HOLOS ENVIRONMENT

USE OF RESONANT CAVITY SPECTROMETER (CRDS) FOR METHANE DETECTION IN IMPACTED AND NON-IMPACTED AREAS

USO DE ESPECTRÔMETRO DE CAVIDADE RESSONANTE (CRDS) PARA A DETECÇÃO DE METANO EM ÁREAS IMPACTADAS E NÃO IMPACTADAS

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Abstract: Methane is one of the main greenhouse gases, impacting a lot on the radioactive forcing, contributing a lot to global warming. Identifying methane generating sources are important in mitigating actions, mainly of anthropic origin. In this work, methane emissions were observed in two distinct areas, one with low anthropogenic impact and the other with high industrial activity. A resonant cavity spectrometer (CRDS) was used to analyze methane concentrations during the months of June and July/2019 in the city of Itanhém and in the months of September, October and January of 2019 in the city of Cubatão.

Keywords: Methane. Resonant cavity spectrometer. Impacted Areas.

Resumo: O metano é um dos principais gases do efeito estufa impactando muito na forçante radioativa, contribuindo muito para o aquecimento do planeta. Identificar as fontes geradoras de metano são importantes nas ações mitigadoras, principalmente de origem antrópicas. Nesse trabalho foi observado as emissões de metano em duas áreas distintas, uma com baixo impacto antrópico e outra com elevada atividade industrial. Foi utilizado um espectrômetro de cavidade ressonante (CRDS) para analisar as concentrações de metano durante os meses de junho e julho/2019 na cidade de Itanhém e nos meses de setembro, Outubro e Janeiro de 2019 na cidade Cubatão.

Palavras-chave: Metano. Espectrômetro de cavidade ressonante. Áreas Impactadas.

1 INTRODUCTION

Methane (CH_4) is one of the most important greenhouse gases, mainly because it plays a significant role in the planet's radiative balance. It is a biogenic gas, but it can be released into the atmosphere by anthropogenic sources (KAVITHA, 2016,

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BARAY, 2018). There are obvious concerns about the impact of CH_4 on the atmosphere, leading to an increase in global temperature related to these different emission sources (IPCC -AR5, 2014). The methane basal concentration from natural sources is around 2 ppm, but this value can be more than double due to different emissions sources (BARAY, 2018).

Coastal areas contribute about 75% of global ocean methane emissions (Bange 2006; Reeburgh 2007). This is due to greater availability of inputs with high sedimentation rates of reactive organic matter from continental sources (BOUSQUET, 2006; EPA 2010).

The concentrations of CH4 in some estuaries can vary due to the entry of fresh waters that have high concentrations of CH4, which mix with sea waters with lower concentrations of CH4, for the general characterization of estuarine waters, suggesting high concentration of methane and low salinity. (DE ANGELIS, 1987; UPSTILL-GODDARD, 2000; MIDDELBURG, 2002). Methane dissolved in fresh water is normally lost at the entrance of the estuary to the atmosphere due to its transport, leaving only a small fraction dissolved in the water column (UPSTILL-GODDARD, 2000; ABRIL, 2002)

In general, methane production is higher in freshwater areas because the high availability of sulfate in marine waters inhibits methane production, in oceans methane starts to be produced in deep waters due to sulfate depletion (MARTENS, 1974).

High methanogenesis in marine sediments has been observed in estuaries that have extremely elevated rates of reactive organic matter sedimentation that can lead to rapid sulfate depletion in the upper layers of the sediments (MARTENS, 1998).

The large spatial and temporal heterogeneity in methanogenesis, methanotrophy and transport patterns makes it difficult to estimate accurate global estuarine emissions of CH_4 (BORGES, 2011). The CH_4 emission patterns in boreal, temperate and tropical estuarine systems revealed high spatial variability depending on their typology and their respective rates of salinity and organic carbon sedimentation (BORGES, 2011). The uncertainties in fluxes at the coastal zone are attributed to low data collection and, lack of sampling in tropical and subtropical latitudes (mainly in the southern hemisphere), the absence of seasonal, annual or interannual temporal studies.

Most studies have been carried out in estuaries dominated by rivers in temperate zones and little is known about CH_4 emissions in systems dominated by seas such as lagoons and coastal bays. Methane concentrations in the water-to-air ratio is well differentiated between coastal regions (open waters), coastal lagoons, swamps and mangroves (BORGES, 2011). The high standard deviations between these ecosystems represent large uncertainties in the estimated flows.

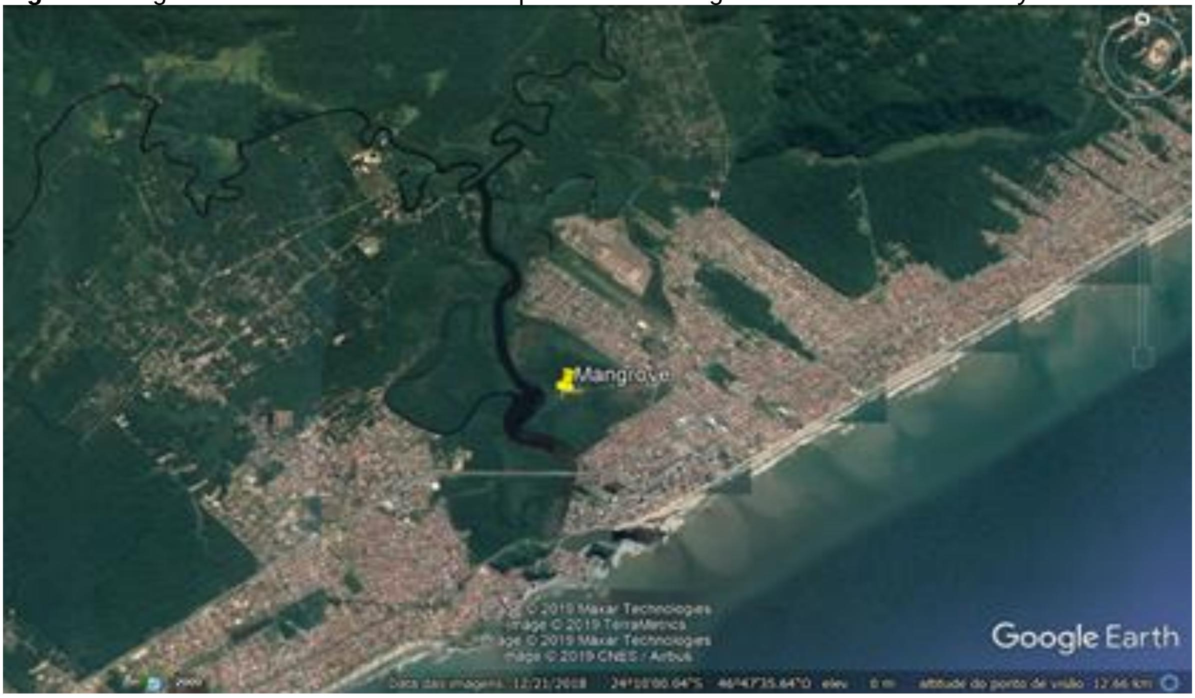
Disruption of the methane balance in the coastal region may be being driven by organic pollution and eutrophication (BANGE 2006; NIRMAL RAJKUMAR, 2008; BURGOS, 2015). Indeed, extremely high methane emissions have been found in some highly polluted systems, especially closer to the wastewater discharge and in locations under the strong anthropogenic influence (NIRMAL RAJKUMAR, 2008; BURGOS, 2015).

CH_4 concentrations and emissions can show different variations (spatial and temporal) in estuaries subject to contamination and eutrophication (NIRMAL RAJKUMAR, 2008). Furthermore, studies comparing pristine and disturbed systems have shown lower concentrations of methane in waters from pristine environments (KRISTENSEN, 2008; ALLEN, 2010).

An increase in CH_4 emissions can be expected is developing countries (mostly located in tropical regions), taking into account the low rate of sewage treatment in these countries and the rapid population growth, especially in coastal regions. Thus, the monitoring and quantification of methane concentrations and fluxes in polluted and eutrophic estuarine systems may become a necessity for understanding the perturbations in the coastal carbon cycle.

Itanhaém, is a city located on the southeast coastland of São Paulo State, belongs to Baixada Santista Metropolitan Region, with a fixed population of 104,351 inhabitants (IBGE,2021). Itanhaém River Estuary is in a good state of preservation, practically free from degrading anthropogenic influences. The mangrove area (Figure 1) has approximately 2.78 km2 and approximately 30% of its area. In general, the mangrove is in a good state of preservation, with high vegetation, good levels of reproductive capacity and specific fauna in expansion. (CAMARGO, 2016).

Figure 1 - Figure shows the data collection point in the mangrove area in Itanhaém city



Source: Google earth pro V 7.1.8.3036. (January 26, 2017). Santos, Brazil. 23°50'57.71"S, 46°23'19.80"W, Altitude do ponto de visão 6.24 km. Digital Globe 2016. http://www.earth.google.com [January 17, 2017]

Cubatão is also part of the Baixada Santista metropolitan area, with a territory of 148 km2. The city is located 57 km from the capital of São Paulo and borders the cities of Santos, São Vicente, São Bernardo do Campo and Santo André. A montainous área and plains form the region, and the maximum height is reached in Serra do Mar, with 700 meters and the minimum height in the plain is approximately 3 meters from sea level. In area, the Cubatão mangrove is the second largest in the Baixada Santista region at 23 km ((Figure 2).

The Cubatão region is an important petrochemical complex with dozens of industrial activities with a high environmental impact, it has 25 large companies in the chemical sector, including an oil refinery, spread over an area of 143 km^2. (HYPOLITO, 2005).

Figure 2 - Figure shows the data collection point in the mangrove area in Cubatão city

Source: Google earth pro V 7.1.8.3036. (November 23, 2021). Cubatão, Brazil. 23°53'49.37"S, 46°24’34.91"O, Altitude do ponto de visão 17.65 km. Digital Globe 2021. http://www.earth.google.com [August 26, 2020]

2 MATERIAL AND METHOD

Ringdow cavity spectroscopy (CRDS) is a direct absorption technique, which can be performed with pulsed or continuous light sources, with greater sensitivity than that obtained with conventional absorption spectroscopy. The CRDS technique is based on measuring the absorption rate in a closed optical cavity with a high merit fator (PALDUS, 2005). The advantage over normal absorption spectroscopy is the intrinsic insensitivity to fluctuations in light source intensity and the extremely long wavelengths that can be performed in stable optical cavities. Over the last decade, the CRDS technique has been shown to be especially powerful in gas-phase spectroscopy for measuring trace gas absorptions or weak absorption of abundant species. This method demonstrates excellent spectroscopy results for atoms, molecules, clusters in many open environments, static gas cells, supersonic expansions, flames and discharges. The sample concentration can be determined using the Beer-Lambert law (BERDEN, 2000).

Its structure consists of a laser, which illuminates the ultra-thin optical cavity, which in its simplest form consists of two highly reflective mirrors. When the laser is at resonance within the cavity, its intensity increases due to constructive interference, so the laser is turned off to allow measurement of the intensity of the exponentially decaying light within the cavity. During this decay, light is reflected back and forth thousands of times between the mirrors, giving an effective length (O'KEEFE, 2009).

The equipment measures how long it takes for light to decay from its initial intensity, and this "touch time" can be used to calculate the concentration of the absorbent substance in the gas mixture in the cavity (TARSA, 2008).

Assuming the switching time of the Pockels cell is short relative to the cavity decay time, the measured cavity output decays exponentially according to the first-order expression:

$$I(t) = I_0 \times exp^{\left[\frac{-t}{\tau}\right]}$$

Where *t* is the cavity decay time constant. If the loss of intensity in the cavity is due to the transmission of the mirrors, we assume that the transmission (T) of the mirror, is given by:

$$T \approx 1 - R$$

So the cavity exit decay time can be related to the *R* via:

$$\tau = \frac{L}{c} \times \left[\frac{\sqrt{R}}{\left(1 - \sqrt{R}\right)}\right]$$

Where is the mirror separation, *c* is the speed of light, and $R = R_1 R_2$ is the reflectance for a two-mirror configuration.

In CRDS, a laser pulse is captured in a highly reflective sensing cavity (usually R > 99.9%). The strength of the trapped pulse will decrease by a fixed percentage during each round trip within the cell due to absorption and scattering through the medium within the cell and losses in reflectivity. The light intensity within the cavity is then determined as an exponential function of time.

For gas measurements based on conventional laser absorption spectroscopy, a laser beam is directed through a sample and the mixing ratio (or molar fraction) of a gas is determined from the measured absorption using Beer's Law, which can be expressed:

$$\frac{I_0}{I_v} = e^{-SL_\lambda P_\phi r}$$

where Iv is the intensity transmitted through the sample at frequency v, I_0 is the laser intensity (reference) before entering the cell, P is the gas pressure, S is the force of the probed transition absorption line, L is the optical path length, c is the mixing rate and f_n is the waveline function of the frequency transition. In this case,

$$\int \phi(v)dv = 1$$

If the laser line width is much narrower than the absorption feature width, high resolution absorption spectra can be recorded by adjusting the laser wavelength over the analyzed feature.

$$x = \frac{1}{SLP}\int ln\left(\frac{I_0}{I_v}\right)dv$$

This strategy has proven successful in determining gas concentrations in mixtures containing various species, in fluxes at high temperatures and pressures, and in a hostile environment, without using calibration gases or reference standards.

3 RESULTS AND DISCUSSION

This study investigated two different situations for methane detection. The first takes advantage of the fact that emissions are close to a petrochemical pole, leaving positive flows, increasing the local atmospheric molar ratio. On the other hand, the second is a region of low environmental impact limiting emissions close to the background. It is worth mentioning the importance of accounting for the dependence of seasonality throughout the year, since the molar ratio change for many gases.

The methane ratio in the Cubatão city showed higher values when compared to the data from Itanhaém city. In October/2019 (Figure 3) we verified values between 1.8 ppm and 2.8 ppm. The month of January/2020 (Figure 4) presented values above 3.0 ppm, above the values expected in the literature, around 1.7 ppm for the atmosphere (WALLACE, 2006).

Figure 3 - Methane ratio in Cubatão city, October 2019

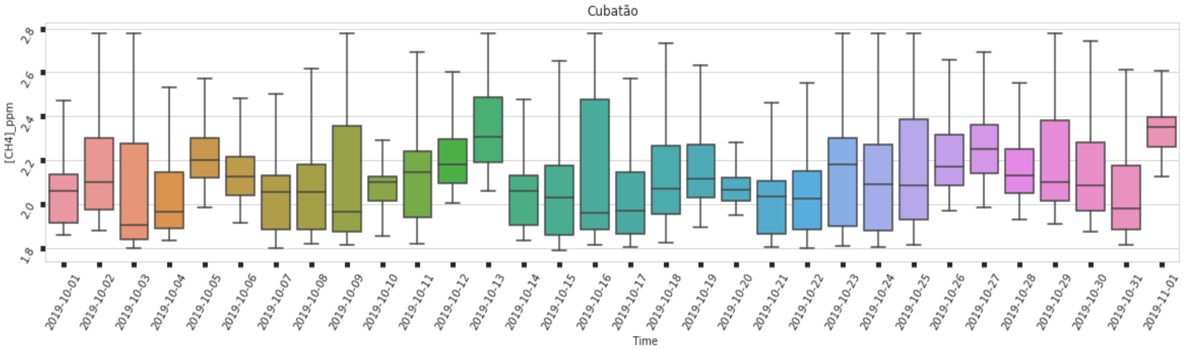


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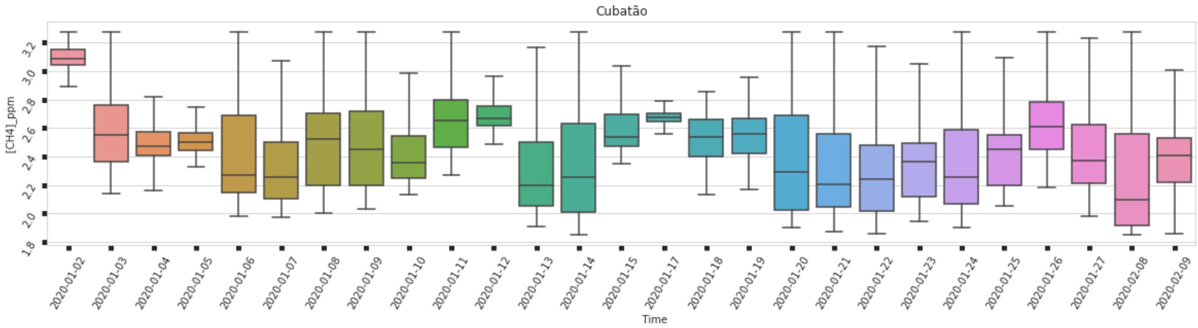
Figure 4 - Methane ratio in Cubatão city, January 2020



In both cases it is quite possible that this is a fugitive emission source of CH_4 from the oil processing plant or from some industrial effluent treatment plant within the raw oil processing site. As commented in Rahimpour, 2012, the flares of the oil derivative production units need to be fuelled with flare gas constantly, where in their majority composition is CH_4. This fact presents indications that one of the possible factors would be an unintentional escape in the flare gas line, as it is approximately 400 m (FACUNDES, 2015) from the acquisition site. The increase in ambient temperature on the surface is also an important fact to highlight, as Segers (1998) confirms that the increase in temperature is directly proportional to methane emission. We emphasize that in this case summer prevailed in Brazil, with a temperature of ~ 36°C at the acquisition site (QUALAR - CETESB 2021).

The Itanhaém region has a large flooded area, which can generate a high amount of methane due to the interaction with decomposing organic matter (EPA, 2010).

We can observe in Figure 5 that the methane concentrations in June/2019 were between 1.8 ppm and 2.6 ppm, slightly higher values compared to July/2019 (Figure 6), where a variation between 1.8 ppm and 2.2 ppm was detected. The higher concentrations of methane in the atmosphere of the Itanhaém region may be caused by the high activity of metagenesis characteristic of flooded regions (UPSTILL-GODDARD,2000).

Figure 5 - Methane ratio in Itanhaém region, June 2019

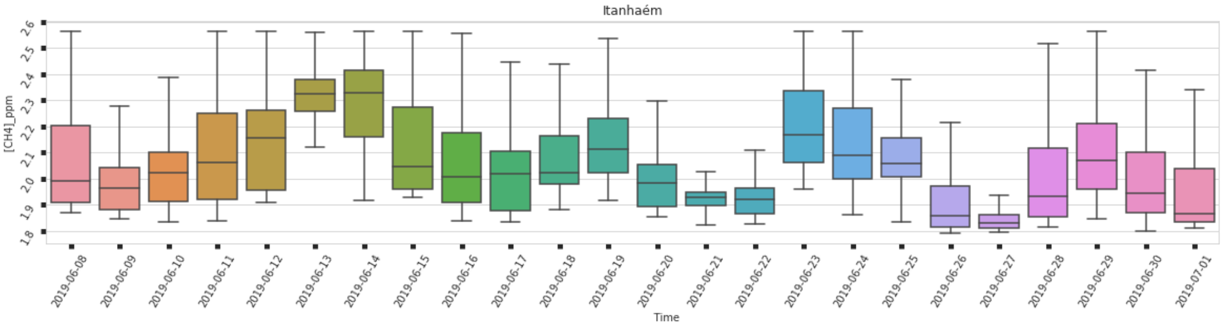
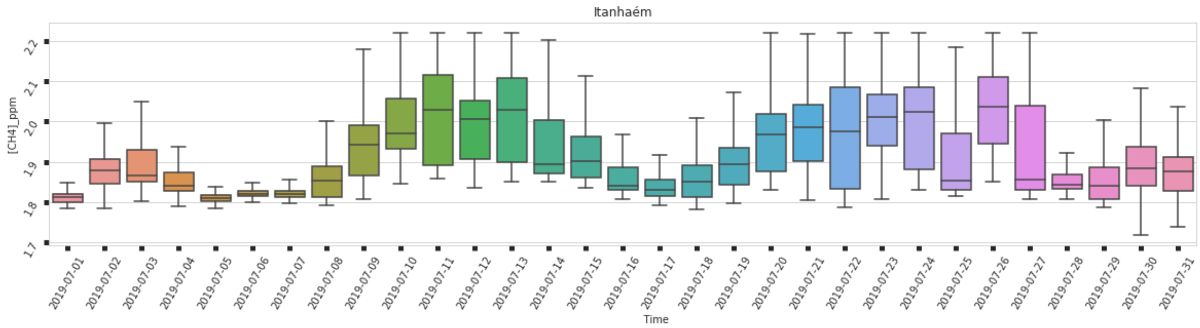


Figure 6 - Methane ratio in Itanhaém region, July 2019



In coastal areas, ecosystem and habitat heterogeneity ensure several pathways of CH_4 transport to the atmosphere, including air-water and soil-water diffusion, escape through the water column, escape at low tide, transport through plants in wetlands and, that is, transport of dissolved CH_4 between tides to and ebb channels (DE ANGELIS, 1993; SANSONE, 1999; ABRIL, 2002; MIDDLEBURG, 2002; BORGES, 2011). In estuaries, the balance between methanogenesis and methanotrophy is driven by highly variable microbiological and physical processes that depend on reactive organic matter inputs present in sediments, availability of electron receptors, hydrodynamics, hydrostatic pressure, salinity and temperature (MARTENS, 1998, BORGES, 2011).

4 CONCLUSION

This study investigated the possibility of characterizing an environmentally preserved and impact-free area and another one impacted by a petrochemical industrial pole, by detecting the CH_4 atmospheric ratio collected during different periods of the year. In the case of Cubatão, we demonstrated how significantly the background line was altered when there is the possibility of escaping methane during the processing of raw oil. The sensitivity of the equipment is evident when comparing the results of the area without impact, Itanhaém.

The comparison of the relationships obtained for the two measurements campaigns, shows significant differences of this atmospheric species, which plays a significant role in the Planet’s radiative balance. The seasonal variability of the periods analyzed is a very important fact, since temperature plays an important role in the environmental biogenicity and methanogenesis of sediments. However, the study should be re-evaluated in other seasons of the year to certify the relationship of the methane cycle with the environment and seasonality in the impacted and impacted areas.

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