Final Report

An investigation of offshore ship emissions of CO from shoreline measurements and a survey of vessel operations

submitted to:

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on May 14, 2010

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Acknowledgments

This Report was submitted in fulfillment of ARB contract number 06-333, An Investigation of offshore ship emissions of CO from Shoreline Measurements and a Survey of Vessel Operations" by The University of California, Davis, under the partial sponsorship of the California Air Resources Board. Work was completed as of May 14, 2010.

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Abstract

The purpose of this research effort was to conduct ambient monitoring of CO and SO_2 at the Bodega Bay Marine Lab on the Northern California coast (55 miles north-northwest of San Francisco) to estimate regional ship emissions from this currently unregulated source of air pollutants. Despite extensive efforts to procure and operate a trace-level SO_2 monitor sufficient for the research objectives, the SO_2 instrument purchased failed to perform to the necessary specifications and consequently did not allow us to make useful ambient measurements of SO_2 along the coast. Because the instrument did not perform according to its advertised specifications, it was returned to the manufacturer who provided a complete refund. Unfortunately, the SO_2 measurement problems did not become fully evident until after concerted and considerable personnel efforts had been expended in laboratory calibrations, field deployment, data analysis, and protracted troubleshooting attempts that ultimately failed. These difficulties depleted much of the resources of the contract and prevented several project tasks from being fully accomplished. Moreover, the failure to measure simultaneous increases in CO and SO_2 concentrations prevented us from identifying the type of engines responsible for the CO spikes, and thus made it impossible to make any inferences about offshore NO_x emissions.

Despite the problems with the faulty SO_2 instrument, we were able to make new measurements of CO and ozone at Bodega Bay which may help to provide baseline air quality data for the offshore environment. Continued detailed analysis of the shoreline pollutant data and the collocated meteorological data have allowed further improvement of the estimation of offshore CO emissions and boundary layer heights. Additional efforts were made to deploy the CO instrument on a Cessna 210 airborne platform in support of a regional greenhouse gas emissions experiment, with the hope that some flights could be performed over the ocean to investigate CO vertical gradients, and thereby help to infer regional offshore emissions. Continuing along those lines, effort was also invested in the analysis of existing datasets of airborne data collected offshore of Northern California (e.g. INTEX-B, DYCOMS-II, ITCT, and ARCTAS-CA.) Approximately consistent results were obtained of ~200 μmol $m^{-2}d^{-1}$ of CO being emitted from the offshore region writ large.

Additionally, a preliminary survey of the local fishing community at Bodega harbor was conducted to ascertain offshore ship traffic frequency, and to develop an inventory of engine types at the local marina. Because of the absence of SO_2 data and the efforts it consumed, the determination of the engine make-up of the local fleet was unsuccessful. However, support of these overall efforts have paved the way for future SO_2 monitoring with improved instrumentation (GC/MS), and integration with the CO and meteorological measurements at the site.

Executive Summary

Ocean-going marine vessels are considered to be the most fuel-efficient mode of transporting goods worldwide, but they also represent one of the most challenging air pollution sources to regulate. It is estimated that 85% of global ship traffic occurs in the northern hemisphere and that 70% of that is within 400 km of land (IMO 1997). In the last decade, ship emissions have been identified as having the potential to substantially influence air quality in many high traffic coastal regions and indeed even globally [Corbett & Fischbeck, 1997; Capaldo et al., 1999; Lawrence & Crutzen, 1999]. More recently, it has been suggested that the developing global inventories of ship emissions are geographically skewed offshore and that in reality twice as much NO_x is emitted by ship traffic and a substantially larger fraction of that is released very near the coast [Corbett & Koehler, 2003]. If this is the case, then it is likely that more and more state and regional air quality managers will become acutely concerned with ship traffic emissions.

Carbon monoxide (CO) is a trace gas of immense importance in mediating the oxidative capacity of the background atmosphere and is often an excellent tracer of combustion. NO_x is central to atmospheric chemistry because it modulates ozone and free radical abundances and thus also influences the atmosphere's oxidative state. SO_x is an important precursor to aerosols, and has a complex fate in marine environments [Bates et al., 1998; Faloona, 2009], where it can substantially influence the cloud albedo [Capaldo et al., 1999; Ferek et al., 1998] and climate. Because of the inherent non-linearity of atmospheric photochemistry and transport, the initial conditions of any air quality model are extremely important to the accuracy of the results. In order to accurately predict air quality throughout California and efficiently regulate pollution sources, it is necessary to better understand the nature and magnitude of emissions of these compounds originating in the coastal waters upwind of central California and in the domain of the air quality models.

Instrumental deficiencies prevented us from making useful measurements of SO_2 along the coast, and failed attempts to rectify the situation consumed a large portion of the project's resources. Nevertheless, in spite of these problems, we succeeded in extending our CO measurements, deploying an ozone monitor at Bodega Bay, and analyzing archived airborne data to bolster our estimates of regional offshore CO emissions. Average levels of SO_2 at the site are most likely no larger than ~200 pptv on long term averages, and ozone fluctuated diurnally from 30-35 ppbv during the late summer with considerable elevations evident during periods when the region was heavily influenced by forest fires. Other efforts supported by this contract include development of marine boundary layer height analysis program, deployment of the CO instrument on airborne studies of greenhouse gas emissions throughout the Sacramento Delta, and deeper analysis of airborne data sets such as that collected during ARCTAS-CA.

Introduction

Continuous, high-rate observations of CO concentrations made by our group at Bodega Bay have indicated considerable onshore advection of pollutant plumes from coastal ship traffic [Cox, 2006]. Nevertheless, the technique developed to estimate CO emissions could not be easily scaled to estimate SO_x and NO_x emissions due to the uncertainty in the engine type of the principal offshore sources. While efforts have been made to quantify offshore emissions of NO_x and SO_x using bottom-up estimates of fuel consumption and vessel activity, many uncertainties in these techniques persist [Corbett & Koehler, 2003], and there have been very few observational studies to substantiate the estimates. Furthermore, unpublished data from Professor Mike Kleeman's group at UC Davis indicate a substantial amount of sulfate aerosols at Bodega Bay, which may originate from ship traffic emissions. On the other hand, recent work in our group has indicated extremely high levels of dimethylsulfide (DMS) at Bodega Bay; thus, the relative sulfur contributions from biogenic versus anthropogenic sources remains highly uncertain. This project directly aligns with research interests of CARB for enhanced understanding of atmospheric processes in the marine boundary layer to improve air quality models of pollutant behavior in California's complex and highly populated coastal environment.

Prior to this study, our research group monitored carbon monoxide (CO) at the Bodega Marine Lab along the coast of Northern California for 18 months (Sept. 2004 – Mar. 2006) with a very fast response and sensitive UV resonance fluorescence instrument. To our surprise, the fast response data revealed the consistent appearance of CO spikes elevated anywhere from 50 – 1000 ppb above background levels (80 – 180 ppbv) while the flow was unequivocally directed onshore. Through past work in our group, we developed a method to accumulate the statistics of these plume spikes, and based on a few assumptions (e.g., the orientation of the CO source line (ship path) relative to the coastline, and that CO is well-mixed throughout the marine boundary layer) were able to estimate the average regional CO emission rate from offshore ship traffic. The apparent mean distance of these CO sources from the coastline appeared to be 2-3 km but some came from as far offshore as 30 km. The regional emissions of CO can then be scaled to the ratio of emission indices between CO and NO_x or SO_2 to derive estimates of the source strengths of these other two species that influence regional air quality more directly. The emissions thus derived appeared to be in the logarithmic vicinity of the estimates from the bottom-up analyses of Corbett et al. [1999] but appreciable uncertainty in the method remains.

There are two main uncertainties in our ongoing work regarding these emission estimates. First, the actual orientation of the ship trajectory as it passes upwind is unconstrained, and therefore inferences about the plumes' width as they advect over the sensor are dubious. Second, the type of engine creating the plumes strongly determines the relative amount of CO and SO_2/NO_x emitted, with diesel combustion releasing more of the SO_2 and NO_x and gasoline more of the CO. Accurate inferences of the regional SO_2 and NO_x emissions thus depend strongly on the source engine type. Because SO_2 data were not collected successfully during this contract and only preliminary surveys of fishing activity were administered, the type of engines responsible for the CO spikes remains unknown.

Despite the failure of the SO_2 measurements, significant progress was made on several other fronts regarding the estimation of ship exhaust emissions offshore of Northern California. Over four additional months of shoreline CO data were collected during the contract and incorporated into an improved methodology for estimating emissions from spike statistics. One of the improvements was in estimating the marine boundary layer depth from the continuous

sounding information provided by the atmospheric sounding system operated by NOAA's Earth System Research Lab. In addition, effort was focused on deployment of the CO instrument onboard a Cessna 210 with other greenhouse gas monitoring equipment to help survey regional emissions. Finally, independent observations of the gradients in CO between the marine boundary layer and the free troposphere above the inversion were compiled from past airborne experiments and used as an independent method of estimating the regional offshore combustion source strength.

Finally, we were able to begin the process of canvassing the local fishing community who access the coastal waters from Spud Point marina in Bodega Bay. Use of the questionnaire was limited, however, as many ship captains reacted negatively to questions regarding their engine emissions, presumably fearing increased regulatory restrictions to an already challenged industry. This experience provided significant insights into the best approach to canvassing the fishing fleet in the future.

From the unsuccessful measurements of SO_2 it is clear that a study of sulfur chemistry along the coast of California, outside of large ports and other industrialization centers, will require instrumentation of very high sensitivity. We suspect that the average concentration of SO_2 at Bodega Bay was below 100 pptv. Such low levels will challenge all but the very best commercially available trace gas analyzers. Furthermore, any study of boating activity by local fishermen should be conducted with the utmost sensitivity to their inveterate circumspection. That community is highly suspicious of excessive governmental regulation and many consider their exact boating patterns to be something of a trade secret.

Results

Due to the failure of the trace level SO_2 analyzer to meet its advertised factory specifications, we were unable to detect any SO_2 in the air at Bodega Bay. The signal was awash with instrumental noise and much effort went into attempts to remedy the situation in order to salvage some meaningful observational data. Nevertheless, not even heavy diurnal averaging could retrieve any signs of the instrument responding to ambient levels of SO_2, let alone transient ship plumes. At the very best, it might be concluded (with considerable caution) that the ambient levels of SO_2 at Bodega Bay are likely to be less than ~200 pptv on averaging periods beyond about 30 minutes. After sending it back to the manufacturer and having their technicians evaluate the unit, they agreed that several problems were found with the unit (Appendix A) and they agreed to a complete refund of the instrument cost.

The failure of the trace-level instrument to perform up to the manufacturer's specifications, however, severely hindered the possibility of achieving many of the goals outlined in the contract. Detection of the problem and attempts to correct necessitated an excessively large expenditure of time and effort. Because it was impossible to purchase another analyzer in the time frame of the contract, and because many of the resources originally allocated to other tasks were required for the labor costs associated with troubleshooting and repair attempts and communications with the vendor, we made a concerted effort to push forward the few lines of research still available on the limited time frame and budget.

Below is a summary of the major tasks originally described in the proposal, along with the shift in emphasis and major findings in each category.

Task I: *Continued analysis of previously collected CO and meteorological data to strengthen ship emission estimation technique.*

Redoubled efforts to extract emission information out of ambient CO measurements were successful, and an additional data set was generated and analyzed for more than 4 months during the Fall of 2007.

I.1 Methodology

A common method of estimating fugitive emissions from line sources is by computing horizontal fluxes of an emitted pollutant such as aerosols from roads [Cowherd and Englehart, 1984; Veranth et al., 2003; Venkatram, 2004]. We extended this idea to mobile and temporary line sources of ship plumes that are advected with the winds during onshore flow at the fixed monitoring site at the Bodega Marine Laboratory (BML) in Bodega Bay, California (Figure 1). UC Davis operates a remarkable facility out on the headlands west of the city of Bodega Bay and its harbor. Measurements were made from a small beach shack away from the main laboratory building. Because CO has a long lifetime (~2 months) and it has been estimated that approximately 70% of ship emissions are within 400 km of land [Sinha et. al. 2003], we believe the CO spikes observed at BML are the result of ship emissions conducted to the site in

the mean onshore flow. Ship emissions are easily detected as ship tracks in satellite images when low level stratocumulus cloud cover is present. Ship tracks are defined as "curvilinear, bright feature[s] in near-infrared imagery that [are] spatially coincident with the effluent plume of a ship," [Durkee et al. 1999]. They occur because the ship emissions produce large numbers

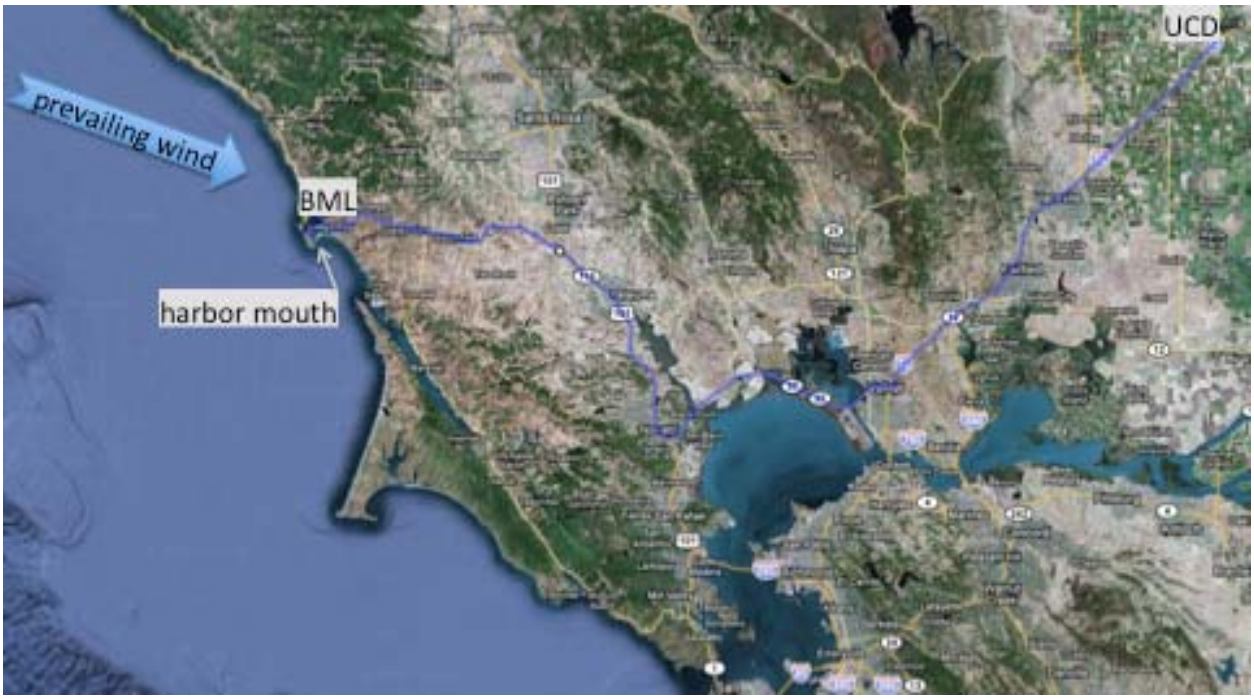


Figure 1. Map of the Bodega Marine Lab and environs. The lab is located west of the town of Bodega Bay approximately 100 miles west of Davis, and 55 miles northwest of San Francisco. The harbor mouth is located on the southern edge of the headlands and thus ships heading north (whether from the harbor or passing by) or heading south (whether approaching the harbor or passing by) will pass offshore of the lab. Thus, only ships with this harbor as their northern terminus would not pass by the BML.

of cloud-condensation nuclei (CCN). The augmented CCN provide more sites for cloud formation and thus lead to regions within the cloud with enhanced liquid water surface area and are thus more reflective in the shortwave region than other clouds not directly impacted by ship emissions. Ship tracks have been commonly observed offshore of California since the mid 1970s but their presence requires not just cloud cover but also a boundary layer that is relatively clean so the contrast of the ship effluent is readily observed [Scorer 1986]. These tracks exhibit obvious plume behavior in that their lateral dispersion occurs gradually, just like smokestacks from industrial plants, and they can persist for up to 36 hours. The chemical nature of such ship tracks has been investigated for many years and their typical characteristics as observed by satellite have been compiled by Durkee et al. [2000]. Figure 2 shows some examples of ship tracks in the clouds and the overall geometry of how ship emissions (many not made visible by the cloud conditions) are commonly advected towards the coast.

An example of a resultant time series of the pollutant CO observed at the coast is shown in Figure 3. The baseline is calculated from the lower 20th percentile in a 20-minute running window. Individual spikes are then identified when the concentration is at least 50 ppb above

the baseline concentration. The geographic significance of the window and threshold and the sensitivity of the results will be discussed later. We attempt to estimate the ship's line source strength from each CO plume encountered by multiplying the enhanced CO concentration of the plume (i.e., minus the background concentration) and its physical size determined from its duration and the wind speed. An outstanding complication is not knowing the exact orientation of the ship exhaust plume with respect to the mean wind that carries it onshore.

Figure 2. Image of ship tracks in marine stratocumulus offshore of California on January 5, 2003 captured by the Moderate Resolution Imaging Spectral Radiometer (MODIS). The many ship plumes not made visible by the clouds are also advected with the mean flow onshore to coastal sites like that at Bodega Bay.

Without any information about specific ship destinations, we assumed that the average ship trajectory is made up of equal components of onshore and offshore directions. Thus, we assumed an average orientation of the plume parallel to the coastline (at BML the coastline lies at an angle of 336° from North.) The CO emission rate per unit length of ship travel, E_{CO}, is thus calculated as the horizontal flux estimated by:

$$E_{CO} \cong \begin{cases} \rho_{air} \cdot \Delta[CO] \cdot \Delta x \cdot z_i , & \Delta x \geq z_i \\ \rho_{air} \cdot \Delta[CO] \cdot (\Delta x)^2 , & \Delta x < z_i \end{cases}$$

where ρ_{air} is the density of air, Δ[CO] is the elevation of the plume above the background (ppbv), Δx is the plume width, and z_i is the height of the marine boundary layer. The plume width is estimated by the observed duration of the plume and the mean wind speed:

$$\Delta x \cong \cos\theta \cdot U \cdot \Delta t$$

where θ is the angle between the mean wind direction and the normal to the shoreline (wind direction minus 246 degrees), U is the mean horizontal wind speed measured at 10 m on the

lab roof, and Δt is the duration of the elevated spike. Comparisons of the lab wind speed to the winds measured by the NOAA buoy 15 mi. offshore (NDBC 46013) indicate that the median buoy winds are only ~30% faster, but because we suspect that most of the ship exhaust is closer than the buoy we use the lab winds in this analysis. The spikes are estimated from a compiled 10 s data set of the meteorological and CO data. Figure 4 illustrates a plan view and a vertical cross section of the plume and its orientation with respect to the wind and the monitoring site. The three dimensional turbulent motions of the marine boundary layer (MBL) will mix the exhaust throughout in a relatively short period (approximately 1000 seconds or about a 4 km horizontal advection length). This is equivalent to a large eddy turnover time and was in fact observed in ship plumes by Durkee et al. [2000]. Because of the inherent three dimensional nature of turbulent mixing, it is assumed that the plume is of similar height as width until the mixing throughout the MBL is achieved.

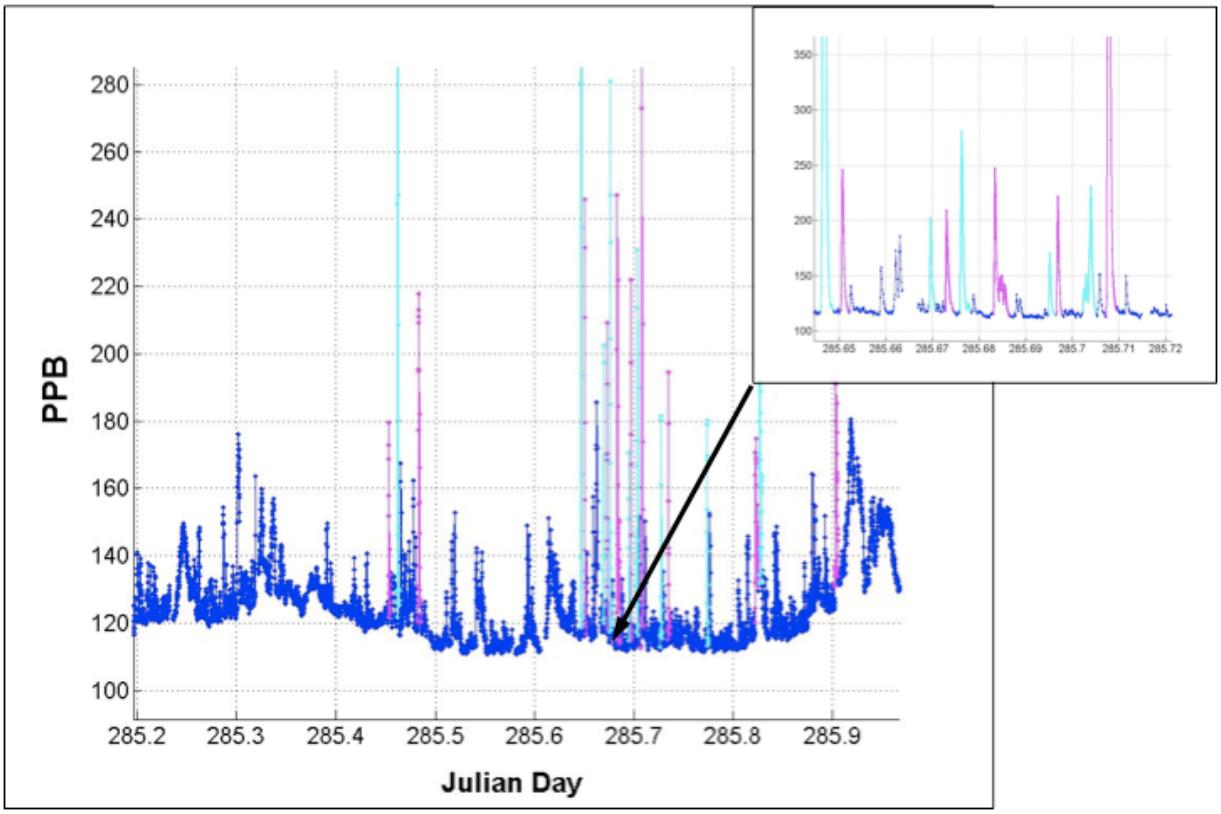


Figure 3. Example time series of CO concentrations from October 2005 indicating the numerous spikes advecting onshore during the day (during onshore flow). The blue is the calculated baseline and the light blue and pink are alternating spikes detected by the algorithm described in the text. The inset is a period of less than two hours showing the very rapid nature (~1 minute) of the spikes.

I.2 Results

The detected plumes from 25 non-contiguous months of CO data are compiled (from September 2004 to December 2007) and used to infer the regional fluxes using the method outlined above. A histogram of the composite data set is illustrated in Figure 5 arranged by plume width. It appears that approximately half of the plumes are of the same size as the MBL

depth (200-500 m typically) or smaller. According to lateral dispersion parameterizations available for over water trajectories, plume widths of 400 m (nearly the median) correspond to approximately 1.5 – 3 km travel distance to the shoreline, with an average wind speed of 4 m/s. This indicates that much of the CO emission plumes at BML appear to be originating from the very near-shore environment, a fact that perhaps is not too surprising given its proximity to the mouth of Bodega Bay harbor.

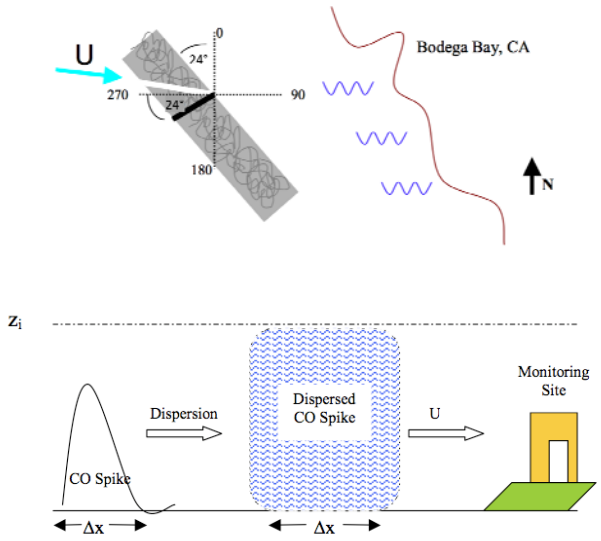


Figure 4. (top) Schematic orientation of ship exhaust plume, coastline, and prevailing wind direction. The diagram below (bottom) shows how the exhaust plume is expected to evolve in the vertical on its transit to the shoreline monitoring site.

The ship plume statistics were compiled for each month of the 25 month time series and a tabulation of the emission rates in mass of CO per linear distance of shoreline were made. In order to convert this to a regional emission rate, the extent of the observational domain offshore must be estimated.

Considering that the running window used to calculate the CO baseline determines the widest plume that could be observed by this technique, and then comparing that to an advection distance based on the mean wind speed and lateral dispersion parameters, we conclude that the farthest offshore range observable using this technique is approximately 25 km (20 minute concentration spike corresponds to 4-5 km plume width, which corresponds to 2 hours advection time and thus 25 km offshore.)

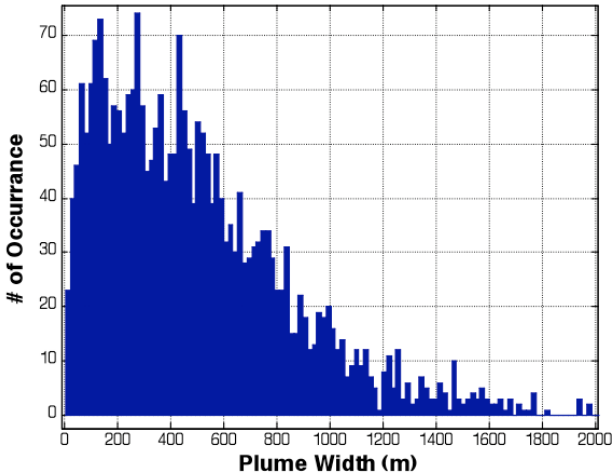


Figure 5. Histogram of observed ship plume widths from 25 months of data, restricted to onshore flow conditions, and corrected for wind orientation with respect to the coastline.

Faloona (2009) provides a compilation of over-water dispersion relationships reported in the literature over the past 40 years. Work by von Glasow et al.(2003) highlights the importance of plume dilution in modeling results of the chemical evolution of ship exhaust in the MBL. The authors, based on their own lateral mixing parameterization, estimated the dilution lifetime of a ship plume (defined as when its contrast to the background has fallen to 5% its initial value) to be ~2 days. It should be pointed out, however, that the plume dilution parameterization developed by von Glasow et al. (2003) is based on only a few ship track cases from Durkee et al. (2000) that spanned a limited plume evolution time and did not agree very well with other common dispersion models. Figure 5 shows the von Glasow et al. (2003) relationship compared with other more common parameterizations such as that from the EPA's Offshore and Coastal Dispersion (OCD) model, and the power laws of Heffter (1965), and the more recent overview by Gifford (1995). The scatter in the data used by each of these is fairly large, but it is apparent that the von Glasow et al. (2003) is too large in the near-field and probably too small in the far-field. The method of using satellite images of ship tracks in marine stratocumulus (Durkee et al., 2000) is complicated because of the requisite coupling between the ship effluent and the ambient cloud field. It is recommended that some average power law of the OCD, Gifford (1995), and Heffter (1965) be used in future work.

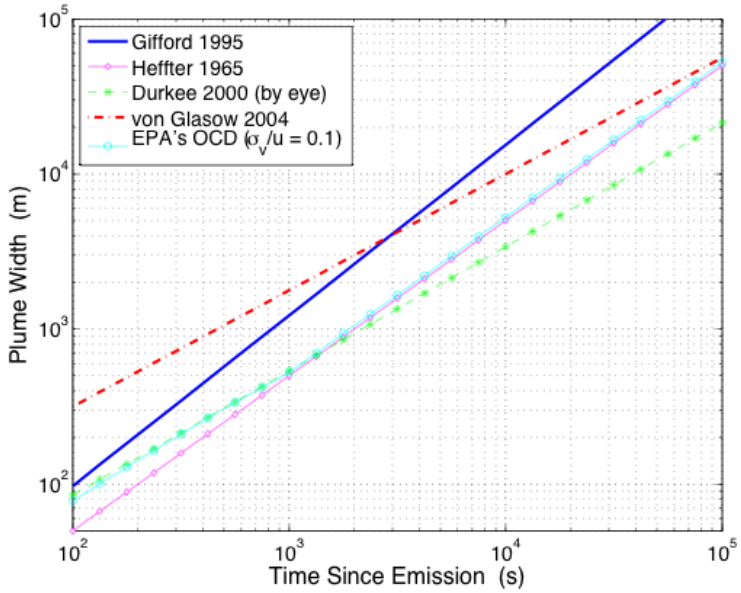


Figure 6. Comparison of several horizontal plume dispersion parameterizations used in marine environments. The EPA's Offshore and Coastal Dispersion (OCD) model is shown normalized to a relative standard deviation of the horizontal wind ($\sigma_v/U = 0.1$)

The cumulative emissions are shown in Figure 7 as a monthly value from the beginning of observations at BML in September 2004 through 2007 (note that this period is not continuous - the line in the figure breaks for the interval between Spring 2006 and Fall 2007 when measurements were not made). A possible fall/winter peak in fishing activity may be inferred from the data, as well as a longer secular trend in CO emissions which may be related to a decline in fishing activity in the past few years. The average daily emission observed during this period, 160 g CO $m^{-1}d^{-1}$, in conjunction with the distance offshore that the method observes (~25 km) leads to an average area flux of CO from shipping of 220 μmol $m^{-2}d^{-1}$.

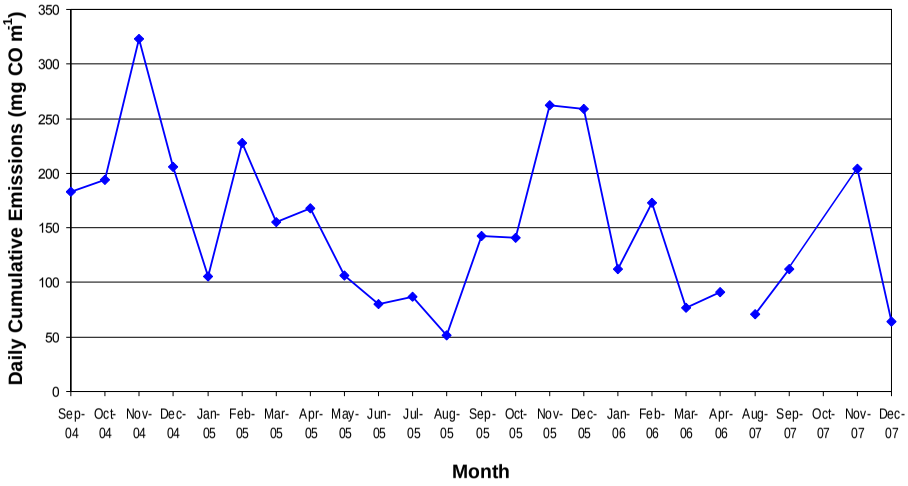


Figure 7. Cumulative daily emissions (g CO m^{-1} shoreline) observed at BML over the 25 month time series. The break in the graph represents 15 months when monitoring did not occur.

This project also permitted continued analysis of the NOAA radio acoustic sounding system (RASS) data at BML and yielded a fairly robust method for determining the boundary layer depth at the site. However, the deeper boundary layers of the winter months defied easy characterization because they frequently exceeded the vertical range of the RASS. Figure 8 shows the mean and median (red and blue lines, respectively) MBL heights determined over the entire period spanning the fall of 2004 to the end of 2007 (note that both figures above have a discontinuity in the data from spring 2006 to the late summer 2007 when this project allowed for continued monitoring). The cyan line shows the percentage of time during onshore air flow that the sounding system was able to select a discernable boundary layer height. The method is much more reliable during the summer months when strong subsidence associated with the Pacific High pressure system restricts the height of the marine boundary layer.

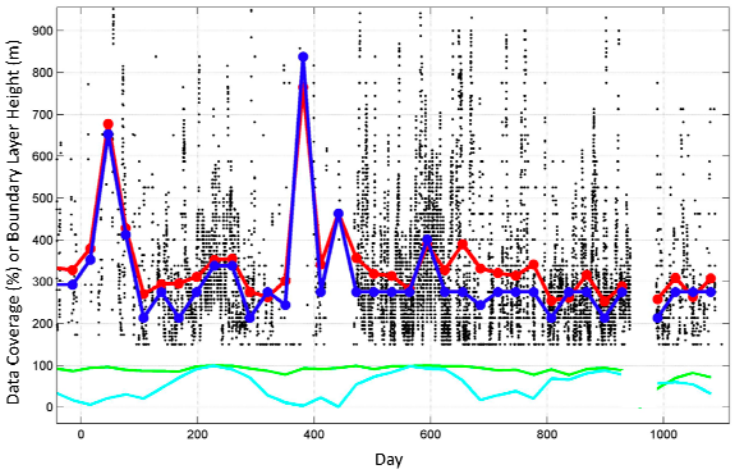


Figure 8. Estimated boundary layer height during the 25 months of data analysis. Black dots are individual 30-minute calculations, the red line is the mean value, the blue line is the median value; the green line shows the percentage of RASS data available during onshore flow, and the cyan line shows the percentage of time that a boundary layer height was discernable when the airflow was onshore.

For the emissions estimates, we used a climatological average when real-time data from the RASS were unavailable. The boundary layer heights near Bodega Bay tend to be a local minimum during the upwelling season (April to October), particularly in the summer months [Dorman et al., 2000]. The inversion heights of only about 250 m in this study compare reasonably well with 180 ± 100 derived by Dorman et al. [2000] for a June & July 1996

dataset. For the winter season, the boundary layer is less clearly defined and varies tremendously with synoptic conditions. We used an average MBL height of 600 m when observations are unable to determine the in-situ height of the MBL.

I.3 Offshore Aircraft Profiles

In order to develop another, independent estimate of the regional offshore emissions of CO, we also investigated historical airborne experiments. Based on an equilibrium of the MBL CO levels achieved through entrainment aloft, we calculated the regional emissions based on airborne observations of the large scale vertical gradients in CO offshore. Data were selected from several experiments with some component flown offshore of Northern California (including DYCOMS-II, INTEX-B, ITCT, and ARCTAS-CA). In selecting data from legs within the MBL, we inspected the HYSPLIT back-trajectories to find air masses that were not likely to have been influenced by nearby continental sources. A sample profile taken with the NOAA WP-3D aircraft during ITCT on May 15, 2002 is depicted in Figure 9, which shows an enhancement of 10-15 ppb CO within the otherwise pristine MBL. A HYSPLIT back-trajectory run for that location and time shows that air mass being over the open sea for the 6 days prior and originating from the Bearing Sea.

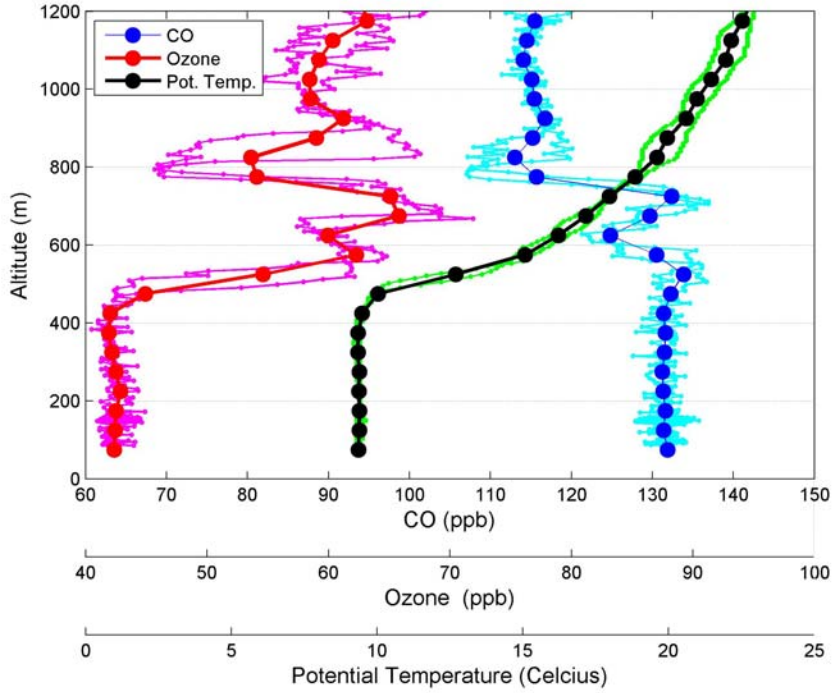


Figure 9. Aerometric profiles observed by the NOAA P-3 aircraft over the ocean about 100 km to the west of Monterey, CA on May 15, 2002.

Based on the average rate of entrainment of the MBL in this region of low level divergence beneath the Pacific High, a dilution time scale of about two days can be inferred (Faloona et al., 2005). Thus, in order to sustain a gradient of CO across the inversion a substantial average surface flux of CO is required. An equilibrium between the surface flux, assumed to be dominated by combustion sources [Day and Faloona, 2009], can be assumed in order to estimate the regional emissions.

$$\frac{\partial[CO]}{\partial t} = \frac{F_0 - w_e \Delta[CO]}{z_i} - k[OH][CO] \cong 0$$

where F_0 is the surface flux (ship emissions), w_e is the entrainment velocity (assumed to be ~0.5-0.6 cm s^{-1}), Δ[CO] is the change (jump) in the CO concentration across the inversion, k is the reaction rate constant for oxidation of CO by the hydroxal radical (OH), and z_i is the depth of the MBL. Because the photochemical lifetime of CO is orders of magnitude larger than the dilution time, the second term in the budget can be neglected and F_0 can be solved from knowing the other parameters. For the conditions depicted in Figure 9, a jump of ~12 ppb CO, we can estimate the average CO emission rate in the region upwind of the sampling site (parallel to the coast approximately 100 km offshore) to be 230 μmol $m^{-2}d^{-1}$. A large compilation of such profiles has been obtained from this analysis and presented in Table 1. Some of the compiled profiles exhibit greater CO in the free troposphere, indicating that differential advection from anthropogenic source regions has obscured the background condition. The averages including these observed profiles is reported but believed to be not as accurate an estimate of the surface CO emissions from combustion. From these airborne surveys, an average emission rate of 240 μmol $m^{-2}d^{-1}$ CO is required by the above MBL equilibrium, and the final extrapolation from our onshore spike estimates at Bodega Bay lead to estimate of ~230 μmol $m^{-2}d^{-1}$. Thus, we believe these independent lines of evidence lead to a reasonably consistent picture of the CO emissions offshore of Northern California.

Table 1. Compilation of CO and other gradients at the top of the marine boundary layer offshore of Northern California from aircraft profiles.

ITCT Profiles
2002

Concentrations are for marine boundary layer (MBL) and "jumps" are change moving from free troposphere to MBL

Date	Julian Time (UTC)	Lat	Lon	Back Trajectory	MBL height, z_i (m)	CO jump, Δ[CO] (ppb)	CO conc (ppb)	O3 jump (ppb)	O3 conc (ppb)	NOy jump (ppb)	NOy conc (ppb)	propane (ppt)	CO Sfc. flux, F_s (μmoles/m²/day)
4/25	115.876	35.38	-126.85	Marine	450	-5	123	-4	38	0.06	0.28	nan	-102
4/26	116.0265	36.96	-122.96	Continental	680	15	138	7	40		0.2	nan	307
4/29	119.7735	36.98	-126.36	Marine	350	3	150	-2	46	-0.03	0.23	nan	61
4/29	119.9502	37.02	-122.88	Marine	700	0	149	0	46	0.05	0.33	nan	0
5/2	122.879	40.08	-124.55	Marine	750	0	135	-23	44	-0.8	0.5	190	0
5/2	122.8855	39.54	-124.21	Marine	750	14	145	-18	42	-0.55	0.65	nan	286
5/2	122.8945	38.87	-123.89	Marine	750	12	144	-15	40		0.6	nan	245
5/5	125.896	41.03	-124.89	Marine	1000	7	180	-7	38	-0.04	0.12	104	143
5/6	126.032	36.87	-122.86	Marine	300	22	120	12	42	0.14	0.32	nan	450
5/6	126.8375	40.65	-124.92	Marine	1000	17	135	0	46	0.1	0.15	306	348
5/8	128.809	35.97	-122.79	Marine?	400	0	140	-13	40	0.15	0.65	390	0
5/10	130.8525	41.01	-126.15	Marine	700	0	125	0	38	0.025	0.16	150	0
5/11	130.997	40.99	-124.21	Marine	400	-5	128	1	40		0.45	nan	-102
5/11	131.9635	40.87	-124.20	Marine	400	10	146	6	48	0.35	1.1	310	NaN
5/15	135.78	35.65	-123.44	Marine	600	15	127	-7	45		0.25	nan	307
5/15	135.867	32.38	-128.48	Marine	600	-13	129	-19	48	-0.34	0.18	158	-266
5/15	135.925	37.38	-126.66	Marine	500	10	132	-19	42	-0.16	0.17	178	204
5/15	135.9705	40.72	-124.54	Marine	450	0	135	-10	41	-0.4	0.3	nan	0
5/17	137.79	35.40	-123.87	Marine	450	13	114	11	34	0.05	0.15	nan	266
5/17	137.8595	30.95	-129.05	Marine	1000	7	107	-22	28		0.13	54	143
5/17	137.9225	34.12	-125.60	Marine	550	8	106	8	31		0.14	62	164
	MEANS				**606.6**	**6.2**	**133.7**	**-5.4**	**40.8**	**-0.09**	**0.34**	**190.2**	**123**
	MEANS of Positive CO jumps				**602.0**	**12.3**	**134.0**	**-1.9**	**40.8**	**0.04**	**0.38**	**189.1**	**259**

DYCOMS-II profiles
2001

Concentrations are for marine boundary layer (MBL) and "jumps" are change moving from free troposphere to MBL

Flight#-Date	Julian time	Lat	Lon	Back Trajectory	MBL height, z_i (m)	CO jump, Δ[CO] (ppb)	CO MBL (ppb)	O3 jump (ppb)	O3 MBL (ppb)	NOy jump (ppb)	NOy MBL (ppb)	propane (ppt)	CO Sfc. flux, F_s (μmoles/m²/day)
RF01-7/10	191.46	31.5	-121.8	Marine	830	11	82	-24	30	nan	nan	nan	225
RF02-7/11	192.46	31.5	-121.9	Marine	750	14.5	79.5	-15	19	nan	nan	nan	296
RF03-7/13	194.46	31.1	-121.6	Marine	650	16	83	-17.5	24	nan	nan	nan	327
RF04-7/17	198.46	29.5	-121.6	Marine	1130	9.5	86.5	-10.5	23.5	nan	nan	nan	194
RF05-7/18	199.46	30.6	-121.8	Marine	900	12.5	87.5	-12.8	27.2	nan	nan	nan	256
RF06-7/20	201.42	30.5	-121.9	Marine	nan	nan	nan	nan	nan	nan	nan	nan	NaN
RF07-7/24	205.46	31.2	-121.6	Marine but 2000m cont	750	-13	80	-24	19	nan	nan	nan	NaN
RF08-7/26	207.04	31.9	-122.4	Marine but 2000m cont	650	4	84	-44	23	nan	nan	nan	82
RF09-7/27	208.96	31.4	-123.7	Marine	nan	nan	nan	nan	nan	nan	nan	nan	NaN
RF10-7/28	209.92	32.5	-122.4	Marine but 2000m cont	nan	nan	nan	nan	nan	nan	nan	nan	NaN
	MEANS				**809**	**8**	**83**	**-21**	**24**				**230**

Task II: *Work with database of ship emissions from Professor James Corbett of the University of Delaware to compare to estimates from Task I.*

This task, involving close analysis of the Corbett ship emissions inventory offshore to compare to the CO emissions estimates made at Bodega Bay, never materialized as effort was necessarily expended on the fundamental Task III objectives. Due to the instrumental failure, much more time was required for Task III, and the data base analysis of Task II was not pursued.

Task III: *Procure and deploy trace level SO_2 analyzer and redeploy CO instrument at Bodega Marine Lab site*.

The original goal of this task was to make fast and sensitive measurements of SO_2 collocated with the CO observations to investigate the ratio of these combustion products in the ship plumes. This would help identify the type of engines (diesel or gas) responsible as well as permit a similar estimation method to be applied to SO_2.

Modified Objective: *Deploy CO instrument onboard a Cessna-210 to assist in regional greenhouse gas emissions estimates*.

Although no useable measurements of SO_2 were made at the shoreline observatory during this project, it did allow us to collect 4-5 months of CO and, additionally, ozone data. The expanded CO data set has been included in the analysis of Task I, and the ozone data are available on the BML data portal, the Bodega Ocean Observing Node (BOON: http://bmlsc.ucdavis.edu/boon/). Figure 10 shows the averaged diurnal ozone measured at BML from the end of June through December, 2008 along with the 2σ envelope of atmospheric variability. These data are filtered for the presence of onshore winds.

Further efforts were also expended in making airborne CO measurements in support of a greenhouse gas surveillance experiment, in the hopes of obtaining vertical profiles near Bodega Bay. The first phase of this experiment was seriously compromised by smoke contamination due to the voracious wildfires that occurred during June 2008. In fact, the ozone data observed at the coast during the fires shows periods in late June and mid July of ozone concentrations elevated by 10-15 ppbv above the mean diurnal profile shown in Figure 10. The periods of elevated ozone were coincident with mesoscale flow patterns that may have swept the fire plumes offshore and then brought them back to the coastline hours/days later. It was not possible to systematically test the ozone instrument response to fire smoke, and thus interferences cannot be ruled out.

Many challenges were overcome during the first week of the aircraft deployment but the results were limited and revealed the likelihood of a small internal leak in the CO inlet. Regardless, the flights were postponed because of the heavy contamination by the biomass burning (forest fire) plumes. The project was then continued during February of 2009 and we succeeded in obtaining more reliable CO data which are valuable for properly interpreting the CO_2 and methane observations with the aircraft.

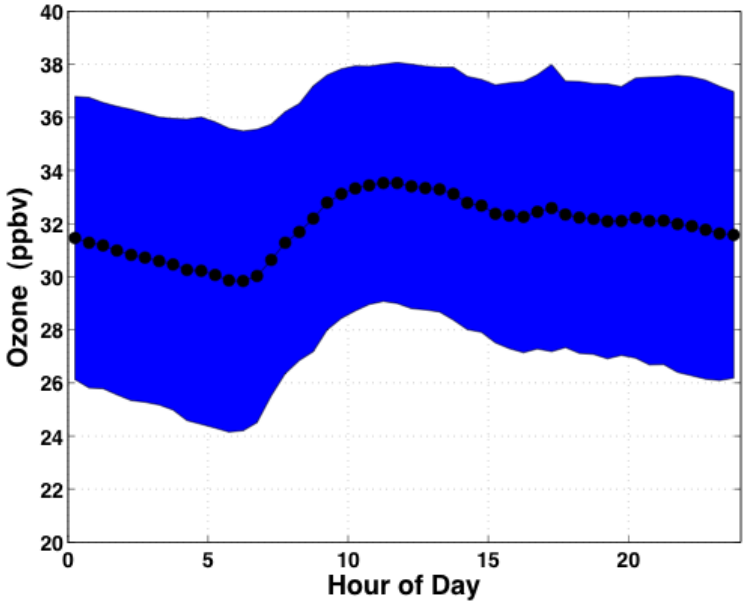


Figure 10. Diurnal ozone profile observed at Bodega Bay from July-December, 2008 during onshore flow. The blue patch represents the ±1σ for each 30-minute bin.

Preliminary airborne CO measurements with our fast CO instrument and the NOAA flask samples taken during one of the flights on February 26, 2009 are shown in Figure 11. Intercomparison of the CO measurements by the two methods indicates promising data quality with the continuous CO analyzer. The ability to accurately detect short-term variations in the CO concentrations should make this instrument suitable for identifying combustion sources in the study area, focused around the delta, as well as along the coast.

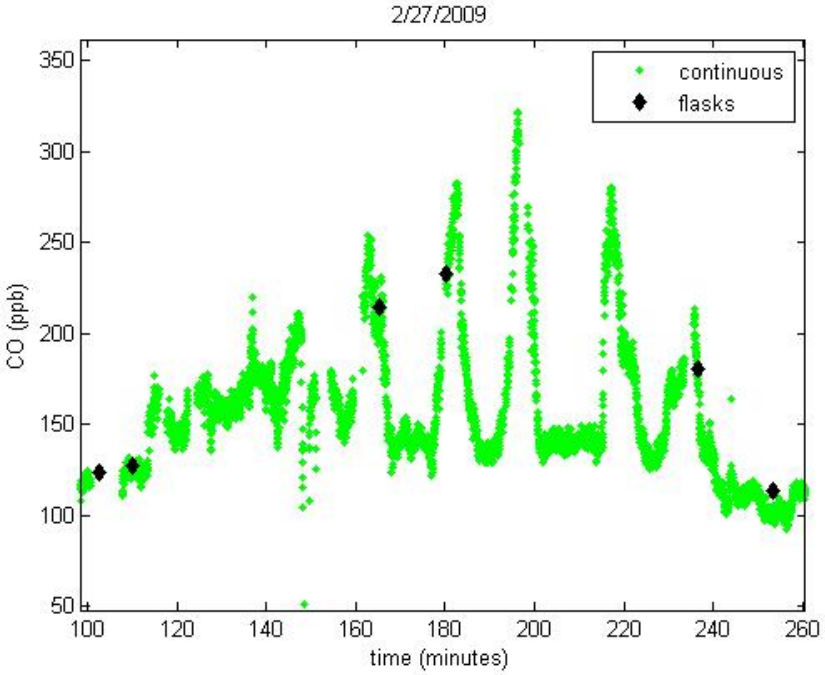


Figure 11. Time series of in-flight CO measurements compared with the grab samples of NOAA's Earth System Research Lab.

Task IV: *Canvas local fishermen about boating patterns and collect specific position data with portable GPS tracking units.*

The original goal of this task was to gather specific information from the users of the harbor on their usage, travel patterns, and engine types to get a better idea of the local boating activity in the region. However, due to the constraints on the contract resources discussed previously, this task was not fully developed. However, the first attempt at convassing local boat owners was attempted in the late summer of 2007 and many lessons were learned. For instance, many of the fishing boat captains reacted adversely to being asked to participate in the survey because, we suspect, a reluctance to provoke further regulatory constraints on an already stressed business. Future surveys might work better if the reasons for inquiry are better explained to not threaten the captains' livelihoods, and if they are distributed via e-mail or postal mail instead of in person. A copy of the survey is provided in Appendix B and the tabulation of the results is provided in an attached spreadsheet.

References

Bates, T.S., V.N. Kapustin, P.K. Quinn, D.S. Covert, D.J. Coffman, C. Mari, P.A. Durkee, W.J. De Bruyn, and E.S. Saltzman, Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the First Aerosol Characterization Experiment (ACE 1). *J. Geophys. Res.*, **103**, 16,369-16,383, 1998.

Capaldo, K., J.J. Corbett, P. Kasibhatla, P. Fischbeck, and S.N. Pandis, Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean, *Nature*, **400**, 1999.

Corbett, J.J., and P. Fischbeck, Emissions from Ships, *Science*, **278** (5339), 823-824, 1997.

Corbett, J.J., P. S. Fischbeck, and S. N. Pandis, Global nitrogen and sulfur inventories for oceangoing ships, *J. Geophys. Res.*, **104**(D3), 3457-3470, 1999.

Corbett, J.J., and H.W. Koehler, Updated emissions from ocean shipping, *J. Geophys. Res.*, **108**(D20), 4650, doi:10.1029/ 2003JD003751, 2003.

Cox, Elizabeth, Contribution of Local Ship Emissions to the Coastal Concentration of Carbon Monoxide at Bodega Bay, CA, MS thesis, UC Davis, 2006.

Dorman, C.E., T. Holt, D.P. Rogers, and K. Edwards, Large-scale structure of the June-July 1996 marine boundary layer along California and Oregon, *Monthly Weather Review*, 128 (6), 1632-1652, 2000.

Faloona, I., Sulfur processing in the marine atmospheric boundary layer: A review and critical assessment of modeling uncertainties, *Atmospheric Environment*, 43 (18), 2841-2854, 2009.

Ferek, R.J., D.A. Hegg, P.V. Hobbs, P. Durkee, and K. Nielsen, Measurements of ship-induced tracks in clouds off the Washington coast, *J. Geophys. Res.*, **103**(D18), 23,199–23,206, 1998.

International Maritime Organization (IMO) Legislation. IMO MARPOL (73/78) Annex VI – Prevention of Air Pollution from Ships. Adopted September 1997, entered into force May 19, 2005. (http://www.imo.org/Environment/mainframe.asp?topic_id=233#annexv)

Lawrence, M., and P. Crutzen, Influence of NO_x emissions from ships on tropospheric photochemistry and climate, *Nature*, **402**(6758), 167–170, 1999.

Smith, Martin D., Spatial Search and Fishing Location Choice: Methodological Challenges of Empirical Modeling, *Journal of Agricultural Resource Economics* **82**(5), 1198-1206, 2000.

Song, C.H., G. Chen, and D.D. Davis, Chemical evolution and dispersion of ship plumes in the remote marine boundary layer: investigation of sulfur chemistry, *Atmospheric Environment*, **37**, 2663–2679, 2003.

Venkatram, A., On estimating emissions through horizontal fluxes, *Atmospheric Environment*, **38**, 1337-1344, 2004.

Wilson, James A., Fishing for Knowledge, *Land Economics*, **66**(1) February, 12-29, 1990.

List of inventions reported and copyrighted materials produced

Glossary of Terms, Abbreviations, and Symbols

ARCTAS-CA - Arctic Research of the Composition of the Troposphere from Aircraft and Satellites, California portion of experiment performed in collaboration with CARB.
BML – Bodega Marine Laboratory (operated by UC Davis)
BOON – Bodega Ocean Observing Node (web portal for BML data)
DYCOMS-II – The second Dynamics and Chemistry of Marine Stratocumulus experiment
HYSPLIT – NOAA's Hybrid Single Particle Lagrangian Integrated Trajectory Model
ITCT - Intercontinental Transport and Chemical Transformation of pollution
INTEX-B – Intercontinental Chemical Transport Experiment
MBL – Marine Boundary Layer
NOAA – National Oceanic and Atmospheric Administration
RASS – Radio acoustic sounding system

Appendix A: Letter from Teledyne regarding failure of SO2 instrument to meet their specifications

4/4/08

Douglas,

I have returned from San Diego and indeed did meet with our engineering staff concerning the problems UC Davis has encountered with the 100EU. As I pointed out in my previous communication to you, API is deeply concerned that the analyzer did not perform to the expectations that UC Davis had set forth.
Upon receipt of the analyzer at the factory, an initial investigation was launched which covered both the physical components and the operational parameters of the analyzer on an as- received basis. Performance data was collected and as each adjustment and repair was made, the performance was checked to determine what improvement was/was not appearing.
This was a long and thorough process. Upon receipt, the noise at zero was well over 200ppt although the analyzer would hold a steady baseline. Listed below are but a few of the findings:

- the reaction cell was disassembled and cleaned.
- wires to the sync/demod board were recrimped to verify connectivity.
  A leak was discovered in the PMT housing.
- The PMT housing was disassembled and thoroughly cleaned.
- The o-rings and gasket for the PMT housing were replaced.
- Upon reassembling, the PMT housing was pumped down to -20psi and then purged with dry N_2.
  All optics was thoroughly cleaned.
- The 214-nm UV filter was found to be degraded- it was replaced.
- The lens holder for the PMT optics was found to be warped, which allowed the lens to changed orientation freely. The holder was replaced and the lens now fits securely.
- The 360-nm light filter for the PMT (used to reduce interference from NO) was replaced with the standard 330-nm filter.

The initial lamp reading upon arrival was less than 2000 mV-far off from the initial factory alignment. The lamp was repositioned for peak performance to its factory value at 4600 mV.

- Recalibrating the PMT afterwards allowed for the HVPS to be at a lower value (700mV down to 550mV) which reduced the gain noise.

After each repair/change, the instrument was reassembled to investigate how each change affected the concentration and stability readings. Additionally, the instrument was zeroed/ spanned after each repair and the lamp, pressure, and PMT were all recalibrated-again after each repair.

The last repair accomplished was for the leak in the PMT housing and the change out of the 360-nm light filter to the 330-nm filter. While each of the repairs listed made an improvement in signal and noise, these two made the most dramatic improvement. After the repair/recalibration efforts, the stability went down to less than 25ppt on zero air-and often under 10ppt. For a 90ppb SO2 span, the stability was 40-50ppt or less.

I have attached a ppt which shows the before and after run on zero air for the analyzer. Its parameters meet our published specifications.
API fully understands the resources expended by UC Davis on this unit. While our records, filled out by our line personnel as the unit is checked out after assembly, show that the analyzer did meet its target specifications upon shipment, UC Davis found otherwise as operation commenced. Why this occurred is now conjecture.
API values a continuing and good working relationship with UC Davis and with this in mind, will refund the amount paid for this analyzer to UC Davis. Please contact Adriana Cunha at 858-642-7725 to begin the process.
Douglas, speaking for API I would like to express our concern over the findings UC Davis encountered. I think you will agree that we have taken these to heart and have done our best to find out the reasons for the problems. Our reputation as a quality supplier of analytical instrumentation is first rate and rarely do we encounter the type of situation that UC Davis has experienced. As I stated earlier, we value UC Davis as a good customer and look forward to a continuing solid relationship.

Best Regards,

Larry Foster
Regional Mgr.
Teledyne API
Ph: 281-907-0664
C: 832-465-6620
Fx: 281-907-0773

Appendix B: Fishing Survey Developed for this project

Survey of Fishing Boat Owner/Operators

* * * Your information will be kept confidential * * *

Name: _____
Address: _____
City: _____ State: _____ Zip code: _____
Phone Number: _____
E-mail address: _____

Vessel Information (please fill out a separate sheet for each vessel that you own or operate)

Vessel Name: _____
Home Port: _____
Vessel Age: _____
U.S. Coast Guard Documentation Number: _____
I am the vessel's…□ Owner □ Operator □ Owner & Operator

Vessel Use: □ Commercial Fishing

□ Recreational Fishing

□ Other, please specify_____

Total Annual Fuel Usage (gallons): 2004: _____ 2005: _____ 2006: _____
Last Engine Maintenance: _____

Propulsion and Auxiliary Engine Information

Engine #	Propulsion (P) Or Auxiliary (A)	Make and Model	Model year	Horsepower	Annual Hours of Operation	Estimated Annual Fuel Usage (gallons)			Engine Exhaust: Wet or Dry [1]	During stop in the ocean: Turn off (yes) or not (no)?
						2004	2005	2006		
1										
2										
3										
4										
5										

Note: [1] "Wet Exhaust" is released at or below the waterline and "Dry Exhaust" is released to the air. If Dry Exhaust, approximate the exhaust height above the waterline.

Which route(s) do you usually take? Please use lines to indicate the route(s) and "*" to indicate places you usually stop on the following graph.

How often do you travel route(s), indicated at left, that you use most frequently?

Route 1:

- □ Everyday
- □ Several times a week
- □ Once a week or less

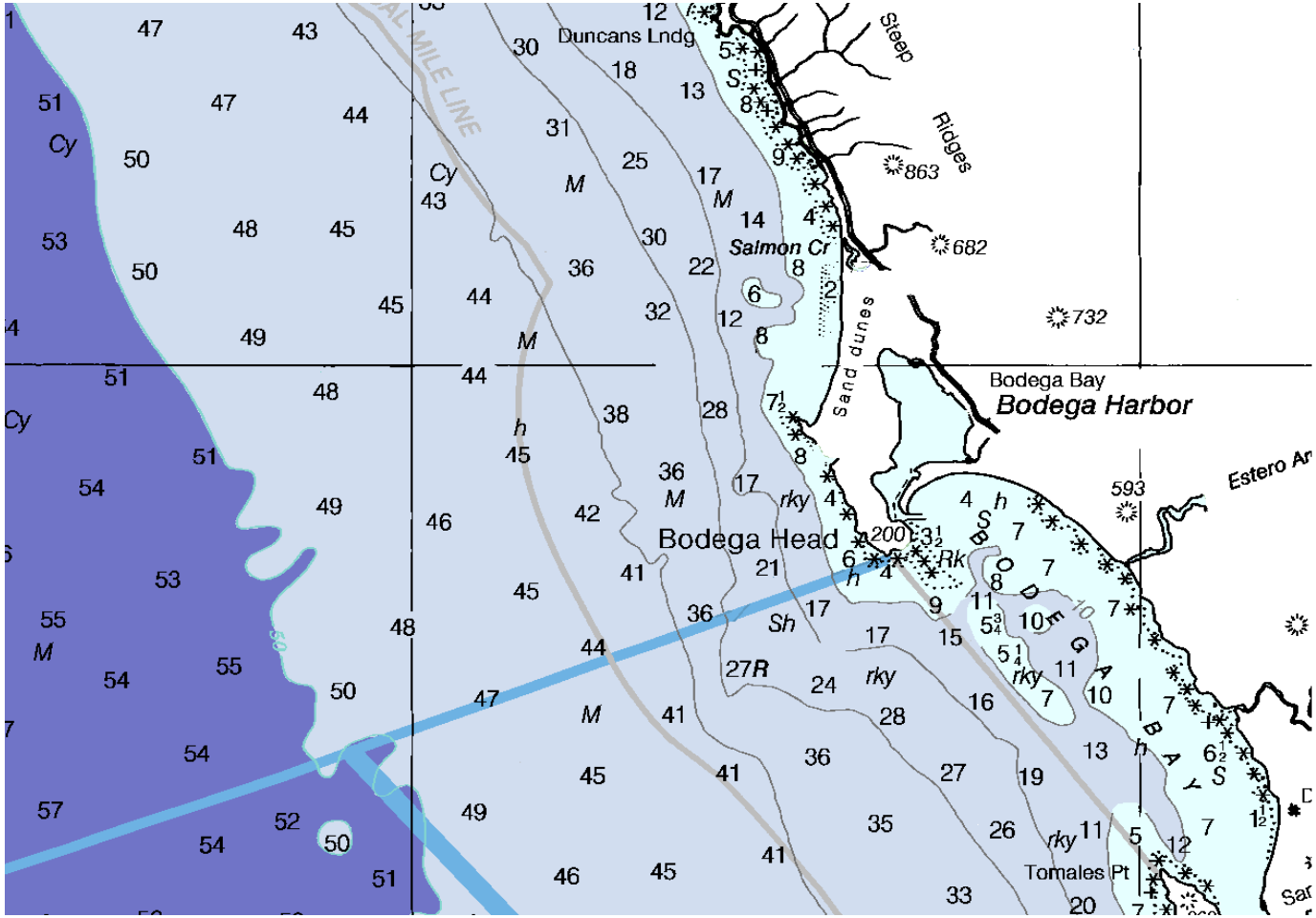
Route 2:

- □ Everyday
- □ Several times a week
- □ Once a week or less

□ I do not have 'regular routes'—they vary day to day.

How often do you go out in groups with other boats?

- □ Never
- □ Sometimes
- □ Often


Duncans Lndg
Steep Ridges
863
682
Salmon Cr
732
Sand dunes
Bodega Bay
Bodega Harbor
Estero Ar
593
Bodega Head
200
Rk
Sh
27R
rky
Tomales Pt
Cy
M
h
S
BODEGA BAY
10
58

Appendix C: Fishing Survey Preliminary Results

1. Vessel Name	Kittywake	?	Valerie	New Sea Angler	Linda Jean	?	Virgina C	Molly
2. Home Port	San Francisco	Bodega Bay	Moss Landing	Bodega Bay	Bodega Bay		Bodega Bay	Bodega Bay
3. Vessel Age	38	8	30	30	24		30	58
4. US Coast Guard Doc #	538939	999	579687	585732	581087		999	357726
5. IMO#	NA	999	999	999	999		999	999
6. Has AIS?	0	1	0	0	1		999	0
7. Plan to Install AIS?	0	999	0	999	999		999	0
8. Owner/ Operator	1	1	1	3	2		999	3
9. Primary Use	3	2	1	3	1		1	1
9. (b) Other Use	Pleasure	999	999	Charter Boat	999		999	999
10. (a) Dale of last engine Rebuild	999	999	999	2003	2006		1997	2005
10 (b) Type of Rebuild	999	999	999	999	New Cummins		999	Major Engine Rebuild
11. (a) Plan to rebuild?	0	0	o	1	0		999	0
11. (b) When rebuild?	999	999	999	2008	999		999	999
12. (a) Repower vessel?	0	0	o	999	0		0	0
12. (b) When repower?	999	999	999	maybe	999		999	999
Engine #	1	1	1	1	1	2	1	1
Propulsion or Auxilary	Auxiliary	Propulsion	999	999	Auxiliary	Propulsion	999	Propulsion
Make & Model	Chrysler Nissan	Volvo Penta	Perkins 4236	Detroit V 892	Izuzu	Cummins	Cummins	371 Jimmy
Model Year	1972	1999	1998	V 892	2004	2005	220	999
Horespower	999	300	85	350	80	340	999	86
Annual hours of operation	10	350	1000	1500	10000	15000	1000	600
Fuel Type	Diesel	Gasoline	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel
Engine Load when on	34 tons	999	999	1500	999	999	999	15
2005 fuel use	5	999	800	10000	1000	999	1000	999
2006 fuel use	4	999	800	12000	1500	999	1000	999
2007 fuel use	0	1750	550	8000	1000	999	101	999
Turn off when stopped?	yes	never	yes	yes	yes	yes	999	no
13 (a) Percent of time less than 3 miles	100	5	0	95		20	0	999
13. (b) % 3-7 miles	0	80	60	999		20	25	999
13. (c) % 7-12 miles	0	80	30	999		20	25	999
13. (d) %12-15 miles	0	90	10	999		20	25	999
13. (f) % more than 25 miles	0	10	0	999		20	25	999
14. Going out with other boats	1	2	3	3		2	3	1
15(a) Engine load berth →fishing	999	7000 lbs	60	1400		22	999	999
15(b) Engine load while fishing	999	999	15	875		24	Crab Pots	999
15(c) Engine load fishing→berth	999	999	65	1400		25	999	999
Respondent comments, if any Fish?			Salmon				Crab	Salmon