the early afternoon, particularly in spring, and weakest in the early morning, especially for the winter, with 60% of pre-sunrise hours during November and December being calm (Fisk, 2008). Land-sea breeze circulation patterns result in a diurnal reversal at WCS with nighttime down slope subsidence flow. Another feature is the cool, dense marine atmospheric boundary layer, which is distinct from the free atmosphere and capped by an inversion. It is particularly apparent in the summer when its thickness varies from 350 to 300 m in the late morning to late afternoon, becoming shallow at night (Dorman and Winant, 2000).

WCS continuously monitors THC with a THC analyzer (Model 400/400A, Beckman Corp., Fullerton, CA) through a glass intake at 4 m height. The data acquisition system digitizes measurements once per second and saves hourly averages. The THC analyzer has a daily, single point, nighttime calibration (8.49 ppm) between 0000 and 0100 PST (Pacific Standard Time; UTC-8 hr). A biweekly calibration includes CH_4 samples at 1.92, 3.87, and 8.47 ppm and a check of the analyzers zero point. Analyzer drift is a few tenths ppm per day. Prior to 4 April 2002, the THC analyzer range was 0-10 ppm; afterwards it was increased to 0 – 25 ppm to capture higher THC values that were observed in the continuous record.

Wind speed (Model 010C, Met One, Grants Pass, OR) and direction (Model 020C, Met One) are measured at a height of 10 m, with a starting threshold of 0.22 m s^{-1}. Hourly averages

are calculated from one Hz measurements. Wind direction and speed accuracies are 3° and 0.07 m s^{-1}, respectively.

In this study, we analyzed hourly THC, wind speed, and wind direction data from 1990 through 2008. Data coverage was relatively complete except for the THC analyzer calibration that resulted in consistent data gaps at hour 0100 PST. Additionally there is a gap in THC data for July-Oct. 1997, and when the station was offline in January 1998 and mid-July through mid-August 1998. Anemometer gaps were infrequent (3.6%), except for a July-December 1995 down period. Given the methodologies used in this study, no gap-filling was necessary. This paper's primary objectives are an overall characterization of the WCS long-term hourly dataset, investigation of local transport processes, and wind sector analysis for insight into the influence of the local marine seeps. Lastly, the multi-year trend in THC values is compared to state CH_4 emissions and AGAGE measurements.

3. **Results**

Mean THC at WCS over the study period (1990-2008) was 2.04±0.49 ppm (Fig. 2A), with a maximum of 17 ppm. Univariate and bivariate histograms were calculated from THC, wind speed, and wind direction data (Fig. 2) and showed numerous positive THC outliers from a normal distribution (Fig. 2A). For example, over 600 (0.4%) measurements exceeded 5 ppm, significantly higher than predicted by a Gaussian model, <0.01%. The sample distribution was significantly right-skewed (skewness=6.42). Wind speeds, u_{10}, at WCS generally were low, with a mode of 2 m s^{-1} and mean of 2.6±1.6 m s^{-1} and with $u_{10} > 5$ m s^{-1} for 7.25% of the data (Fig. 2B). The dominant wind directions were from the NNE-E and SW-W (Fig. 2C), with the

strongest winds being easterlies and westerlies (Fig. 2D). Weak winds occurred for all directions, with a high probability for light NE winds.

< Insert Figure 2 about here >

The bivariate histograms illustrate the strong dependency of WCS THC concentrations on wind direction and speed. The highest THC values were recorded for low wind speeds (Fig. 2E). Also, the THC measurements show a strong directional dependency such that higher THC values more likely arise when the winds are from seep field directions (>130° and <240°).

Assessing whether particular THC measurements at WCS are representative requires characterization of the temporal variability in THC, wind speed, and wind direction. Hourly wind speed and direction show clear seasonal modulations of the diurnal (sea breeze) cycle: stronger onshore winds occur during the day and light northern offshore winds occur at night (Figs. 3A & 3B). Inter-annual variations of the wind speed and direction are far less apparent, although the intensity and extent of stronger springtime wind speeds does vary between years, e.g., in 1991 there were 266 observations of wind speeds greater than 7 m s^{-1}, but 115 for 1994. Unlike the relative multi-year constancy of the wind data, there is a striking long-term trend of decreasing THC until the late 1990s, at which point the trend reverses. High THC values also show a strong seasonal modulation in terms of the hour of the highest concentrations (Fig. 3C). THC subsets for different timescales from year (2006) to day (Figs. 3 D-F), illustrate the high frequency variability in the data as well as the bimodal diel signal (Fig. 3F), which has variable amplitude and tends to be more distinct in the morning (Fig. 3A).

< Insert Figure 3 about here >

Bivariate column-standardized frequency histograms by parameter (wind speed, direction, THC) and time (hour, month, year) provide more detail on the trends over different

timescales and the relationship between parameters (Fig. 4). The afternoon sea breeze has the narrowest range of wind directions (i.e., most consistent) of any time of day and the broadest range in wind speeds (Figs. 4A & 4D). The greatest range for THC occurs near 0900 and 2000 PST while lower values tend to occur in the afternoon (Fig. 4G). In terms of seasonal trends and varying day length (sea breeze duration), during the summer, southwest winds are the most frequent, while northeast winds are dominant in the winter (Figs. 4B & 4E). Summer wind speed has a broader peak than in winter months (Fig. 4E); however, winds greater than 7 m s^{-1} are most frequent in the spring due to synoptic weather systems. THC shows a more subtle seasonal pattern, with little variability in peak values, although summertime THC values generally were lower (Fig. 4H). THC shows a comparatively dramatic shift in the long-term trend near 1997, with a decrease in probability for high values prior to this date and an increase afterwards (Fig. 4I), and no corresponding interannual surface-wind trend (Figs. 4C & 4F).

< Insert Figure 4 about here >

To assess the seasonal variability, data were detrended by subtracting the 53-week moving average, and then the least-squares fit for a four harmonic function was determined for the 13-week moving average (Artuso et al., 2007). This was repeated for each hour of the day, with the best harmonic fit for the afternoon (R^2>0.6, maximum R^2=0.69 at 1200 PST), low nighttime correlations (e.g., 0200 PST, R^2=0.28) and poorest agreement in the morning (0800 PST, R^2=0.07). The seasonal peak-to-peak amplitude for 1200 PST was estimated as 0.24 ppm, with a peak in January and minimum in July. Higher frequencies contributed negligibly to variability in this smoothed data.

Diurnal THC trends were investigated for summer and winter months for a four-year period (2005-2008) of relative interannual stability (Fig. 5). Analysis included using a narrow (2

$< u_{10} < 2.3$ m s^{-1}) wind speed filter to partially control for wind speed effects on THC, illustrated in Fig. 2E. The range chosen maximizes the hourly sample size to at least 30 observations. The summer-filtered THC hourly averages were unimodal with highest values in the afternoon, whereas the unfiltered version was bimodal with peaks in the morning and evening. Corresponding resultant wind vectors demonstrate that the filtered winds were strongly meridional in the afternoon compared to the unfiltered data. A similar pattern was evident for winter months, although the THC peak was narrower in time than in the summer.

< Insert Figure 5 about here >

The multi-year trend when viewed in terms of THC averages for 5° wind-direction bins, $\mu_{THC}(\varphi,yr)$, where φ is wind direction (degrees azimuth), shows the strongest THC levels arising from the seep field direction (Fig. 6A). The overall THC trend shows a general decrease from all seep field directions until ca. 1998; however, the decrease is not uniform with φ, exhibiting a greater relative decrease from the seep field's periphery. Specifically, $\mu_{THC}(\varphi,yr)$ narrows in amplitude and half-width. At the minimum (1997), the highest THC levels was from ~195°, i.e., the direction of the Seep Tent Seep area, which was the most active and intense seep in the 1990s. Support that $\mu_{THC}(\varphi,yr)$ variability is related to source dynamics is provided by the absence of multi-year trends in mean wind speed by direction, $\mu_{THC}(\varphi,yr)$ (Fig. 6B). Further, because averages are calculated for wind direction bins, shifts in wind direction cannot explain the THC trends beyond shifts in the angular distribution.

< Insert Figure 6 about here >

The directional THC maximum values, $max_{THC}(\varphi)$, for the dataset show agreement with the detailed, sonar-derived COP seep locations (Fig. 7B). Peak values corresponded with the 215-245° sector, which included near seeps (Shane) and more distant (HolOil and Platform

Holly) (ref Fig. 1B). The highest value was for ~152.5° (La Goleta and inshore seeps). Mean THC, $\mu_{THC}(\varphi)$, is far more homogeneous, with a broad SSE peak (Fig. 7A). Elevated $\mu_{THC}(\varphi)$ also are observed for the N-NE wind directions. Restriction by year (2005 & 2006) to most closely correspond with the sonar survey (2005) and wind speed (2-4 m s^{-1}), resulted in similar average and maxima trends (Fig. 7C) and further evidence of symmetry between the major (onshore) and minor (offshore) modes.

< Insert Figure 7 about here >

THC positive outliers were further analyzed for temporal patterns within the last five years. Numerous outliers exceeding 10 ppm THC occurred, with 339 above 5 ppm. Occurrence of high values slightly increased from 2004 to 2007 and may have leveled off in 2008 (Fig. 8A). In terms of seasonal and diurnal variation, summer months have fewer positive extremes compared to November and March (Fig. 8B) and hourly outlier probabilities peaked at ~1000 and ~1800 PST (Fig. 8C).

< Insert Figure 8 about here >

The 53-week, smoothed THC data for WCS (all values and only THC greater than or equal to 3.0 ppm) was compared with the state of California CH_4 emission inventory (CARB, 2008) (Fig. 9). The unfiltered THC record and CARB inventory showed a similar general decrease until the late 1990's and then a reversal, although there are deviations in the growth rate and multi-year variability. THC measurements significantly above global background (> 3.0 ppm, i.e., having a strong seep contribution) showed a poorer agreement with California emission trends.

< Insert Figure 9 about here >

4. Discussion

4.1. Diurnal and Seasonal THC Trends

On a diurnal basis, THC outlier analysis (Fig. 8C) and hourly averages (Fig. 5), all show a morning and evening peak in THC values, with low afternoon values. This pattern most likely arises from diurnal land-sea breeze circulations and variability in mixing height. In the morning, the boundary layer generally is thinner while winds are light, enhancing THC at WCS. Also, there could be nocturnal CH_4 accumulation over the seeps that late morning winds advect towards WCS. During the afternoon, the mixing height increases and winds are stronger, leading to a dilution effect. Finally, the evening reversal in wind direction could lead to re-circulation of the seep-enriched air with the concomitant decrease in the boundary layer thickness enhancing THC. However, the summer diurnal THC signal is unimodal for constrained wind speeds (Fig. 5A).

Seasonality of WCS data (Fig. 4) likely reflects a combination of cycles in background concentrations, seasonal cycles in transport and mixing depth height, variability in seep field emissions, and seasonal rain and synoptic system patterns. The strongest signature of the seasonal cycle was for THC data at 1200 PST (peak-to-peak amplitude of 0.24 ppm with summer low). The THC cycle is relatively in phase with the average seasonal cycle for baseline, afternoon CH4 measurements at Trinidad Head, CA (41.05°N, 124.15°W) and Point Arena CA (38.95°N, 123.74°W) (GLOBALVIEW-CH4, 2008) showing the effect of regional cycles; however, background THC cycles can only partially explain the THC seasonal cycle, given that its amplitude is an order of magnitude smaller. Meteorology likely explains some of the variation; for constrained wind speeds, summertime shows a single THC mid-day peak, such that

the 1200 PST value is greater than in winter months (Fig. 5). Some of the seasonality likely is source driven, related to storms (discussed below) and for long time scales, seasonal changes in the hydroxyl radical CH_4 sink.

4.1. Geology and Seepage

Data clearly show that the Coal Oil Point seep field is the dominant THC source at WCS (Fig. 6). Not only does the angular distribution of seepage show very good correspondence with sonar mapped seepage emissions (Fig. 7), but THC levels for winds from the seep field directions have THC values far higher than values for this latitude (or other directions). Underlying the seep WCS data trends are potential processes due to synoptic events and geology, which can affect emissions by altering subsurface hydrocarbon pressure (Leifer and Boles, 2005). Careful analysis of wind data showed an absence of long-term interannual trends (Fig. 4C & 4F), indicating that transport likely played a negligible role at these timescales for WCS THC.

Likely external (environmental) processes with the potential to affect seep field emissions are primarily storm-related. Specifically, storms can scour the seabed, thereby eroding tar caps sealing migration pathways. Storms also may affect seepage through swell-related hydrostatic pumping (Leifer, unpublished observations, 2009). Finally, an interesting hypothesis is that rains could affect seepage through aquifer recharge. Rock strata run from the coastal plain under the seabed and are penetrated by faults onshore (Jackson and Yeats, 1982) and offshore (Leifer et al. 2009, *submitted*), providing potential pathways to transmit aquifer pressures to seep migration. Monthly probabilities of high THC events show peaks in November and February-March (Fig. 8B), which could be related to storms and rainfall occurring during the winter rainy season.

On the interannual time scale, internal geologic processes likely are the dominant forcing for WCS THC. These changes occur over the full azimuthal range of the seep field (Fig. 6)

suggesting field-wide changes, which therefore most likely relate to deep migration processes. Thus, a decrease in seepage implies seabed emissions are greater than resupply from the Monterey Formation deep under the channel, leading to depressurization of near seabed reservoirs. Conversely, an emission increase must result from an increase in deep migration, due to opening of new pathways in which seismic processes may play a role. Observations since the 1940s (Fischer, 1978) suggest slow changes on decadal and longer time scales.

The data showed a decrease both in emissions and azimuthal width through 1997, when seepage appeared to arise largely from the Seep Tent Seep area (Fig. 6E), which in the 1980s was responsible for ~10% of the entire seep field emissions (Boles et al., 2001). To understand this change, we applied the conceptual seep resistance model (Leifer and Boles, 2005) to the overall seep field. In this application, dominant and thus high permeability pathway(s) supply each seep area. Then, decreasing seep field emissions tend to focus seepage through the highest permeability (strongest) seep areas, i.e., the Seep Tent Seep.

Thereafter, THC levels increased in tandem with an increase in the broadness of elevated $\mu_{THC}(\phi,yr)$ associated with the seep field and opening or re-opening of new pathways, an example being Trilogy Seep Area which first was observed in the WCS data in 2001. This corroborates sonar surveys in 1995 and 1999 that showed an absence of emissions from the Trilogy Seep area (Leifer et al., 2009, *in prep*). Additionally, the spatial distribution of seepage in relation to the WCS station will influence THC concentrations.

4.2 Comparison to regional trends and the impact of non-seep sources

There clearly are similarities between estimated California CH_4 inventory trends; however, there also are significant deviations (Fig. 9). The emission inventory is constructed

using a bottom-up approach with the overall trend resulting from underlying trends between 1990 and 2004 of decreasing residential and transportation emissions and increasing agricultural emissions (CARB, 2008). The effect of these trends is evident in the WCS THC data for observations from non-seep directions (e.g., 90° Fig. 6A). Although the estimated emission trend is fairly monotonic, the WCS THC trend (particularly for maxima) shows strong and persistent structure on multiple timescales (peak in 2002-2003) that clearly are not expressed in the inventory trends (Fig. 9). In comparison, a general overall increase in annually averaged CH_4 from 1990 through 1999 was followed by a period of relative stability except for significant increases in 2003 and 2007 (GLOBALVIEW-CH4, 2008). This trend was evident for reference marine boundary layer estimates (GLOBAL-VIEW 33.367° N) and baseline measurements at the background air observatories Trinidad Head, CA (41.05°N, 124.15°W) and Point Arena, CA (38.95°N, 123.74°W). The notable global growth event of 1997-1998 was linked to *El Niño*-related emission increases from wetlands, rice agriculture, and biomass burning; while the Northern Hemisphere 2002-2003 increase has been associated with biomass burning (Rigby et al., 2008).

Aside from regional and global variability, other non-seep local sources could have an impact at WCS. These include wildfire, and nearby biogenic and anthropogenic sources. In the Santa Barbara region, several wildfires have occurred during the study period: the *Gaviota* (3,010 ha; June 2004), *Zaca* (97,210 ha; July 2007), *Gap* (3,820 ha; July 2008), *Tea* (785 ha; Nov. 2008) fires (http://cdfdata.fire.ca.gov/incidents/). Local biomass burning could potentially explain the elevated $\mu_{THC}(\varphi, yr)$ for terrestrial wind sectors, i.e., 0 to 45°, in 2004 and 2007-2008 (Fig. 6); but not the greater $\mu_{THC}(\varphi, yr)$ from seep directions. Further, elevated THC in 2003 did not correlate with any local fires, while comparison of monthly THC averages (with and without

outliers, $0° < \varphi < 45°$) with the timing of fires was inconclusive. The coastal location and low sampling height of WCS likely reduces local fire effects on THC. Potential nearby biogenic sources include the Devereaux Lagoon, which would influence wind azimuths 90-180°. However, the $\mu_{THC}(\varphi, yr)$ demonstrate that this influence is negligible in comparison to the dominating seep emissions (Fig. 6).

Anthropogenic sources include urban, vehicular traffic, shipping, and local fossil-fuel related-facilities. Urban sources should correlate with population density (Fig. 7 - primarily to the east, Isla Vista). For the Isla Vista sector, mean THC values are relatively low. Relative to the seeps, vehicular traffic, focused along Highway 101 (Fig. 7 - tangential to WCS at ~0°), appears negligible and further, the diurnal THC pattern is inconsistent (Fig. 3C & 5).

Shipping-related THC emissions were estimated at ~3 Mg day^{-1} for the entire Santa Barbara channel. This estimate was based on a consistent NOx to THC ratio (Eyring et al., 2005) and is an order of magnitude smaller than seep field output, 40 Mg day^{-1} (Luyendyk et al., 2005). Moreover, shipping emissions largely arise from international waters in the Channel center, dozens of kilometers more distant. The nearby Ellwood Marine Terminal oil storage tanks (Fig. 1, 260 m at 310°), the Ellwood Oil and Gas Processing Facility (3.5 km at 325°) and a natural gas storage field (6 km at 83°), showed no persistent or highly significant effect on WCS THC in this analysis.

The $\mu_{THC}(\varphi)$ and $max_{THC}(\varphi)$ showed symmetry between peaks at 190° and 30° (Figs. 6 and 7), which suggests the latter, secondary peak is seep-related. Given the coastal location and occurrence of wind reversal in the evening from southwest to northeast winds (Fig 3), we propose this trend could result from re-circulation of marine air parcels with elevated THC values, back downslope in the evening, although local terrestrial sources cannot be ruled out.

4.3 Future efforts and implications

There are many directions for further analysis of the WCS THC dataset. These include synthesis with other existing data and field experiments to elucidate local spatio-temporal dynamics, source appropriation, and to test various hypotheses. For example, spectral analysis of hourly THC data to identify dominant frequencies (hourly to semi-decadal) and coherence and phase with respect to transport, mixing depth, and tidal forcing. Sonar maps from different years, aerial remote sensing data, meteorology and surface current data, and other air pollution monitoring station measurements along the coast will aid interpretation.

Further analysis of WCS data could be used to discriminate between diffuse emissions from the downcurrent dissolved CH_4 plume and from bubble plumes. Because the diffuse emissions depend on atmospheric and oceanic conditions, this dependency can be studied, e.g., the effect of wind speed on direct and indirect fluxes. More detailed analysis also can investigate temporal trends in $\mu_{THC}(\phi)$ to test hypotheses related to hydrocarbon migration (vent sealing, opening, blowouts, etc.) and the role of synoptic and geologic processes.

Several methods could be used to discriminate between anthropogenic and natural THC sources at WCS, specifically, isotopic analysis and CO and CO_2 measurements. WCS data could be modeled to infer source strength (Zhao et al., 2009) and integrated vertical-column CH_4 measurements used to control for diurnal boundary layer variations (Wunch et al., 2009). Forward modeling based on sonar-derived seep maps could identify spatial shifts in seep activity through comparison with WCS data. Planned modeling efforts will address regional influences and the fate of COP seep gas over longer time-scales.

Seepage is widespread in S. California (Fischer, 1978; Hodgson, 1987), with geogenic emissions recognized as a primary source of hydrocarbons (Killus and Moore, 1991). Source profiles determined from canister grab samples as part of the SCCCAMP Sept-Oct 1985 study, show that NMHC geogenic sources outweighed the anthropogenic (auto-related) for all sites except for interestingly, Goleta, CA (16%), which is closest to WCS (Killus and Moore, 1991). This could be due to the location and timing of the samples (0630-0700 PST & 1330-1400 PST) in contrast to the WCS THC peak values (Fig. 3).

COP emissions are conservatively estimated at 0.015 Tg CH_4 yr^{-1} (Clark et al., 2009), from 1994-1995 sonar maps, with our findings suggesting higher contemporary values. This compares to top-down estimates for Los Angeles County of 0.2± 0.006 (Hsu et al., 2009) and 0.6 ± 0.1 Tg CH_4 yr^{-1} (Wunch et al. 2009). The discrepancy between the top-down and bottom-up emission estimates (Hsu et al., 2009) could be due in part to underestimation of geologic emissions in Los Angeles and surrounding counties. While, the WCS data shows the importance of the COP seep field, estimates are largely lacking for other California geologic sources, currently budgeted at 1-2% of California CH_4 emissions.

5. Conclusions

In this paper, we present an eighteen-year total hydrocarbon (THC) record at the West Campus Station (WCS) air pollution monitoring station that provides insight into geologic marine seep dynamics and the importance of such sources for CH_4 emission inventories. Analysis of WCS data shows a strong THC dependence on local transport processes and variability at diurnal to interannual time scales. High wind speeds occur in the afternoon and were correlated with lower THC levels, likely due in part to dilution and convective mixing.

Elevated THC tends to occur in the morning and evening with a seasonal shift in timing corresponding to changing day length. A seasonal cycle was observed, which was strongest for afternoon hours with a maximum in January and minimum in July with a peak-to-peak amplitude of 0.24 ppm.

Although there is relative constancy in wind direction and speed over the 18 year record, average annual THC with respect to wind direction, $\mu_{THC}(\varphi,yr)$, showed a decrease both in seep extent and strength until circa 1997 at which point there was a reversal. These changes were concluded to arise primarily from long-term, deep geologic processes. Additionally, analysis of $\mu_{THC}(\varphi)$ suggested evening recirculation of CH_4-enriched air from the seeps at WCS. Other sources including urban, fires, and biogenic were not found to significantly affect WCS THC in comparison to the seeps.

This study illustrates the value of long-term municipal air pollution monitoring station data, beyond ensuring compliance of anthropogenic point sources. Using the variability in THC with wind direction provides insights into emissions from other local sources and long-term patterns. Analysis of similar datasets for other sites should be considered to improve our understanding of long-term source variations (Graedel and McRae, 1980). This study shows that COP seep field emissions are locally and regionally significant and exhibit multi-year trends, thereby highlighting the need for further studies of regional geological emissions.

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FIGURE CAPTIONS

Fig. 1. A) Location of West Campus Station (WCS), Los Angeles (LA), and Mt. Wilson on a surface wind vector map for coastal Southern California from METOC/Geophysics Branch, Naval Air Systems Command Weapons Division (www.weatherflow.com/navair/analysis.html, with permission). Blue vectors are interpolated from yellow observation sites, gray shading represents topography. **B)** Water-column, bottom-bounce normalized sonar return, σ, amplitude map of gas plumes in Coal Oil Point (COP) seep field (logarithmic color scale). Offshore seep trend was surveyed Sept. 2005, inshore trend July 2006. From Leifer et al. 2009, *submitted.* WCS is located on **C)** COP coastal plain, nearby to Elwood Marine Terminal storage tanks (EMT).

Fig. 2. Histograms of **A)** Total hydrocarbon, **B)** wind speed, and **C)** wind direction. THC histogram inset shows enlarged view for 1-4 ppm range and a probability plot indicating samples' departure from Gaussian. Bivariate relative *f*, frequency, histograms for **D)** wind direction and speed, **E)** THC and wind speed, and **F)** THC and wind direction, using a discretization scheme for direction of 0 to 360° in 5° bins, speed 0 to 15 m/s in 0.3 m s^{-1} bins, and concentration 0 to 18.0 ppm in 0.3 ppm bins. **G)** Enlarged *f* histogram for THC and wind direction, for THC 1.6 to 3.6 ppm in 0.1 ppm by 1° direction bins, with low probabilities ($<3.125\times10^{-5}$) not shown.

Fig. 3. Hourly **A)** wind speed, **B)** wind direction, and **C)** THC values for 1990-2008 record shown as color-scale values within an hour vs. day grid, with start of year indicated on x-axis. THC color range has gradation for values between 1 and 3 ppm, reflecting majority of the data. Data gaps are shown as gray, see text for details. Temporal subsets shown for **D)** year 2006, **E)** July 2006, and **F)** 7, 15, and 25 July 2006.

Fig. 4. Bivariate column-standardized frequency histograms shown as color scales for wind direction, wind speed, and THC as a function of hour (PST), month, and year (1991-2008). Colorbar shows normalized probability. Gray is used to indicate lowest probabilities, with white markers for null values and black for THC calibration at 0100 PST.

Fig. 5. Hourly THC averages and standard errors for **A)** summer (May-September) and **B)** winter (October-February) for 2005 through 2008. Wind-speed filtered data (green), restricted to 2 to 2.3 m s^{-1}, shows a single mode and highest THC values. Quiver plots show resultant hourly wind vectors for summer **C)** and winter **D)**. Note, averaging can lead to vectors shorter than scalar filter limit.

Fig. 6. Azimuthal **A)** average THC, **B)** wind speed for 5° wind-direction bins by year.

Fig. 7. Average **A)** and maximum **B)** THC values for 5° binned wind direction overlain on study region image © Google – Map data Santa Barbara terrain, with sonar contours (see Fig. 1B). Blue to red color scale for **(A)** is 1.7 to 2.7 ppm and for maximum values **B)** is 0 to 17 ppm. Filtered data 2-4 m s^{-1} for 2005 and 2006 presented in **C)**, unsmoothed 1° data (yellow) and smoothed 3° moving average (black).

Fig. 8. Probability of elevated values for **A)** year, **B)** month, and **C)** hour for 2004-2008.

Fig. 9. THC 53-week centered moving averages for unfiltered data (gray, left axis) and only observations greater than or equal to 3 ppm (black, left axis + 2 ppm). Masked moving average for mid-1997 through mid-1998 on account of data gaps. X-axis labels refer to start of year. Bar chart of CH_4 emission estimates from CARB California inventory for 1990 – 2004 in units of MMT CO_2 equiv. per year (CARB, 2008).

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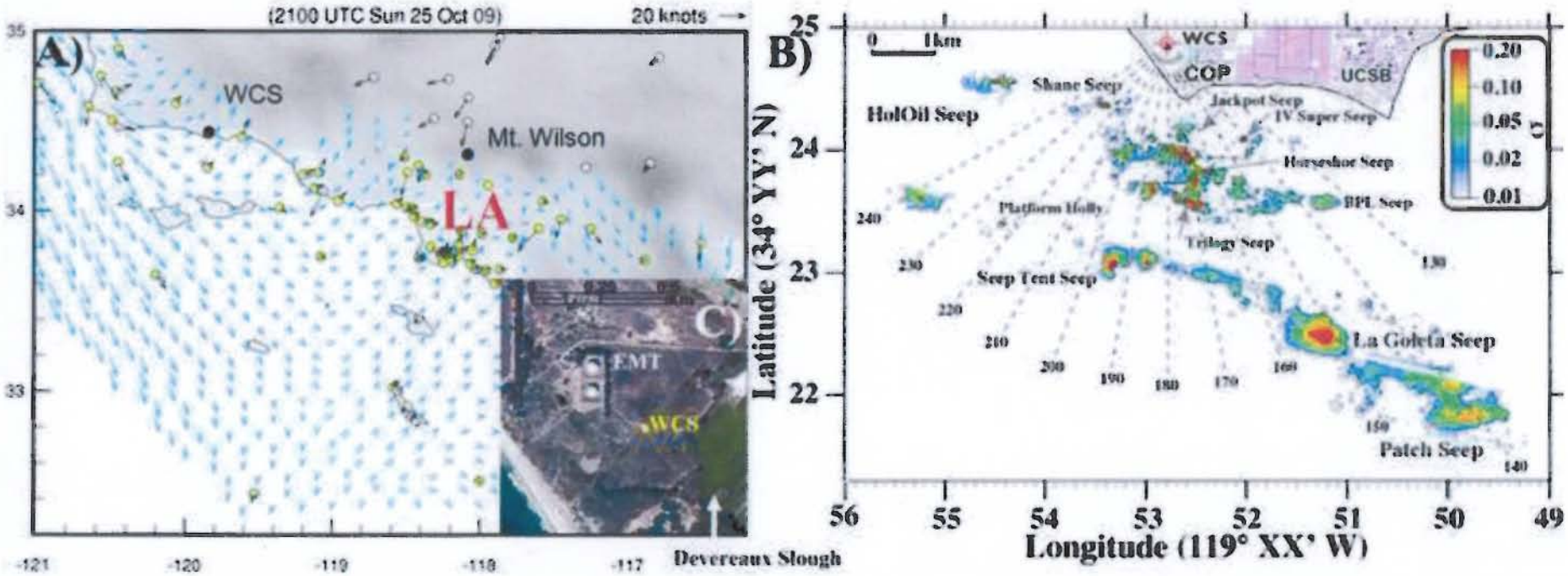

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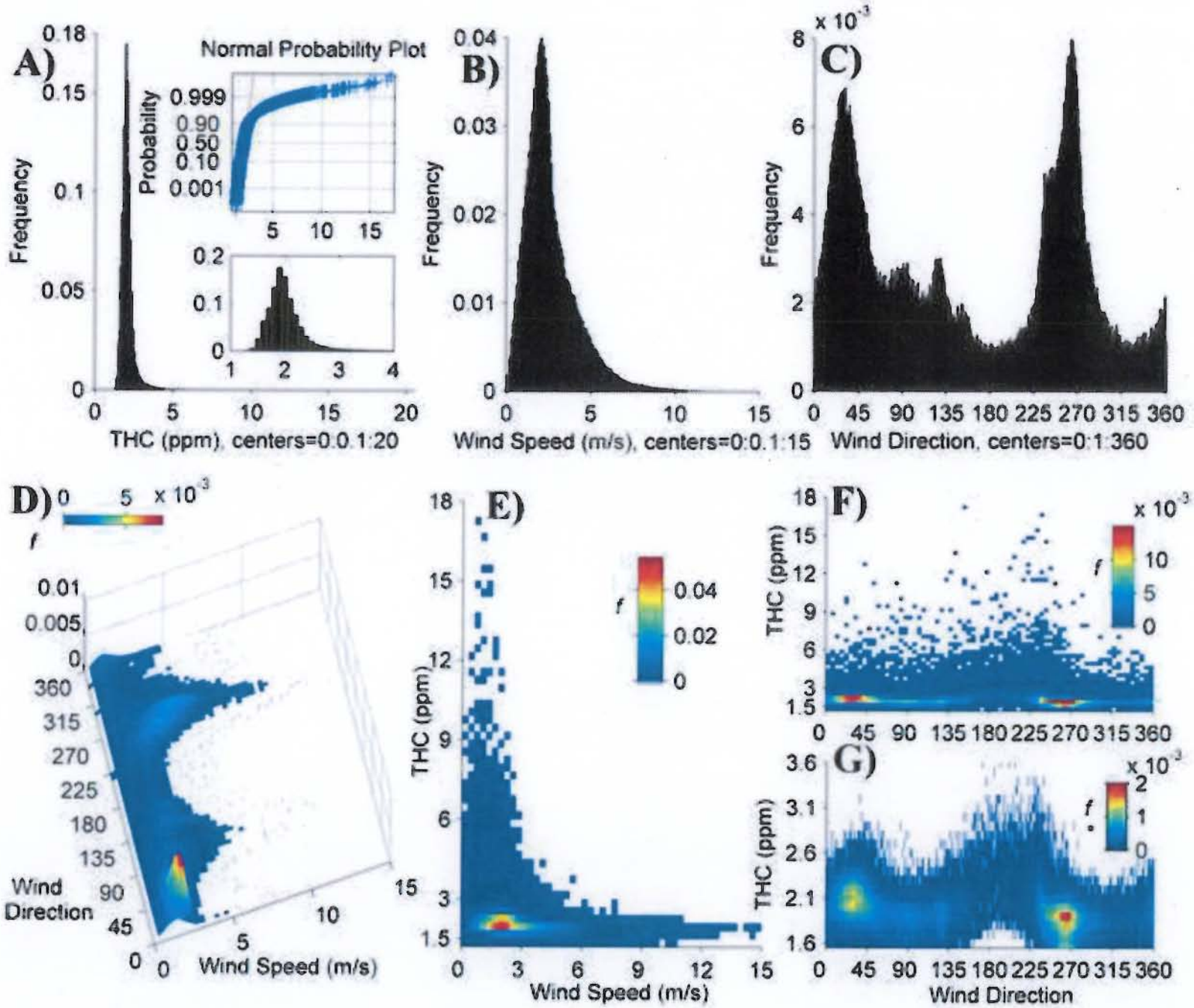

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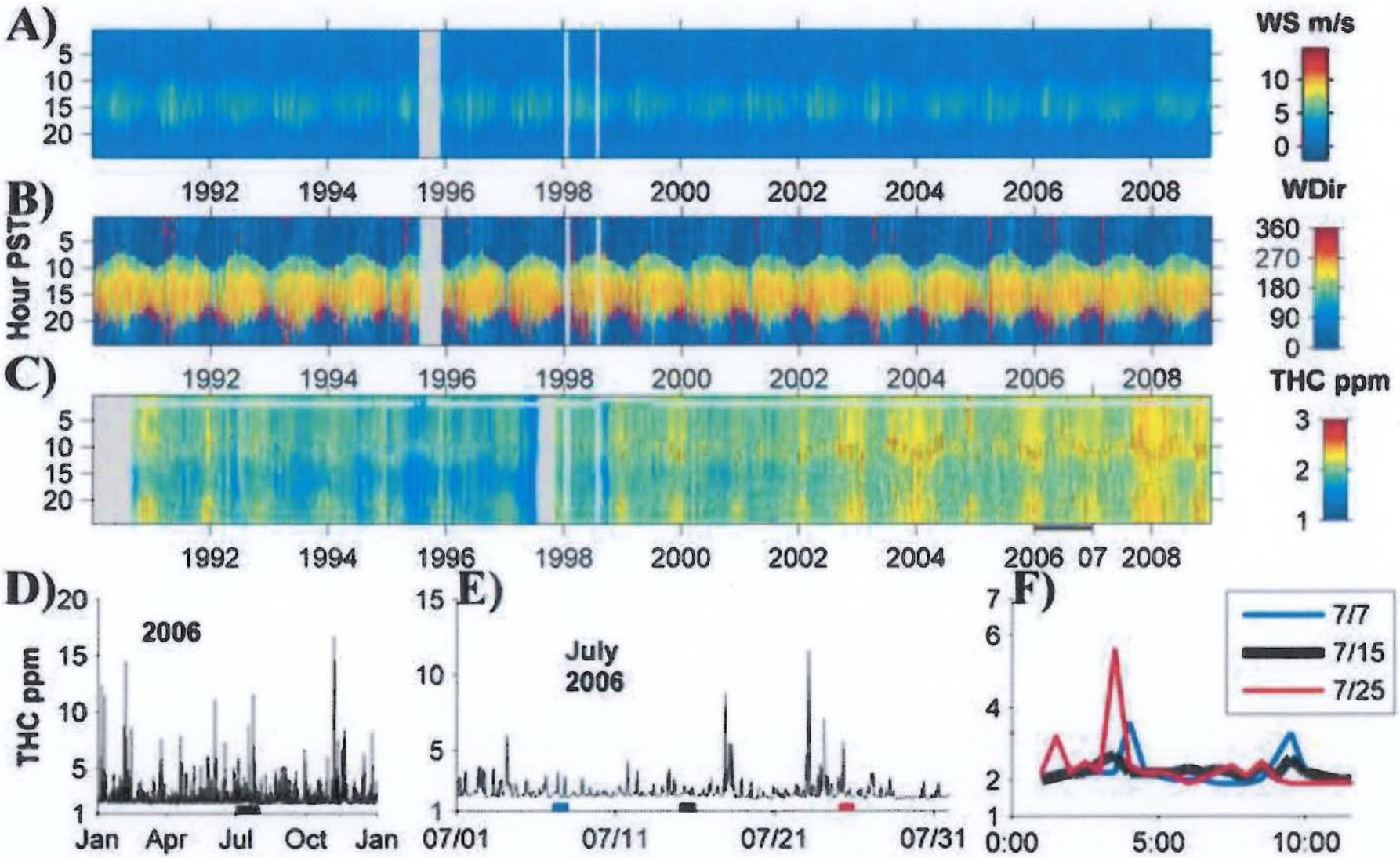

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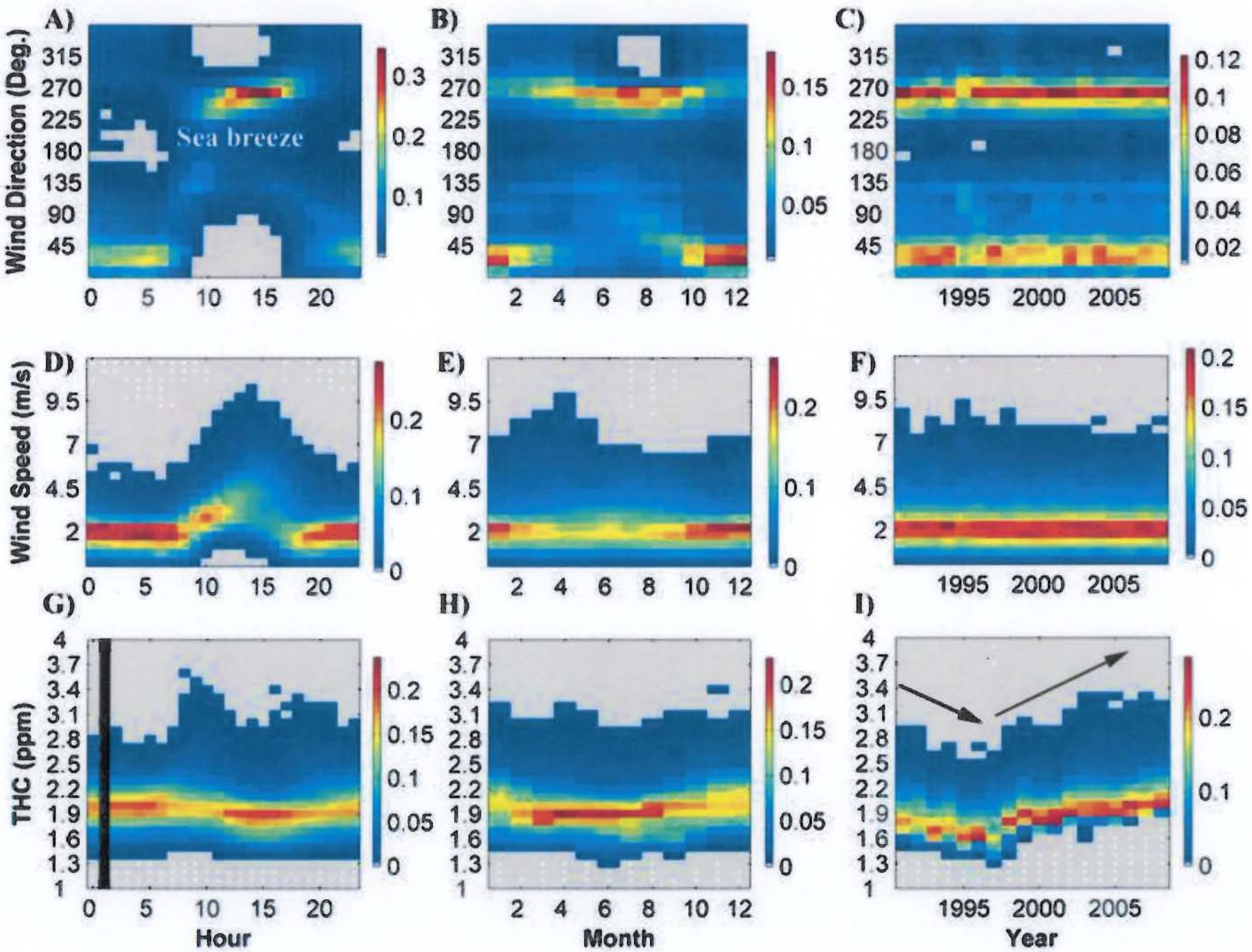

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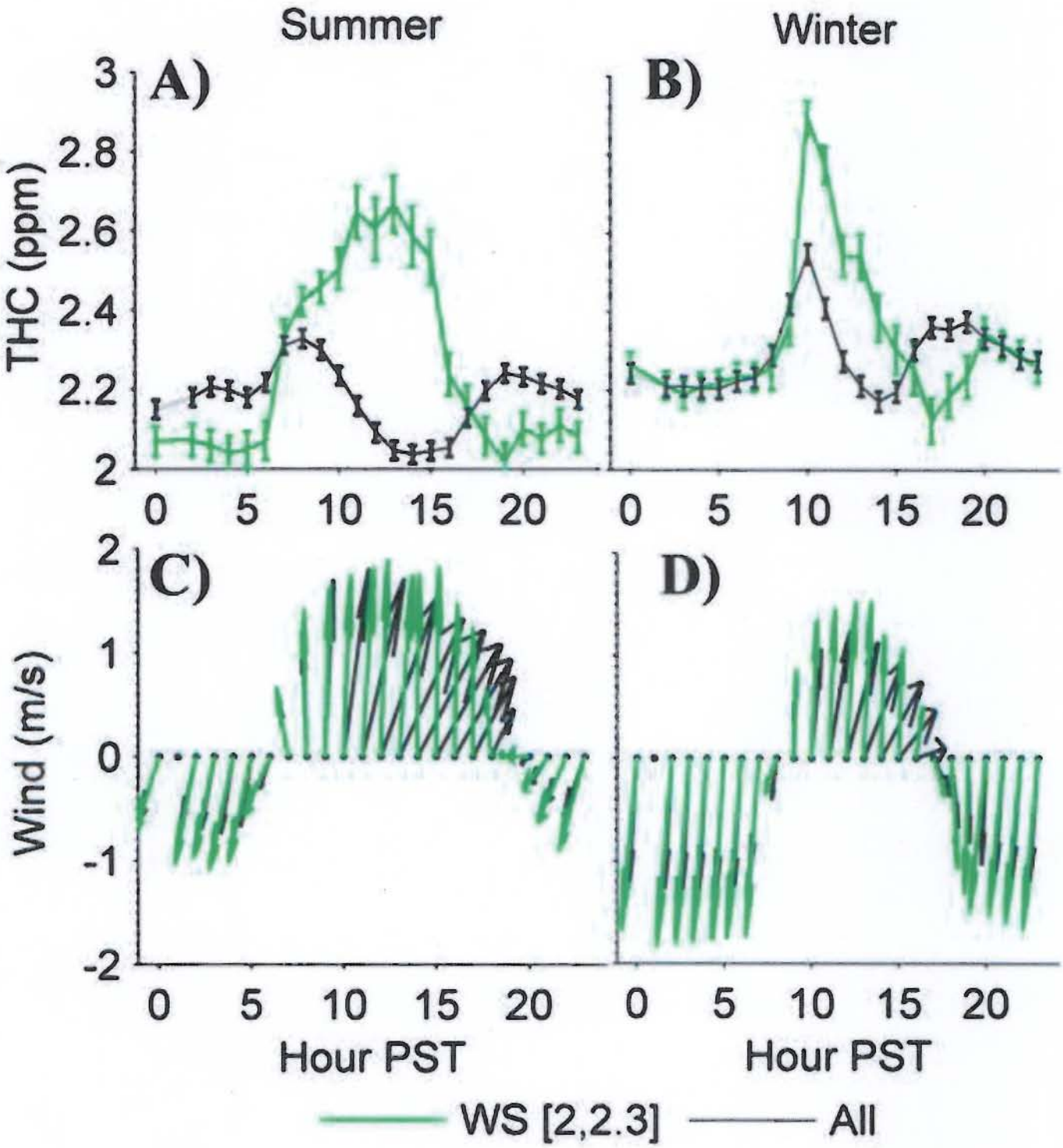

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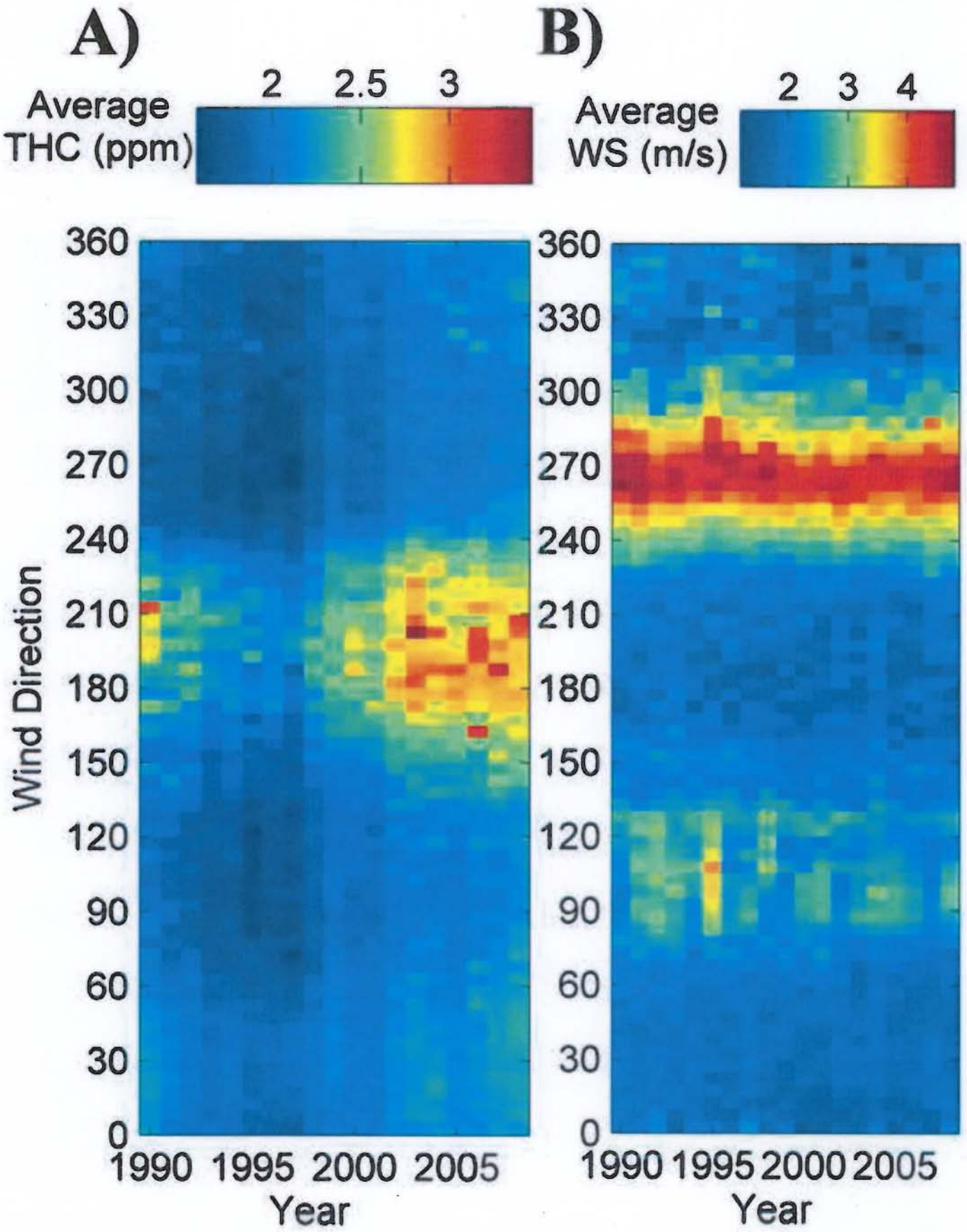

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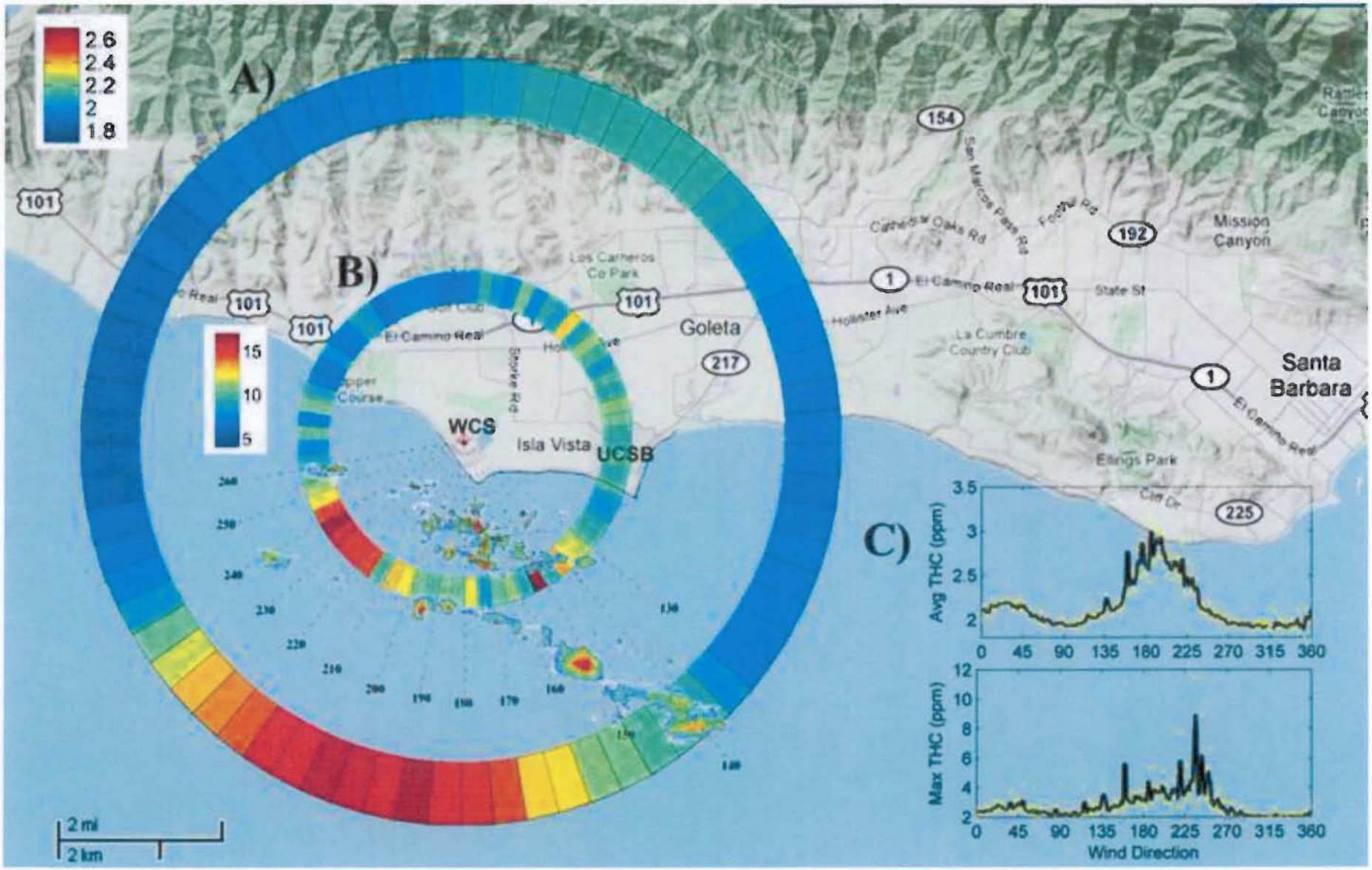
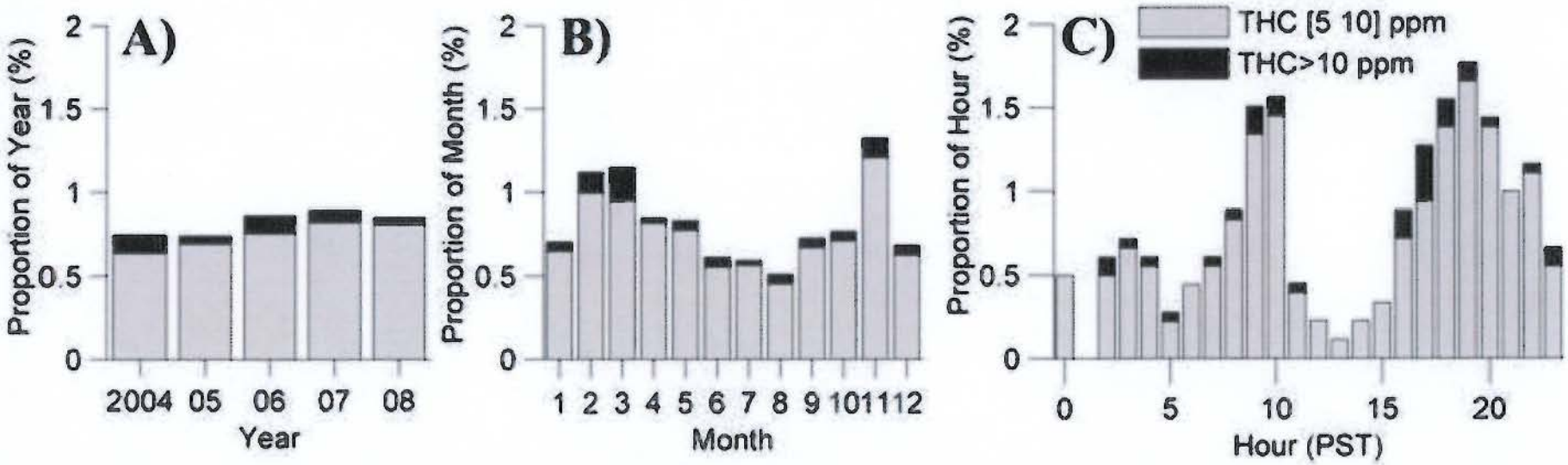
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