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MONITORING GREENHOUSE GASES IN COMANDANTE FERRAZ ANTARCTIC STATION, KING GEORGE ISLAND

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Abstract: *This document presents the results of the monitoring of Greenhouse Gases (GHG) at Brazilian Antarctic Station Comandante Ferraz (EACF). The samples were taken near the Ozone and Meteorology Modules, weather conditions, such as direction and intensity of the wind, being annotated. For measurements of the concentration of GHG, a collection system that used a diaphragm pump, with samples of air being stored in stainless steel cylinders, was used. Concentrations of gases of interest in the samples collected were determined by the ozone gas chromatography laboratory, in São José dos Campos/SP. Furthermore, a continuous infrared monitor (model LI-820 Licor Gas Analyzer) was installed in the Ozone Module. There was great stability of the concentration values obtained by liquor, in that the average for these records were 378.8 ± 2.0 ppm (parts per million by volume), very close to that reported at NOAA's (National Oceanic and Atmospheric Administration) polar station (385 ppm). Analyses of nitrous oxide (N_2O) collected in the cylinders in the months of January to March 2010 resulted in an average of 334.7 ± 2.0 ppb (parts per billion by volume), very close to that reported by NOAA as a global average (323 ppb), however it was noted that this value was virtually constant in all samples, which reflected in low standard deviation, revealing an offset in our pattern to be given in subsequent samples. Samples collected in cylinders in the same period and analyzed for methane showed an average 1,791.4 ± 38.0 ppb. This value is higher than expected for the region (1,750 ppbv). However there was a wide variability in the samples (represented by the standard deviation) reflecting local sample point, mainly in the samples collected near the station. CO data did not pass in the validation tests, mainly due to their long storage time. As the CO is reactive and can undergo alteration inside the cylinder through other compounds, the storage time led to reactions inside the cylinders, causing the invalidation of the samples for this gas.*

Keywords: greenhouse effect, carbon dioxide, carbon monoxide, methane, Antarctica

Introdution

The Earth can be considered a body in thermal equilibrium, so the radiation absorbed by the surface must be distributed by it so that the balance is maintained. The Earth's surface, heated, re-emits the absorbed radiation through wavelengths greater in the infrared range, called planetary radiation. On its way into space, some of this radiation is absorbed by the atmosphere, warming it. Only 6% of the radiation emitted from the surface escapes directly into space, especially in the spectral region known as the "atmospheric window" between 7 and 14 μm, where the absorption by CO_2 and water vapour is weak (Vianello & Alves, 1991). The heated atmosphere emits radiation in all directions and a fraction of this radiation is absorbed by the surface again, contributing to further warming, the greenhouse effect.

Among the various greenhouse gases, the main ones are carbon dioxide (CO_2), which is responsible for more than 60% of the increase of temperature, methane (CH_4), nitrous oxide (N_2O), and CFCs 11 and 12. The GWP of a gas is an

index that expresses how effective this is for the greenhouse effect. It is measured in terms of the effect of the introduction of a molecule in the atmosphere (or gram) of gas over the effect of the introduction of a molecule (or gram) of CO_2, calculated for a certain time period (integration period). This calculation also takes into account indirect effects, such as chemical reactions that act as sink for gas, but that generate other greenhouse gases. For carbon dioxide, GWP is set to 1. Thus to say that the GWP of CFC-12, for an interval of 100 years, is 10,600, is equivalent to saying that the addition of a molecule of CFC-12 is equivalent to adding 10,600 molecules of CO_2.

The increase in the concentration of the gases responsible for global radiation absorption, called greenhouse gases, is causing a further rise in temperature, which can lead to an environmental imbalance. It is estimated that the increased concentrations of some gases (such as carbon dioxide, methane, nitrous oxide and CFCs) is responsible for a rise of about 0.3 °C in average global temperature per decade (with an uncertainty of 0.2 to 0.5 °C per decade), maintained their current growth rates (Cotton & Pielke, 1995).

Besides the natural variations of the atmosphere, there are variations in the concentrations of certain gases by interference of man. The most typical example is the case of the stratospheric ozone layer and the increase of Greenhouse gases. Artificially produced chemicals and greenhouse gases emitted in the industrial era just reacting and dramatically affecting the chemistry and dynamics of the atmosphere, producing environmental impacts such as a slow and progressive reduction of the concentration of ozone at all latitudes and the increase of the surface temperature of the Earth.

However, in the current frame of Global Changes, other complementary information about the variation of atmospheric parameters is necessary to measure the impact of these changes in the atmosphere and so that the environment can be assessed and quantified.

The Antarctic environment is in the region of lowest global human impact. Due to its condition and its remote low-impact feature, this region is taken as reference for studies of global dispersal of pollutants and products from the earth's crust, oceans and volcanic eruptions. Thus, maintenance of natural conditions in this region is of vital importance for understanding the impact of large scale impacts occurring in various continents and potentially those that have an influence on the Antarctic region.

The gases CO, CH_4, N_2O and CO_2 are greenhouse gases and their monitoring is essential over time. Moreover, these gases may be used for monitoring environmental pollution produced in the region of Antarctic Station Comandante Ferraz (EACF).

Materials and Methods

For the measurements of concentration of greenhouse gases, which began in November 2009, a system of collection with a diaphragm compressor pump was used, with air samples being stored in stainless steel cylinders using an electropolishing procedure. Figure 1 shows the process of collections in the vicinity of EACF (62.11° S and 58.41° W).

The frequency of sampling was weekly and the sampling was done in pairs, with two cylinders being pressurized in sequence. The pairs of samples collected were considered valid only when the difference in the mixing ratios between the two cylinders was at most 5%. At the time of sampling, the weather conditions, like the wind direction and intensity, were recorded. The detailed meteorological data at the time of collection, such as wind speed, temperature and humidity were obtained through the address www.cptec.inpe.br/antartica.

The samples were brought to the Ozone Laboratory at the National Institute for Space Research (INPE) to be analysed. To determine the mixing ratio of methane a chromatograph Shimadzu GC-14A equipped with a flame ionization detector (FID) and two columns of stainless steel 1/8 inch in diameter, were used. The first column, 2.5 m, was filled with silica gel and was used to minimize the total analysis time for the retention of water vapour, CO_2 and carbon compounds heavier than methane. The second was a column packed with zeolite 5Å molecular sieve (5 angstrom), 3.0 m in length, which was responsible for the gas chromatographic separation of the sample. The standard gas used was purchased from NOAA (National

Figure 1. Collect the air samples using stainless steel cylinders with electropolishing internal pressurized to 2 atm, near (left, on the beach) and far from the station (right).

Oceanic and Atmospheric Administration), and showed a concentration of 1749.4 ± 4.5 ppbv. The sample was injected through a sampling loop of 2.2 mL. The speakers operated at 100 °C and the detector at 120 °C. The chromatographic gases used for the FID(H_2, N_2 and synthetic air) had a high purity (99.999%). The relative accuracy obtained in the analysis of three aliquots of each sample was 0.7% or better (Alvalá *et al*., 2004; Marani & Alvalá, 2007). A detector of oxide of mercury was used for determining the mixing ratio of CO, with a relative precision of 3.5% or better for analysis of three aliquots (Kirchhoff *et al*., 2003). To determine the mixing ratio of N_2O and CO_2 a gas chromatograph equipped with electron capture detector (ECD), with relative accuracy of 0.7% or better, was used. All standard gases used were obtained from NOAA.

In addition, a continuous infrared carbon dioxide monitor (model LI-820 Gas Analyzer) was installed near the ozone module (100 m distant from EACF), which provided instantaneous concentrations of gas and that should remain at the station performing the monitoring of the concentration of atmospheric CO_2. The Licor determines the concentration of CO_2 every second, but for this monitoring, the daily averages were chosen.

Results and Conclusions

Because it is monitoring work, its continuation is necessary so that the behaviour of greenhouse gases can be duly studied. The monitoring is important because it may give indications of the impact of human presence in this region of Antarctica. In terms of results already obtained, we observed a greater stability of CO_2 concentration values obtained by the Licor, and the average for these observations were 378.8 ± 2.0 ppm (parts per million by volume), very close to that observed in polar station NOAA (385 ppm). There were problems with pump parts in June 2010 and a new pump was planned to reach EACF by November 2010 for monitoring to continue. Figure 2 shows the daily averages of CO_2 obtained in EACF using cylinders (between December 2009 and January 2010), while in April, May and June, the data corresponds to daily averages obtained using the Licor equipment.

The analysis of nitrous oxide (N_2O) in the cylinders collected from January to March 2010 resulted in an average of 334.7 ± 2.0 ppb (parts per billion by volume). This value was found to be 10 ppb above the global average of NOAA (323 ppb), but observed that this value was almost constant in all samples, which resulted in low standard deviation, revealing a shift in our pattern to be given for the next samples.

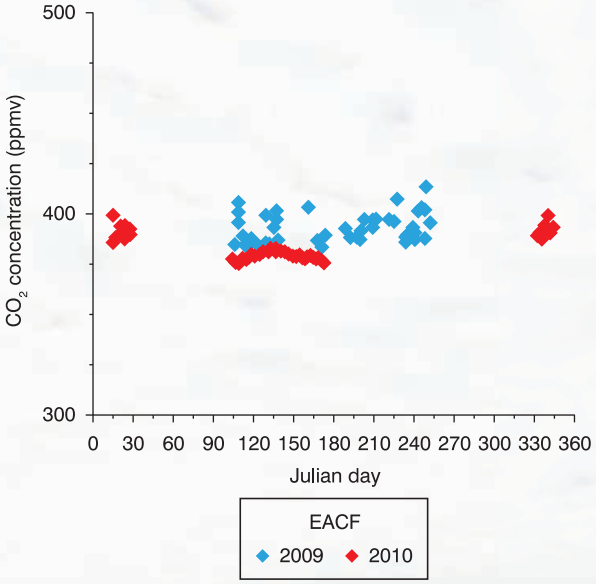

Figure 2. CO_2 (March 2009 to January 2010), obtained from samples collected in drums (purple) and those obtained by continuous monitoring (blue).

The samples collected in cylinders in the same period and analyzed for methane exhibited an average of 1791.4 ± 38.0 ppb. This value is higher than expected for the region (1750 ppbv). However there was a large variability in the samples (represented by standard deviation) reflecting the local sampling, mainly in samples collected near a station with favourable wind.

The CO data did not pass the validation tests, mainly due to long storage time. As the CO is reactive and can undergo alteration inside the cylinder through other compounds, the storage time led to reactions inside the cylinders, characterizing the samples as invalid for this gas. As a result, one of the difficulties was to perform the analysis of samples in smaller time intervals. Delays and changes in flight dates to support the work and difficulty in dispatch, resulted in cylinders being collected from São José dos Campos at shorter intervals, particularly during winter.

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CONSIDERING NEW PARAMETERS IN THE STUDY OF ATMOSPHERIC IMPACTS AT ADMIRALTY BAY

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Abstract: *The purpose of this research is to deepen the investigation of atmospheric impact as a result of aerosol and gas emissions at Comandante Ferraz Brazilian Antarctic Base (henceforth EACF). As a consequence of a campaign during 2009/2010 summer and re-analysis of 1998 filters (whereby there became available an annual set of continuous samples), levoglucosan (the product cellulose pyrolysis) as an indicator of burning of organic material by the Brazilian Station was verified. The numeric model of atmospheric dispersion used for Admiralty Bay was suitable for study of the impact on the atmosphere in Admiralty Bay and in zoned areas of biological importance within the Antarctic Specially Managed Area of King George Island, using a simulation with stations and ships operating simultaneously. The preliminary results of the chemical analyses for carbonyls and BTEX have shown that the direct atmospheric impact zone of EACF, due to these chemicals, is restricted to a radius of a maximum of 400 m, falling sharply in all directions*

Keywords: King George Island, atmospheric impact, air polution, levoglucosano, BETEX

Introduction

An Antarctic Specially Managed Area (ASMA) of greater interest for the Brazilian Antarctic Programme has been delineated around Admiralty Bay and covers the location of 2 permanent research stations: EACF (Brazil) and Arctowski (Poland) and 2 of a smaller size, which operate only during the austral Summer: Machu Picchu (Peru) and Pieter J. Lenie-Copacabana (U.S.A), (Weber & Montone, 2006). All these stations have power generating systems operated on the basis of the burning of fossil fuels (with the exception of Copacabana) and also incinerate organic waste. These operational pattern make the stations sources of research related to local pollution. The Brazilian base is the one which sustains a greater amount of human activity due to the great number of research scientists and technical support professionals, who are based there every year, together with their logistical maintenance support systems, personnel transport carriers, and materials. Admiralty Bay also receives several tourist ships that contribute to the increase of the local atmospheric pollution. The orography of the region is characterised by fjords surrounded by mountainous areas, which results in a large basin area making difficult the dispersion of pollutants generated there, especially during periods of high atmospheric stability. In this research work, we present the results of new simulations using the mathematical model of atmospheric dispersion presently in use, ISCST3 (Industrial Source Complex - Short Term Version 3), and the employment of chemical markers (levoglucosan, total BTEX and total carbonyls) representative of the anthropic activities at ASMA.

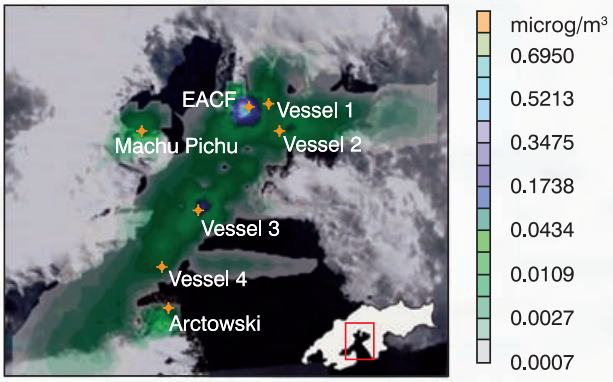

Figure 1. A modelled scenario of atmospheric dispersion using multiple sources in the interior of Admiralty Bay/King George Island.

Preliminary Results

Atmospheric dispersion model

The mathematical atmospheric pollutant dispersion models are important tools for understanding the behaviour of some gaseous and particle pollutants using data from the study of topography, emissions and meteorology. These models estimate the impact of one or more sources on the air quality of a certain region. The dispersion model used in this research was the ISCST3 (Industrial Source Complex - Short Term

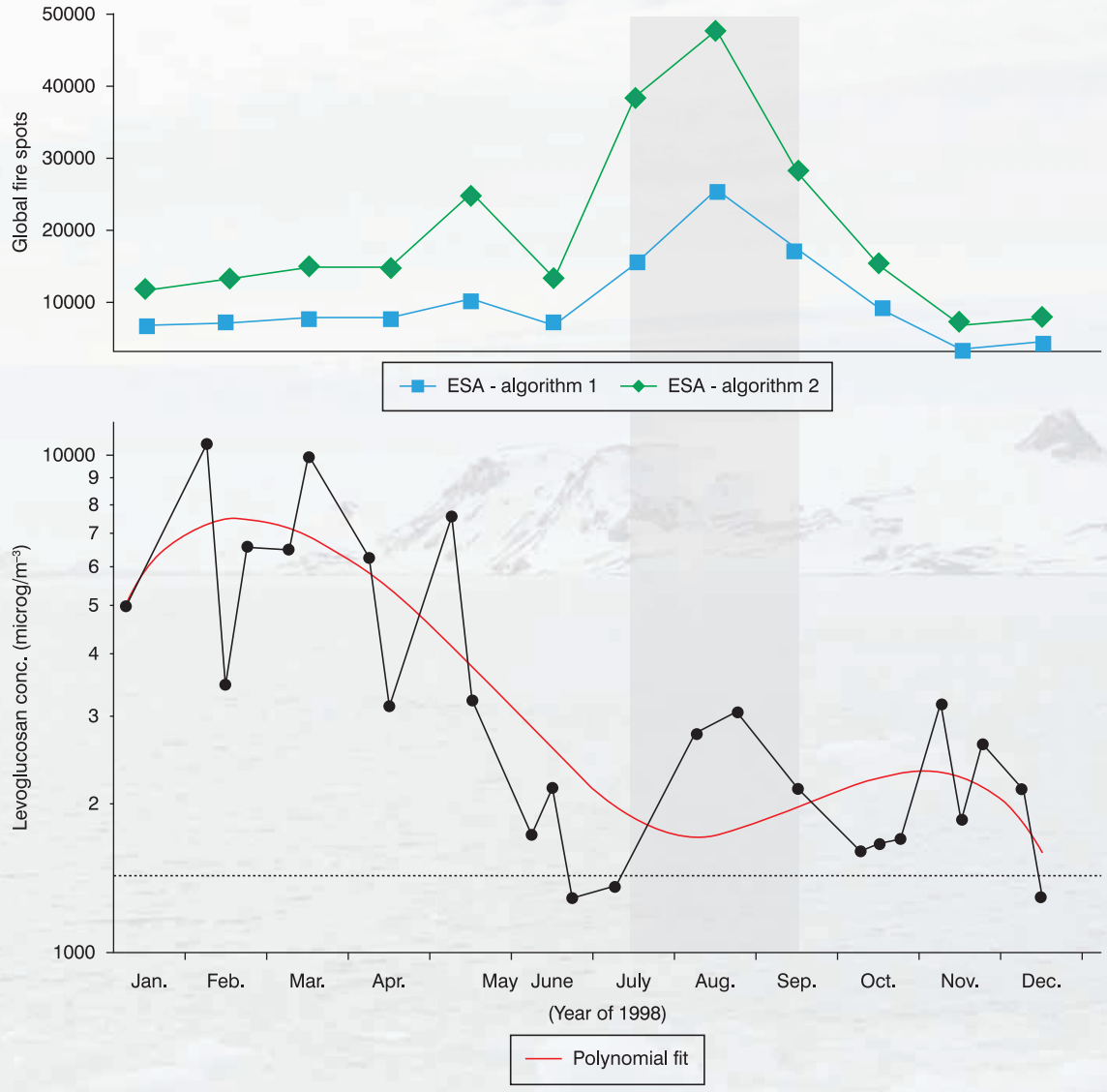

Figure 2. (Upper) seasonal average of global fire spots; (bottom) inter-annual concentrations of Levoglucosan in 1998 measured at EACF.

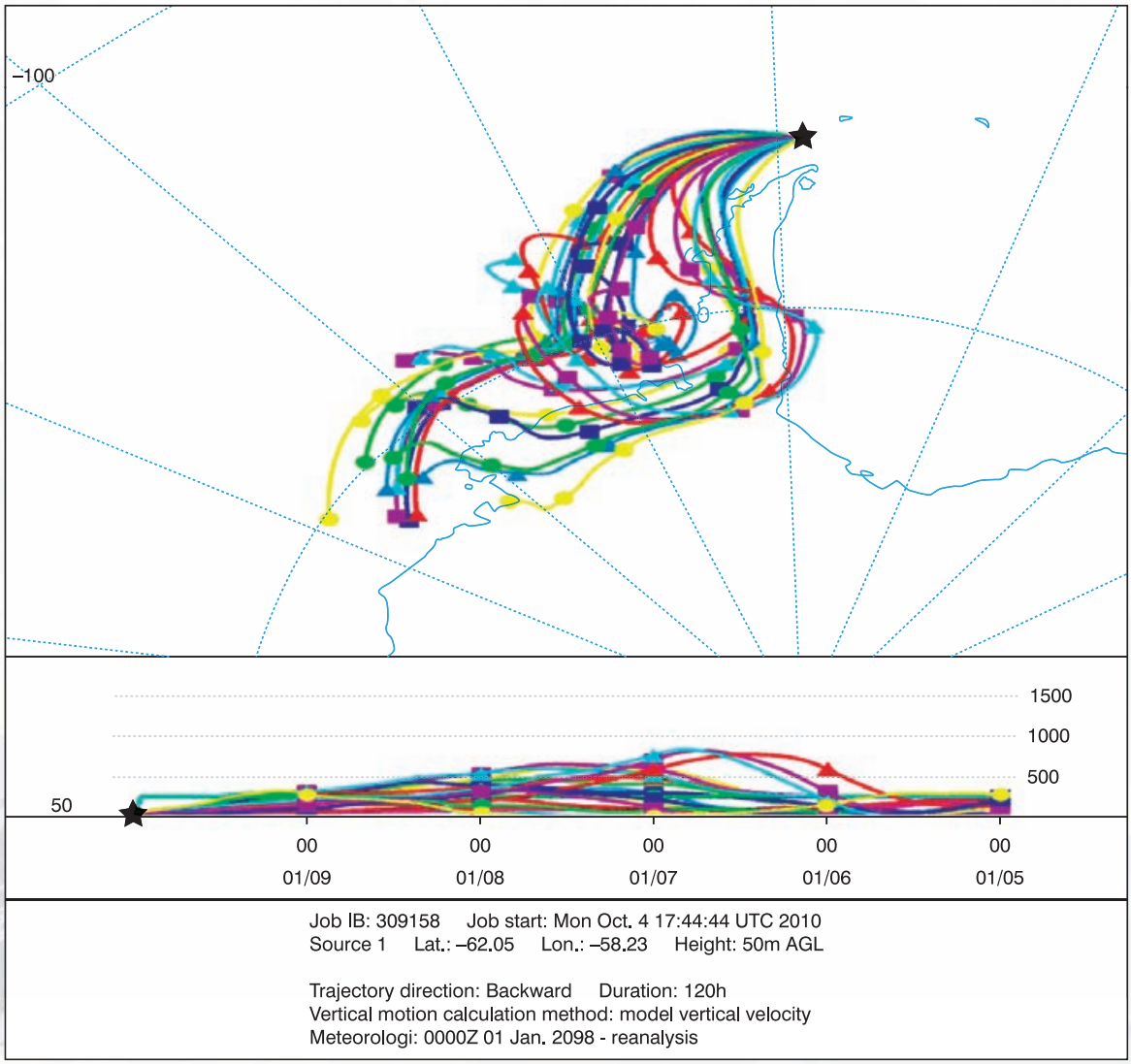

Figure 3. Back-trajectory model (Hyspit/NOAA), during the the increase of Levoglucosan levels over the King George Island in January 1998.

Version 3), a Gaussian Plume Model in a steady-state condition that can be used in the evaluation of pollutant concentrations and/or in the deposition fluxes from a great variety of complex sources (Vidal, 2008). In this study, the plume model was configured for a critical scenario whereby 3 scientific stations and 4 ships were operating simultaneously in Admiralty Bay. The result is shown in Figure 1 and considers an average distribution of local wind, topoghaphy and the predominant classes of stability. It can be observed that in these circumstances, apart from local impacts, an important part of Admiralty Bay receives the combined atmospheric impact of these pollutants sources.

Chemical tracers: Levoglucosan

Levoglucosan (1,6 anhydro-β-D-glucopyranose), the product of cellulose pyrolysis, has been studied as a forest and agricultural biomass burning tracer due to its resistance to weathering and its dispersion in the atmosphere during occurrences of slash-and-burn. Another potential source of levoglucosan in Antarctica is the practice of organic

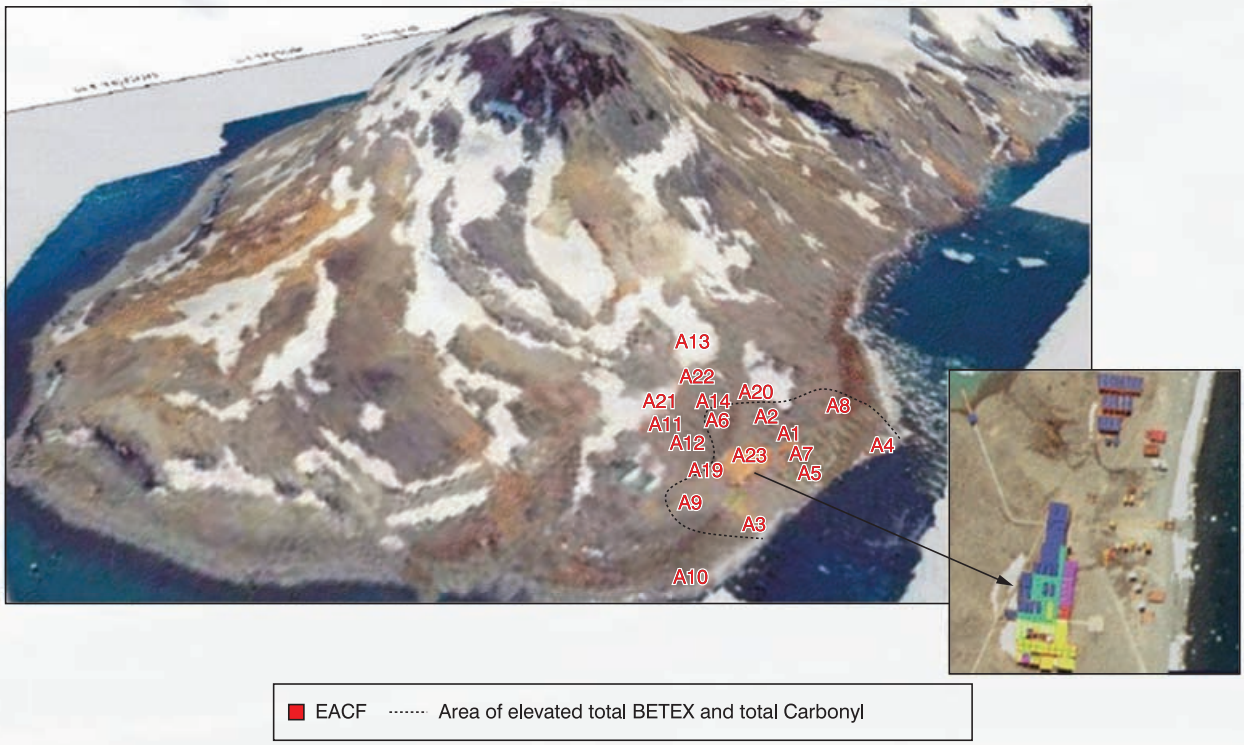

Figure 4. Spatial distribution of the atmospheric samples during the first phase of the 2009/2010 summer at EACF. The dotted contour line indicates where significant increases of BTEX and Carbonylic compounds were observed. The lower square close up detail, to the right, shows EACF and the reserve fuel tanks.

waste incineration by the research stations. An analysis undertaken concerning the filter samples in 1998, whose monitoring spanned a complete annual sequence, showed that the level of greater concentration of levoglucosan coincided with the period of greatest human activity at EACF, at which moments the incinerator is used with greater frequency. From the seasonal point of view, the peaks of Levoglucosan differ from the occurrence of peaks of the forest slash-and-burn, not only in South America/Africa, but also in terms of worldwide slash-and-burn, according to the database of the European Space Agency – ESA, Figure 2. Considering that the displacement time of the plumes of smoke from slash-and-burn between South America and the Antarctic Peninsula occur in approximately 7-15 days, the time lag observed does not justify a continental origin for the levoglucosan, making the incineration of organic waste at EACF the most probable cause.

Trying to corroborating the hypothesis concerning the relevance of the local sources related to levoglucosan, regarding long distance displacement, the Hysplit/NOAA model was used with in order to investigate the nature of the back-trajectories of the air masses, referring to the sample dates that show high concentrations. A typical structure is shown in Figure 3, calculated for January 2008. In this case, it was verified that during the periods of high level of Levoglucosan, the air masses that prevailed over the King George Island were basically from polar-oceanic nature, justifying, in principle, the influence of forest slash-and-burn over that region.

Carbonylic and monoaromatic hydrocarbons

In general the main carbonylic compounds in the troposphere are formaldehyde, acetaldehyde and acetone, and the first is considered carcinogenic by IARC. The monitoring of these compounds is an American regulatory ruling by USEPA. In the vicinity of EACF, 14 air samples

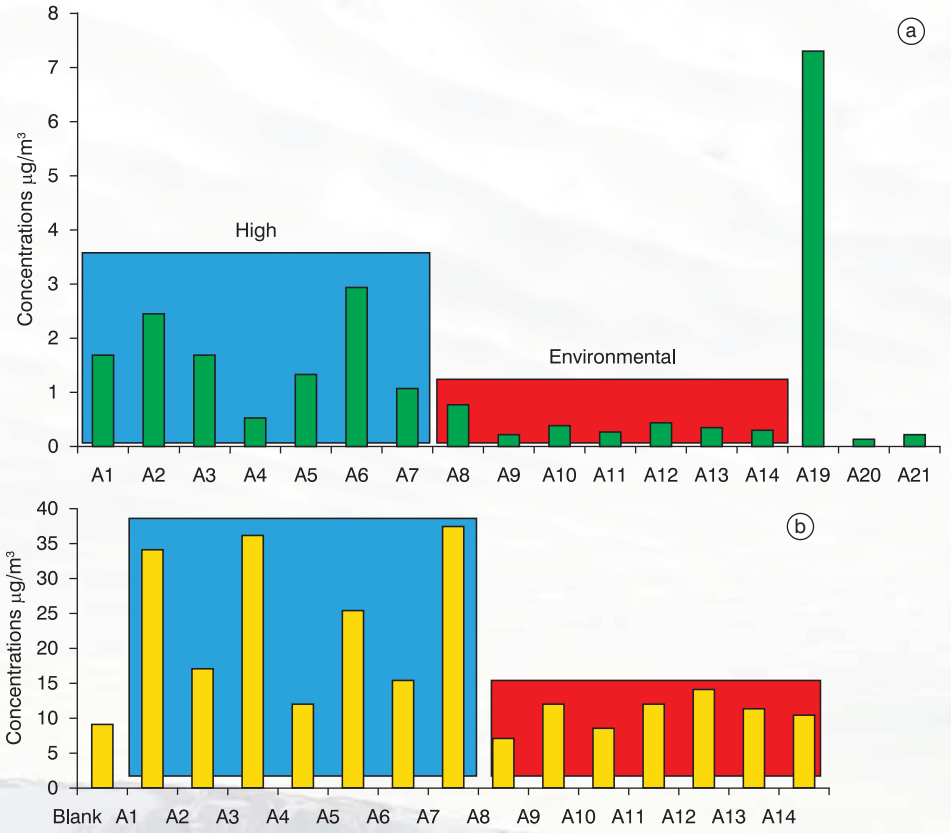

Figure 5. a) Total BTEX and b) Total Carbonyl. The colored rectangles distinct the samples with higher values and the environmental levels. The identification of the samples refers to Figure 4. Sampling station A19 was set close to the emission point.

were collected and analysed according to USEPA(1997) methodology. The results showed the presence of these compounds, mainly inside a 200-400 m radius from EACF (Figures 4 and 5). The same occurred for BTEX, aromatic hydrocarbons present in diesel and with high resistance to environmental degradation and and high volatility. In sub-polar environments the latter form becomes more persistent, since the low temperatures delay their degrading process. Among the 21 air samples analysed for BTEX, an analogue spatial distribution behaviour for the carbonylic compounds was observed.

A cluster analysis between the results of the atmospheric chemical pollutants and meteorological data obtained in situ (in the case, pressure, humidity, wind intensity, air temperature and solar radiation), indicated the presence of 3 groups when a tolerance limit of 0.35 was adopted; that is, a first group that relates pressure and relative humidity

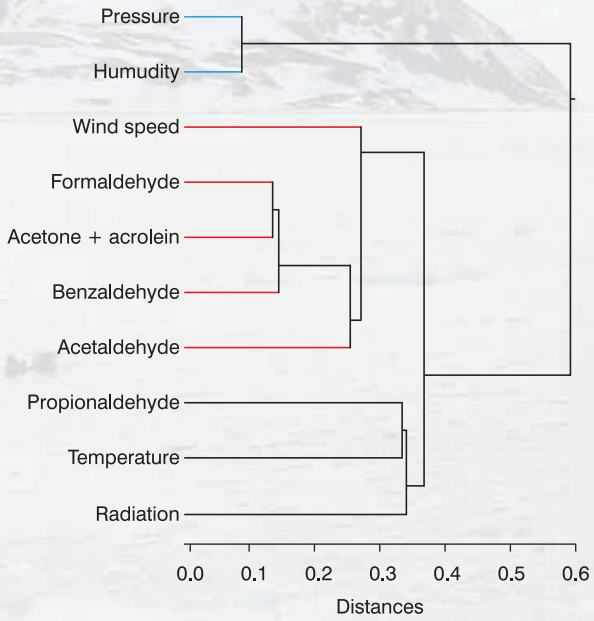

Figure 6. Cluster analysis of Carbonylic Compounds and meteorological data for the 2009 summer around EACF.