

# EMISSION OF VOC AND GHG BY BIOREMEDIATION OF SOIL CONTAMINATED WITH DIESEL

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## ABSTRACT

Bioremediation processes have been credited for reducing high levels of organic contaminants from soils. However, during bioremediation of diesel contaminated soils, for instance, diesel is converted to volatile organic compounds (VOC) and greenhouse gases (GHG), which means that such remediation technique contributes to the greenhouse effect. The ongoing construction of a large petrochemical industrial region in Rio de Janeiro Metropolitan Area (COMPERJ) and the transportation of large volumes of oil byproducts (mainly diesel), have raised deep concerns regarding accidents that may result in soil and air contamination. When the problem comes, remediation techniques shall be applied. The objective of this study was to characterize the emission of GHG and VOC during bioremediation of soils contaminated with diesel oil in pilot scale. Soil samples contaminated with 0.5, 2.0 and 4.0 w/w% diesel oil were kept during 3 months in glass reactors (2 L internal volume) kept under anaerobic/anoxic conditions. The soil moisture was controlled at 80% of field capacity. Bioremediation processes were investigated with nutrient's adjustment (biostimulation), no adjustment (natural attenuation) and sterilized soil (abiotic process). The gases emitted from different reactors were collected in activated carbon cartridges and the GHG were collected in Tedlar bags. The chemical analyzes were performed using a gas chromatograph (Agilent 7690) with multi-detection using FID for CH<sub>4</sub>, ECD for N<sub>2</sub>O and TCD for CO<sub>2</sub>. VOC were analyzed using a mass spectrometry detector (Varian 450GC MS220). The results indicated that gaseous samples contained high concentrations of CO<sub>2</sub> but low concentrations of CH<sub>4</sub> and N<sub>2</sub>O. The differences in composition of the gas emitted from the reactors regarding CO<sub>2</sub> were statistically not significant. Preliminarily, regarding VOC emissions, such as alkanes and alkenes (both branched), cycloalkanes, and aromatic substituted (such as ethyl benzene), the compounds with higher emissions were cycloalkanes and branched alkanes.

## KEYWORDS

Air emissions, Greenhouse effect, Soil bioremediation, VOC, GHG.

## 1 INTRODUCTION

Soil contamination is the result of the industrial progress that society has undergone during the second half of the last century and the rapid population and economic growth presented at the beginning of the present century. In the list of USA environmental national priorities existed in the mid-90s, over 1,200 contaminated areas with the possibility to increase to 32 000 sites [1]. In the largest Brazilian cities like Rio de Janeiro and São Paulo, the INEA (Rio de Janeiro Environmental Agency) [2] and CETESB (São Paulo Environmental Agency) [3], have reported several contaminated areas. The petroleum industry introduces toxic pollutants in the environment during several processes, such as exploration, exploitation, transportation, storage, and refining. The environmental and health problems resulting from pollution of soil and water with petroleum are well known, but the impacts in the atmosphere are poorly studied. Large quantities of volatile organic compounds (VOC) are released into the atmosphere during accidents and also during treatment processes of contaminated soil and water. To address the issue raised by remediation technologies and their potential to release pollutants to the atmosphere, the bioremediation technique and the soil from the region where the Petrochemical Complex of Rio de Janeiro (COMPERJ) has been constructed were chosen as case study. COMPERJ is a petrochemical complex being built in the region of Itaboraí at the Rio de Janeiro Metropolitan Area which aims primarily to increase the domestic production of petrochemicals. COMPERJ will be responsible for processing 450 thousand barrels a day of crude oil with a high flow of transportation of raw material and end products. Consequently in the risks for pollution related to oil spills are expected to increase considerably.

The emissions released during remediation of contaminated soils are not a new issue. The bioremediation of oil-contaminated soils has shown good performance, and usually, the microorganisms get all the credits for the removal efficiency. Losses due to evaporation or breakages of contaminants into lighter molecules with subsequent volatilization with no interference of microorganisms are not estimated. With the fast development of environmental problems related to emissions of VOC and GHG, few studies assessing this aspect began to be done. According to [4], many VOC are released during storage of waste for energy, for instance. In that investigation VOC were quantified and it was found alarming emission values during the storage, such as high concentrations of CH<sub>4</sub> (7 ppm) and CO<sub>2</sub> (60 ppm). Likewise, the present study seeks to quantify VOC and GHG released during bioremediation process of soils contaminated with diesel oil. The specific objectives of this study are: (i) to assess the conversion of heavy into lighter hydrocarbons under three different microbiological conditions (abiotic processes, natural attenuation and biostimulation); (ii) to assess eventual temperature variations in the reactors during the experiments due to the applied treatment strategies; (iii) to characterize the emission patterns and quantify VOC and GHG; (iv) to check the residual contaminants in the soil after treatment with the purpose of estimating mass balance.

## 2 METODOLOGY

### 2.1 Soil characterization

The soil used in the study was collected at COMPERJ region and characterized at EMBRAPA laboratory according to its methodology [5]. All soil samples were collected on the same day and

under similar sampling conditions, in similar mass quantities, then mixed and stored in a polyethylene bag.

According to EMBRAPA, the representative soil of the region is a Cambisol. This type of soil is characterized by an incipient developing of B horizon. The sample represented the surface layer (0-20 cm) of the Cambisol. It has a sandy loam texture, with 120 g kg<sup>-1</sup> of clay and 798 g kg<sup>-1</sup> of sand. The elemental analysis of this soil indicated a low content of organic carbon (8.4 g kg<sup>-1</sup>) and a C/N ratio consistent with a well humified soil organic matter (10). The acid pH (5.3), the low base saturation (8%), the high aluminium saturation (58%) and the low content of phosphorus are consistent with a tropical soil condition. In that context, the high amount of aluminium found in the soil sample (0.7 cmolc kg<sup>-1</sup>) can facilitate the biodegradation, since this metal can act as electron acceptor. Regarding the extraction of other metals by Mehlich 1 solution (HCl 0.05 + H<sub>2</sub>SO<sub>4</sub> 0.0125 mol L<sup>-1</sup>), the levels of Fe, Mn, Zn and Cu were within the range found in Rio de Janeiro State [6]. The levels of Cr, Cd and Pb are within the normal range in Brazil. Co and Ni were below the limit of detection of the technique.

## 2.2 Experimental setup

In order to assess air emissions from diesel contaminated soils with no interference of microorganisms (abiotic processes-AB), under natural conditions (natural attenuation-AN) and, with stimulation of the indigenous microorganisms (biostimulation-BI), three different setups (AB, AN, BI) were prepared as described below.

**Abiotic Processes (AB):** The soil pH was adjusted to the neutrality (around 7.0) as described in the literature [8, 9]. After that, the soil was subjected to the action of sodium azide (5% w/w) during 1 h and then, the soil was autoclaved for 2 h. The water used for moisture adjustment was also autoclaved.

**Natural Attenuation (NA):** The soil was tested with no chemical or thermal sterilization.

**Biostimulation (BS):** The soil pH was adjusted to the neutrality (around 7.0) as described in the literature [8, 9]. The soil had its pH adjusted, no sterilization was performed, and nutrients were added. Phosphorous (Na<sub>3</sub>PO<sub>4</sub>) and Nitrogen (Urea) were added according to the literature, where some authors [10-15] suggest the ratio of 10 mg P per 100 mg soil and 2.5 g of Nitrogen per 100 mg of soil.

Emissions of VOC and GHG from bioremediation processes were obtained using 2 L glass reactors coupled at the top with coconut shell charcoal (CSC) cartridges and Tedlar bags. The emissions were measured during treatment of 1.0 kg of soil artificially contaminated with commercial diesel oil. The commercial diesel oil (with 5% of biodiesel) was chosen due to the increasing diesel B5 production in Brazil, and consequently the increasing potential for accidents during the first year of COMPERJ's operation. The diesel B5 concentrations in the treated soil were 0.5%, 2.0% and 4.0% w/w.

The reactors were assembled following three different treatments: reactors for abiotic processes (PA), to verify the emissions from soil with no microbial activity; in this treatment, the soil was sterilized with sodium azide at 5% and autoclaved for 2 h); natural attenuation (AN) to address the degradation processes with no interference; and biostimulation (BI), where the contaminated soil had nutrients (N and P) and pH corrections in order to enhance the microbial activity. CSC

cartridges (double bed 400/200 mg) were used to trap VOC, which had been volatilized during the process. Three L Tedlar bags were coupled after these cartridges. Tests were conducted during 3 months in triplicates.

### 2.3 Sampling

The reactors were kept locked during 90 days with no contact to the air. The samples were collected after 30, 60 and 90 days and analysed for light VOC (adsorbed on the CSC cartridges), greenhouse gases (collected in Tedlar bags). The remaining hydrocarbons in the contaminated soils after 90 days were also analysed. The gases retained in the cartridges were extracted with dichloromethane at ultrasound bath for 10 min. The hydrocarbons in soil were extracted using cyclohexane in a Soxhlet extractor for 4 h.

### 2.4 Chemical analyses

The analyses of VOC from samples obtained with CSC cartridges and n-alkanes from the soil were done using a Varian 450 gas chromatograph coupled to a Varian 220 mass spectrometer (ion trap), under the following conditions: injector at 320° C; mobile phase He 1.8 mL min<sup>-1</sup>; VF5MS column 30m x 0.25 mm x 0.25 μm; column temperature of 40° C for 4 min, followed by heating at 10° C min<sup>-1</sup> to 300° C and stabilizing for 5 min; 1.0 μL splitless injection. The mass spectrometer has operated in SCAN mode (35-450 m/z), with trap temperature at 250° C, transfer line at 280° C, and manifold at 40° C. Quantification was made by the external standard method. GHG were analysed in an Agilent 7890 gas chromatograph with multiple detector (flame ionisation detector for CH<sub>4</sub>, thermal conductivity detector for CO<sub>2</sub>, and electron capture detector for N<sub>2</sub>O).

## 3 RESULTS AND DISCUSSION

### 3.1 Temperature

The temperatures reached by the soil mass during different treatments showed variation considered negligible. According to Jacques [15] in anaerobic systems, electron transfer reactions occur with low energy release. No supply of oxygen occurred during 90 days in locked reactors, which is supposed to setup conditions for the establishment of anaerobic environment. The highest temperature observed in biostimulation reactors occurred at the end of the experiment, but it did not exceed 23 °C. For the other reactors, the temperature did not exceed 22 °C. During the experiments the ambient temperature was kept at 20°C.

### 3.2 GHG emissions

The high concentration values for GHG (CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O) were observed even after 90 days of treatment as shown in figures 1, 2 and 3.

**CH<sub>4</sub>:** Different treatments (AN, AP and BI) resulted in less variation regarding methane concentration in samples obtained after 30, 60 and 90 days from reactors containing soil with high contamination (4% diesel B5) when compared to those from reactors with soils with lower contamination (0.5% diesel B5). This result suggests that the sampling procedure should be checked.

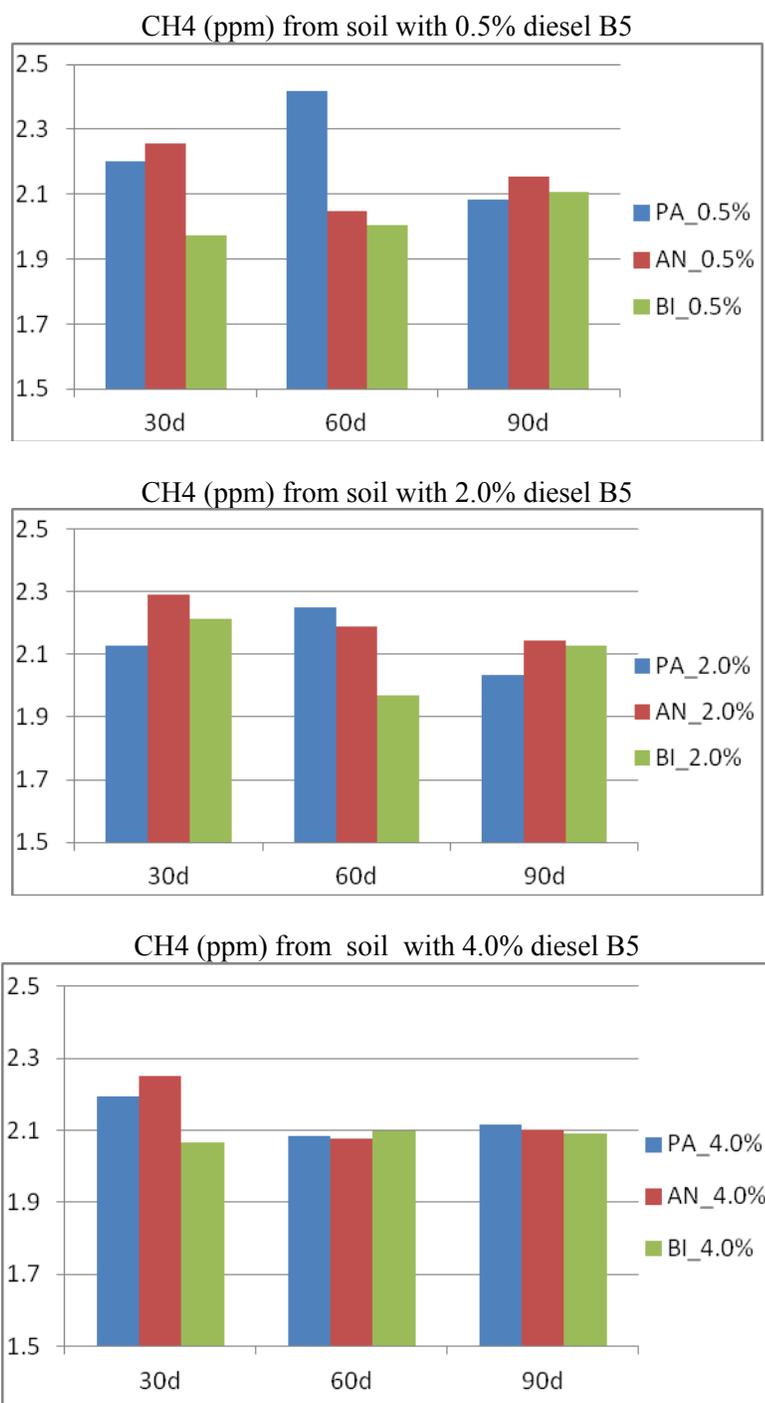


Figure 1. CH<sub>4</sub> (ppm) is samples from reactors with soil contaminated with 0.5%, 2.0% and 4.0% diesel B5 after 30, 60 and 90 days of treatment by PA, AN and BI.

**CO<sub>2</sub>:** The concentrations (in ppm multiplied by 100) of CO<sub>2</sub> are shown in Figure 2. It was observed a trend for reduction in samples from all reactors, regardless the initial concentration of

the contaminant in soil and the treatment applied. The higher the initial diesel B5 concentration in the soil, higher concentrations were observed after 30 and 60 days of treatment. However, by the end of the experiment, all treatments were releasing around 4.5 ppm CO<sub>2</sub>.

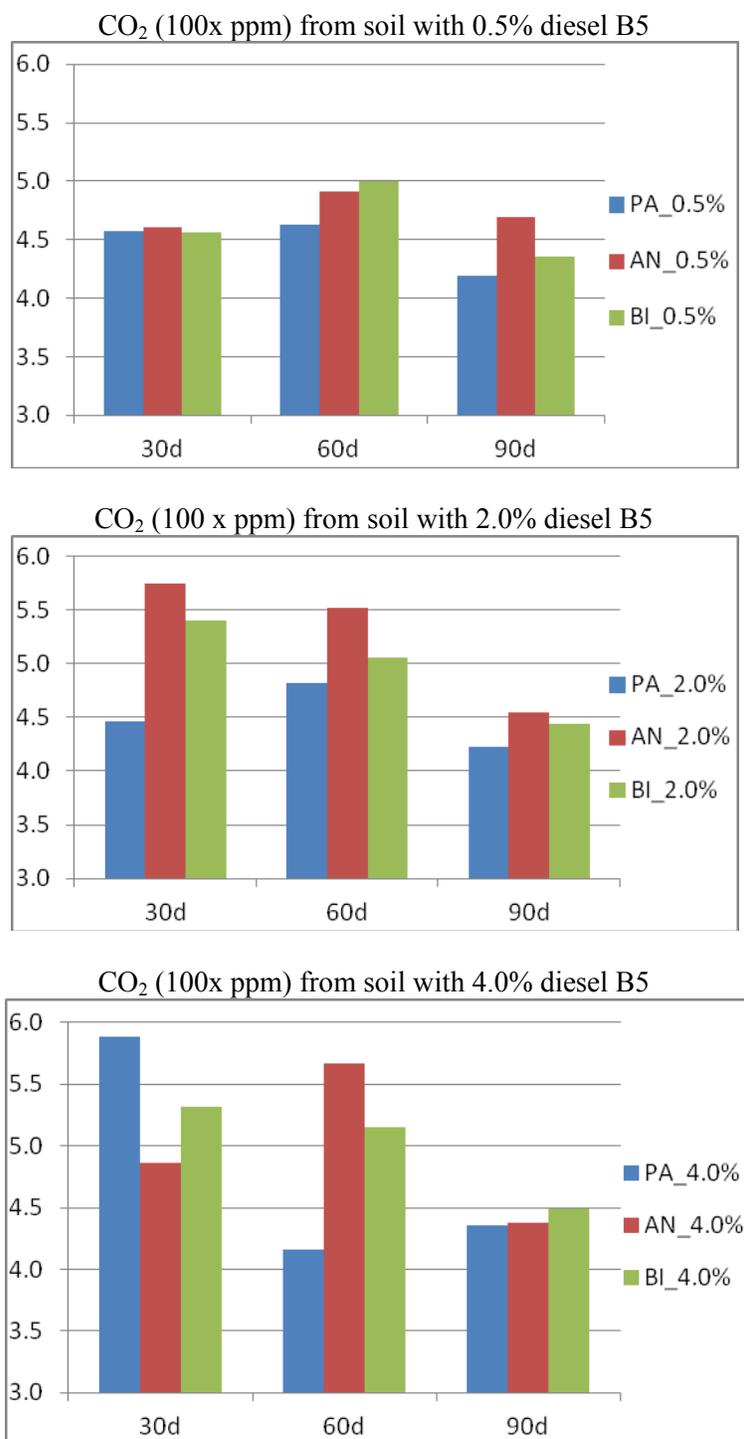


Figure 2. CO<sub>2</sub> (ppm) from reactors with soil contaminated with 0.5%, 2.0% and 4.0% diesel B5 after 30, 60 and 90 days of treatment by PA, AN and BI.

**N<sub>2</sub>O:** Regardless the treatment applied (AP, NA, BI) or the initial concentration of contaminant in the soil, after 30 days of treatment the concentration in the sample was about 20% higher than those found after 60 and 90 days of treatment. A plateau of N<sub>2</sub>O concentration around 0.30 ppm was reached in samples obtained after 60 and also after 90 days of experiments.

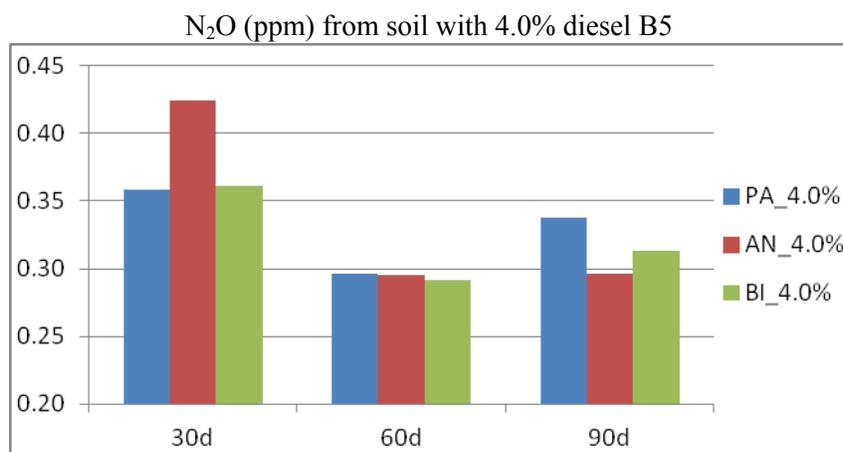
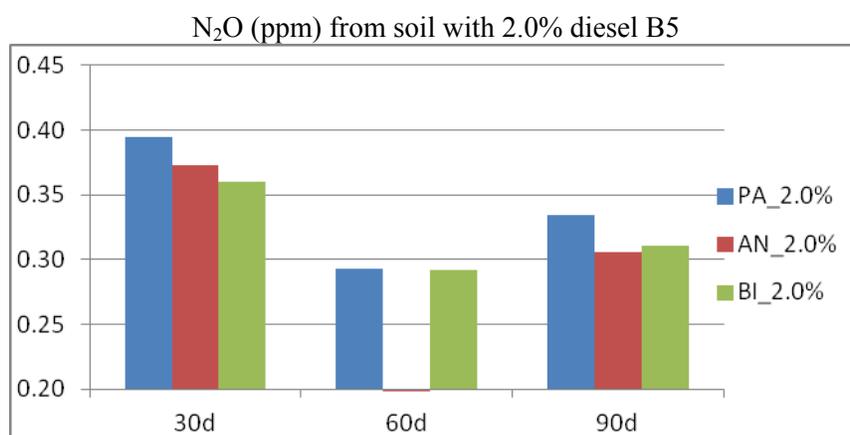
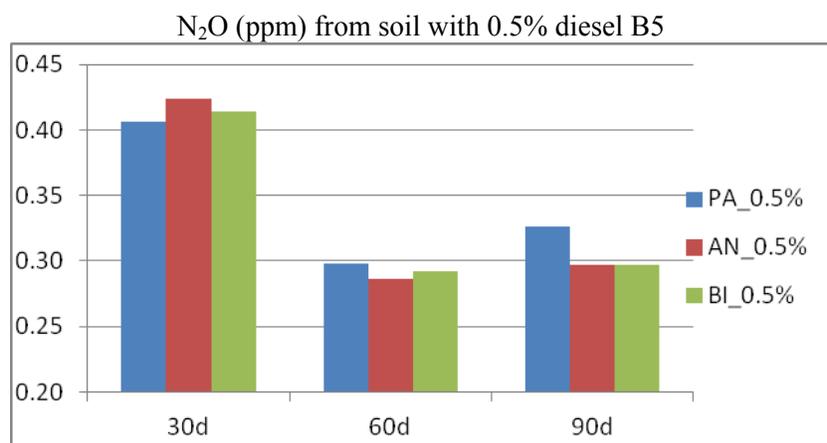


Figure 3. N<sub>2</sub>O (ppm) from reactors with soil contaminated with 0.5%, 2.0% and 4.0% diesel B5 after 30, 60 and 90 days of treatment by PA, AN and BI.

The results suggest that the studied gases were generated by the anaerobic processes according the literature [17].

### 3.3 Remaining contamination in soil

Figure 4 shows some remaining n-alkanes concentrations (ppm) extracted from soil at different reactors after 90 days of treatment (soil contaminated of 2% diesel B5). Although the relative abundance of each remaining compound is kept in all treatments, the soil that underwent biostimulation (reactors BI) showed consistently less remaining n-alkanes than the soil from natural attenuation reactor (NA) and abiotic process reactor (PA), suggesting that higher degradation occurred in BI.

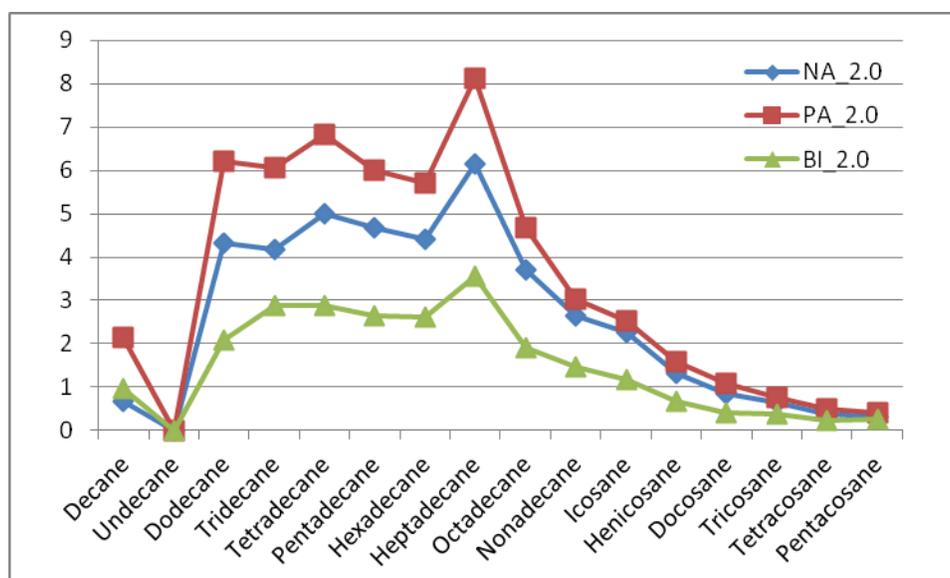


Figure 4 – N-alkanes (ppm) extracted from soil initially contaminated with 2% (w/w) diesel B5 obtained from reactors PA, NA and BI after 90 days of experiment.

Regarding VOC, a more detailed observation about decane, or instance reveals that the concentration of decane in soil after the experiment is < 2 ppm in both NA and BI reactors and a just above 2 ppm in PA reactor. This indicates that most decane (existing or generated during degradation or larger alkanes) was emitted as gas as observed in Table 1. These emissions were no longer observed at 60 or 90 days of treatment.

Table 1.  $C_{10}H_{22}$  (ppm) after 30 days from the Abiotic Processes (PA), Natural Attenuation (NA) and Bioestimulation (BI) reactors with 0.5%; 2.0% and 4.0% diesel B5.

| Treatment | 30 days (ppm) |
|-----------|---------------|
| PA_0.5%   | 2.39 ± 10.61  |
| NA_0.5%   | 18.15 ± 10.61 |
| BI_0.5%   | 10.15 ± 10.61 |
| PA_2.0%   | 11.99 ± 10.61 |
| NA_2.0%   | 14.48 ± 10.61 |
| BI_2.0%   | 36.04 ± 10.61 |
| PA_4.0%   | 1.34 ± 10.61  |
| NA_4.0%   | 5.01 ± 10.61  |
| BI_4.0%   | 17.55 ± 10.61 |

Since the microbiota was not quantified in different treatments it is not possible to guarantee that the emissions from abiotic process reactor (PA) are only due to abiotic processes. This is due to the fact that application of sodium azide and thermic treatment do not guarantee total and prolonged sterilization. This is particularly true due to the fact that the diesel or any other type of petroleum-based product can add to the soil microorganisms.

In relation to greenhouse gas emissions it is necessary to perform the experiment for aerobic processes to verify the generation of GHG as described by Nakawa & Andréia [16].

#### 4 CONCLUSIONS

This investigation demonstrated that emissions of VOC occur under anoxic/anaerobic conditions. The possibility of conversion of larger into smaller hydrocarbons of during the experiment should be considered. Further studies should be conducted in order to confirm the absence of active microbiota in sterilized soils. Regarding to emissions GHG, it is premature to say that the entire contents of generated gas comes from biological processes. It is more likely that an initial different population of microorganisms colonize the soil after sterilization takes place due to the low residual effectiveness of the applied sterilization procedures.

There is no doubt, however, that the contribution with GHG coming from bioremediation processes is not negligible and it should be better estimated in full-scale treatment plants.

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