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CARBON DIOXIDE AND METHANE LEVELS IN SURFACE WATERS ALONG THE SÃO VICENTE ISLAND IN COASTAL REGION OF SÃO PAULO STATE

Elaine Cristina Araujo[1], Izabel da Silva Andrade[1] Fernanda de M. Macedo[4], Thaís Corrêa[1], Thais Andrade[1], Elisabete S. Braga[3], Maria de F. Andrade[2], Eduardo Landulfo[1]

[1]*Nuclear and Energy Research Institute*
elaine.c.araujo@usp.br
izabel.andrade@usp.br
correa-thais@usp.br
thais.andradedasilva@usp.br
elandulf@ipen.br
[2]*Institute of Astronomy, Geophysics and Atmospheric Sciences*
maria.andrade@iag.usp.br
[3]*University of Sao Paulo, Institute Oceanography, Brazil*
edsbraga@usp.br
[4]*FATEC - Faculty of Technology of the State of São Paulo*
fernanda.m.macedo@alumni.usp.br

Abstract: Various studies explore the relationship between the rising levels of CO_2 and CH_4 (greenhouse gasses) in the atmosphere and climate changes, and how these increases are connected to human activities. The escalation of these gas species may have implications for the environment. Concerning coastal systems, the rise in greenhouse gas emissions could impact the environment through multiple pathways because the atmosphere and superficial ocean waters also have significant exchanges. The main purpose of this work is to study Greenhouse gasses (GHG), such as CO_2 and CH_4, on the superficial waters of the coastal region of São Paulo coast. The data were collected in situ on a vessel provided by the Institute of Oceanography of São Paulo University (IOUSP). The campaign was conducted in spring 2022 (10 -11 October) in the south of the coast of São Paulo state, traveling through cities with anthropogenic impacts in principal Santos city, which is located the main port of Sul America. For these in situ measurements a portable gas analyzer Microportable Greenhouse Gas Analyzers (LGR-ICOS ™ GLA Series) - was used to detect the CO_2 and CH_4 spectra through the Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique.

***Keywords*:** Methane, Carbon Dioxide, Estuary, GHG, Microportable Gas Analyzers.

INTRODUCTION

According to the IPCC 2013, carbon dioxide concentration increased from 278 ppm in 1750 to 390.5 ppm in 2011, making it one of the largest contributors to the anthropogenic greenhouse effect. Another important gas in the process of greenhouse effect is methane (CH_4), which had an increase since the pre-industrial era (1750), from 722 ppb to 1803 ppb in 2011 [1]. This escalating concentration of greenhouse gasses (GHGs) and their significant impact on radiative forcing has spurred extensive research into GHG dynamics, particularly in coastal areas and estuaries. Coastal regions, comprising only 7% of the total ocean surface, play a crucial role in biogeochemical cycles linking continents, the atmosphere, and oceans [2]. The main purpose of this work is to study Greenhouse gasses (GHG), such as CO_2 and CH_4, on the waters of the coastal region of São Paulo. The data were collected in situ on a vessel provided by the Institute of Oceanography of São Paulo University (IOUSP). The campaign was carried out in October 2022 on São Vicente island, where the cities of Santos and São Vicente are inside, two cities with greater anthropic impact in the Metropolitan Region of Baixada Santista. For these in situ measurements a portable gas analyzer - Microportable Greenhouse Gas Analyzers (LGR-ICOS ™ GLA Series) - was installed in the vessel Alpha Delphini for to detect the CO_2 and CH_4 concentrations through the Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique.

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METHODS

The Delphini I Campaign, which took place in an approximately 28-hour Journey along the cities São Vicente and Santos in the Coast of São Paulo state, Brazil. The route crossed the coast of cities with greater anthropic impact in the Metropolitan Region of Baixada Santista. (Figure 1).

For data gathering, a portable gas analyzer - Microportable Greenhouse Gas Analyzer LGR-ICOS™ GLA Series - was used. This instrument has a high sensibility, resulting in a very fast gas flow response time (1 second) [3], it's based on the Off-Axis, Integrated Cavity Output Spectroscopy (OA-ICOS), where the light beam is placed at an angle off the axis of the cavity and its output signal is a sinusoidal modulation in light intensity, it's a technique that is widely utilized for gas detection due to its rapid response, high sensitivity, and stability [4], achieve obtain a precision of <0.9 ppb (1 second) for CH_4 and <350 ppb for CO_2 (1 second).

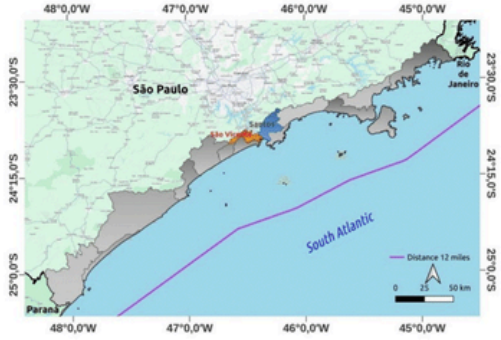

Figure 1. Map coast of São Paulo. In highlight the cities São Vicente and Santos

Figure 2. Vessel Alpha Delphini IOUSP, in destak the position inlet of portable gas analyzer

A Teflon tube of ¼ was coupled to the INLET, which extended up to about ~8 meters above sea level and was positioned above the cabin of the captain of the vessel at half ship. At the end of this tube a PFA 47-mm Savillex filter holder was attached, and inside this support a Zefluor membrane of 2.0 µm was used (Figure 2).

FINDINGS AND ARGUMENT

Data was continuously obtained during the campaign, which was divided into two days. The initial day (10th, october) of the project was spent around the Port of Santos, and the measurements began at 3 pm. The vessel returned to the pier about 8 pm. The GHG analyzer maintained continuous measures until the second day around 7 am and the journey was around Santos submarine emissary and São Vicente city. The campaign finished on October 11th at approximately 6 pm. The analysis inserted a minimum and maximum limit by calculating the Interquartile Range (IQR), which is the difference between the Third Quartile (Q3) and the First Quartile (Q1) - representing the amplitude of the interval in which the central half of the data is concentrated, ignoring the extremes (Figure 3 and 4).

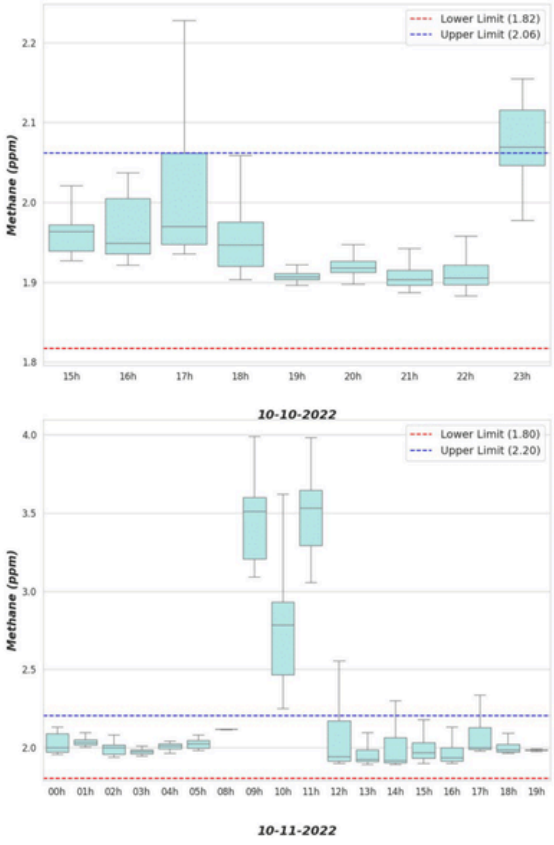

Figure 3. Boxplot for daily data of CH4 concentrations per hour for the two days of campaign.

After excluding highly descriptive data, methane values on the first day of the campaign mostly remained within the lower and upper limits calculated by the interquartile range (1.82 ppm and 2.06 ppm,

respectively), deviating from this range only after 10 pm. Regarding CH_4, in the second day of analysis, most data points still fell within the range established by the interquartiles. However, between 9 am and 12 pm, it was evident that values significantly exceeded the maximum limit, reaching up to 4 ppm (Figure 3).

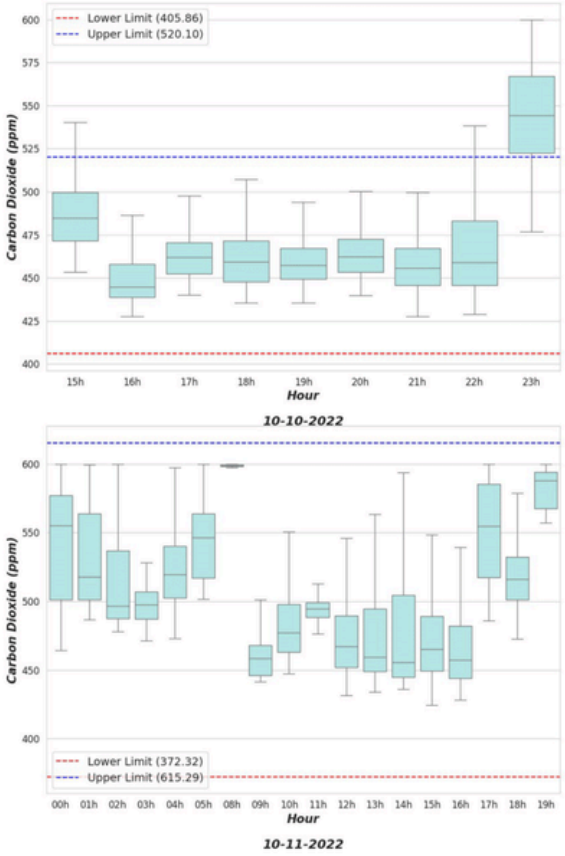

Figure 4. Boxplot for daily data of CO2 concentrations per hour for the two days of campaign.

Carbon dioxide data exhibited results that surpassed the upper limits of the interquartile range, which was approximately 520 ppm, peaking close to 600 ppm by 11 pm on the first day of measurement (October 10th). On the final day of the campaign, concentrations did not surpass the maximum interquartile value of around 615 ppm. However, there were very few data points within this range between 6 and 9 am, suggesting that most of the data during this time exceeded 600 ppm (Figure 4).

The highs methane data, were recorded when the vessel was positioned between the cities of Santos and São Vicente. It is noteworthy that these two cities are the most populous in the region, and between them lies the submarine outfall of Santos, where residential sewage is discharged. As for CO_2, concentrations exceeding 500 ppm occurred when the vessel navigated through the channel of the Port of Santos, near the ferry crossing, and in close proximity to bulk carriers.

CONCLUSIONS

The data presented here are from the first campaign that utilized a portable GHG analyzer to assess CO_2 and CH_4 concentrations in the Santos and São Vicente cities. The campaign aimed to explore a coastal region heavily influenced by anthropogenic factors, such as a high population density and proximity to the Port of Santos. Despite being the initial use of this equipment in the region, the results were promising, as they revealed high concentrations of both gasses that align with potential sources near the vessel. However, it is crucial to consider certain factors in future research. Parameters like wind direction should be accounted for to pinpoint the origins of the highest concentration peaks in each region. Additionally, conducting more extensive sampling over multiple days in the same areas would facilitate a more thorough analysis of the results.

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