Inferring episodic atmospheric iron fluxes in the Western South Atlantic

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1. Introduction

It has been proposed that the micronutrient Fe plays a key role as limiting factor for phytoplankton growth rate and structuring plankton communities in the world oceans (Moore et al., 2002). A deficiency of Fe in seawater may prevent the complete biological assimilation of available nitrate and influences plankton species composition in open-ocean environments. The “Fe hypothesis” was postulated by John Martin in 1991 who stated that phytoplankton may not grow at optimal rates in some ocean areas, characterized as high nutrient low chlorophyll (HNLC) (Bucciarelli et al., 2001). At those sites the major phytoplankton limiting factor is attributed to dissolved Fe in the euphotic zone. An important parameter in the delivery of terrigenous material (including Fe) from land to the sea is the surface winds and it is believed to be the dominant factor at most remote ocean sites (Duce and Tindale, 1991; Sarthou et al., 2003). An evidence of this process is the occurrence of mineral types as kaolinite and illite in sea bottom sediments off the coast, where no or very few fluvial sources could be associated to (Prospero, 1981). Although some studies have inferred the atmospheric Fe deposition flux into the Western South Atlantic (WSA), based on models and considerations of dust emission from the Patagonian semi-desert (e.g.: Erickson et al., 2003), so far no reproducible experiments have been conducted to measure the in situ Fe flux in the ocean to validate the estimates. In this work we analyze data obtained from four oceanographic cruises concerning the Fe concentrations and fluxes, associations with terrigenous elements, potential anthropogenic sources and the atmospheric transport between South America and WSA continental shelf.

2. Study area

Oceanographic campaigns were basically developed over the continental shelf within the latitudinal band 22°–62°S. The
continental land associated to that encloses part of Southeast Brazil, South of Brazil, the coast of Uruguay and Argentine, up to the South Shetland Islands, at Northern Antarctic Peninsula. One of the major continental influencing region of this study is the Patagonian semi-desert. Its climatology is controlled by the persistent westerly winds that blow from the Pacific Ocean, though the Andean Cordillera where they discharge most of their water content, and continuing as dry winds to the East (Iriondo, 2000). The annual precipitation at the semi-desert domain is less than 200 mm and it is concentrated in the fall-winter seasons. The partial lack of soil moisture, sparse vegetation cover and strong surface winds provide the appropriate conditions for dust emission (Gaiero et al., 2003). In general, dust activity (resuspension) is higher during the summer, although winter and fall events have also been reported (Gassó and Stein, 2007). Aerosol samples were collected on board the Oceanographic vessel ‘Ary Rongel’ of the Brazilian Navy. Data were obtained underway from the City of Rio de Janeiro/Brazil to King George Island in the South Shetland Islands.

3. Methods

Total Fe flux was obtained from both in situ aerosol measurements over sea and modeled data that estimated deposition velocities and wet precipitation at the study region. The dry component of the Fe flux was estimated by a simple model based on the Fe concentrations determined at the fine and coarse aero-dynamic modes, sampled during the oceanographic cruise of 2003, 2004 and 2005, multiplied by the corresponding deposition velocities of 0.001 m s⁻¹ and 0.02 m s⁻¹, according to Duce et al., 1991. Especially for the 2002 campaign, the Fe Mass Median Aerodynamic Diameter (MMAD) was calculated using a six-stage cascade impactor. In this case, the deposition velocities for each aerosol diameter was estimated by a model proposed by Slinn and Slinn (1980), which considers the marine environment characteristics and measured in situ wind velocity. Since in the geographic context of this work, precipitation is expected to occur, the wet component of Fe flux was estimated using daily precipitation rate maps averaged for one month (November for the year 2003, February for 2004 and October for 2005). Precipitation data (enclosing: 40°–70°W and 22°–60°S) were provided by the NOAA/ESRL, at the website http://www.cdc.noaa.gov/, and superimposed to the ship tracks in a geo-referenced system (ARC VIEW).

3.1. On board aerosol sampling

Atmospheric samplings occurred during the following oceanographic campaigns: one in the period October–November of 2002, that covered the latitudinal band 22°–52° S, specially conducted to integrate aerosols into six aerodynamic diameters; followed by 3 main campaigns: the first between October 29th and November 15th, 2003; the second between February 15th and March 6th, 2004; and the third between October 21st and November 5th, 2005. Mean distances between the ship tracks and coast line varied from 300 to 900 km. During all campaigns, the samplings were performed using a wind sector control system to prevent from the ship’s exhaust contamination. The aerosol inlet (a cylindrical tube of 20 cm length and 15 cm width) was used to prevent the filters from sea spray. It was positioned at the top of the ship (10 m a.s.l.), 50 m away from the ship stack’s emission, while the pumping unit was installed inside the ship and consisted of: (1) one high volume pump (one-head GAST model); (2) an air flow monitor; and (3) a wind sector sampling control that is an electronic device connected to an anemometer (installed besides the inlet compartment), a datalogger, a two-way electrical valve and the pumps. The system was programmed to interrupt the aerosol sampling any time the wind direction is inside an angular sector (“named “dirty sector”) of 60° centered at a line between the inlet and the ship’s exhaust. Therefore, if the wind turns to the “dirty sector” the air flow connection between the filter holder and the pump unit is interrupted through a two-way electrical valve. In parallel we used an aethalometer (Magee Scientific, model AE-10) to monitor the aerosol black carbon (BC) in 30 min-resolution. Both aerosols and BC inlets were positioned together. BC data allowed investigating the effectiveness of the aerosol discrimination system. Data of BC of these campaigns were discussed in Evangelista et al. (2007). Particularly during the 2002 campaign we used a six-stage cascade impactor, with operational flow rate of 12.5 ± 0.6 L min⁻¹ and cutoff diameters of 19.9, 9.9, 4.7, 2.4, 1 and 0.64 μm. Fe concentrations were analyzed by PIXE technique, Dias da Cunha et al. (1998). For 2003 and 2004 campaigns, a “May cascade impactor” (May, 1975), was used to collect particles in two aerosol size ranges: 0.5–2 μm and 2–8 μm. In this system, airborne particles are forced to collide, by inertial impaction, over a glass plate coated with a thin silver film. Detected particles were individually analyzed by EPMA (Electron Probe Micro-Analysis) to determine the elemental mass concentration. Additionally, a stacked filter unit composed by a two-stage filter holder, to collect aerosols in fine and coarse modes (Nuclepore, 1987) was used. Aerosols were deposited onto sequential Nuclepore polycarbonate membrane filters of 47 mm of diameter. Each holder was composed by an upper filter with membrane pore size of 8 μm and a bottom filter of 0.4 μm. In this system the collection efficiency is a function of the aerosol aerodynamic diameter, and the cutoff diameter is defined at a 50% efficiency collection (Parker et al., 1977). Considering our air flow range of 12–17 slpm (standard Liter per minute), the cutoff diameter for the coarse mode is ~ 2 μm (John et al., 1983). For the above air flow, the inlet characteristic provides an aerosol cutoff diameter of ~ 10 μm (Cahill et al., 1979). This allowed the selection of particles with diameters (dp) < 2 μm and 2 < dp < 10 μm for the fine and coarse modes, respectively. The use of this technique is particularly valid for samplings of short duration conducted at remote regions, where atmospheric aerosol collection is typically very low. Filters containing particles were submitted to EDXRF technique. A summary of the aerosol techniques and oceanographic cruises is presented in Table 1. Calibration and inter-comparisons of PIXE and EDXRF are described in Calzolaia et al. (2008).

3.2. Bulk elemental analysis

The particles impacted on each stage of the cascade impactor were analyzed using a proton beam of 2 MeV using an electric current of 10 nA, generated by a 4 MV Van de Graaff electrostatic accelerator installed at PUC-RIO, Brazil (PIXE technique). Elemental composition of airborne particles collected by the two-stage filter unit were analyzed by a Spectrace-5000 equipped with a Rh-anode X-ray tube that generates a 17.5 W. For the determination of Fe, a high voltage of 35 kV, current of 0.35 mA and acquisition time of 10,000 s was used (EDXRF technique). Other details of EDXRF are presented in Spolnik et al. (2005).

<table>
<thead>
<tr>
<th>Aerosol Sampler</th>
<th>Measuring Technique</th>
<th>Year of Oceanographic Cruises</th>
</tr>
</thead>
<tbody>
<tr>
<td>six stage cascade impactor</td>
<td>PIXE</td>
<td>2002</td>
</tr>
<tr>
<td>two stage “May impactor”</td>
<td>EPMA</td>
<td>2003</td>
</tr>
<tr>
<td>two stage stack filter unit</td>
<td>EDXRF</td>
<td>2004</td>
</tr>
</tbody>
</table>
3.3. Individual particle micro-analysis

Particles collected by the two-stage “May cascade impactor” were submitted to automated EPMA (Ro et al., 1999; Godoi et al., 2004). Electron beam was obtained from a JEOL 733 electron probe micro-analyzer that employed an accelerating high voltage of 10 kV, current of 1.0 nA and measuring time of 20 s. Samples were previously conditioned in liquid nitrogen to reduce destructive effects (mainly the carbon enriched particles) while submitted to high energy electron beams. Quantification by EPMA (including Z-low elements as C, N and O) was made using a Monte Carlo iterative simulation and by the hierarchical cluster analysis performed by an Integrated Data System – IDAS, described in Bondarenko et al. (1996). In EPMA, abundance percentage observed refers to percentage of all particle number counted.

Some distinctive particle types were named according to their major chemical species and concentrations. Since EPMA allows determining the chemical species, at least semi-quantitatively, some individual particles were identified as internally or externally mixed particles. Soil dust abundances were estimated by summing the aluminum and silicon contents in wt% containing trace concentrations of Fe, Ca, K, Ti or Mn (<10% wt). Carbonaceous particles were separated in three different groups of species: biogenic, carbon-rich and organic particles. Particles are identified as organic when the C content is about the same magnitude of O (>70% wt). Mixed organic compounds and soil dust (>10% wt) were found in our samples and were labeled soil dust + organic. The presence of organic coatings over particle was demonstrated earlier for particles suspended in seawater by using an indirect method, but with TW-EPMA we could determine the existence of these layers directly in the X-ray spectra. Fe-containing particles are also encountered and two different types of Fe-containing particles were identified: Fe2O3 and Fe metal. Most of Fe metal particles contain 70–80% of Fe with some C and O, due to surface oxidation. In this work, all Fe-containing particles are denoted by “FeOx.” Regarding Fe-containing particles internally mixed with sodium chloride, we designated as NaCl–FeOx. Particles were identified as CaCO3 when the stoichiometry ratio of Ca, O and C were kept >70% wt. Sodium chloride (sea salt) particles were abundant in coarse and fine modes, which is clearly a fingerprint of the high marine influence on the sampled aerosol. This occurs due to the so-called bubble bursting or sea spray process that transports water drops from bursting white caps into the air, after which crystallization takes place and some salts remain airborne. Therefore, sea salt should be the main constituent in the coarse mode fractions of marine aerosols, except during great episodes of continental dust transport near shore (Fitzgerald, 1991). Since the low-Z EPMA is used for the analysis of a microscopic volume (picogram range in mass for a single particle of micrometer size), the elements at trace levels could not be reliably investigated. Thus, we do not include elements with less than 1.0% of elemental concentration in the procedure of chemical speciation.

3.4. Air mass back-trajectories

At the latitudinal bands where aerosol samples were integrated, the air mass back-trajectories were estimated using NOAA/HYSPLIT Model (Hybrid Single-Particle Lagrangian Integrated – available at http://www.arl.noaa.gov). Ending point for trajectory analyze was at mid-latitude coordinates, 10 m a.s.l. We used the default meteorological dataset of HYSPLIT, this is, the NCEP/NCAR reanalysis (2.5° lat/long 6 hourly). These trajectories provided information on the retrospective pathway of the air masses before reaching the ship. We run HYSPLIT twice each day (0:00 h and 12:00 h a.m.) for 5 days backwards. An ensemble dispersion product was also used to investigate the uncertainty level attributed to an individual track event, during main peaks of Fe concentration.

4. Results and discussions


Table 2 summarizes sampling data of aerosol’s collection during 2003, 2004 and 2005 campaigns.

### Table 2
Sampling data of 2003, 2004 and 2005 oceanographic campaigns at the Western South Atlantic.

<table>
<thead>
<tr>
<th>Start of sampling</th>
<th>End of sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Year</strong></td>
<td><strong>ID</strong></td>
</tr>
<tr>
<td>2003&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1AB</td>
</tr>
<tr>
<td>1CD</td>
<td>Oct 30th</td>
</tr>
<tr>
<td>1EF</td>
<td>Nov 9th</td>
</tr>
<tr>
<td>1GH</td>
<td>Nov 11th</td>
</tr>
<tr>
<td>1IJ</td>
<td>Nov 13th</td>
</tr>
<tr>
<td>1LM</td>
<td>Nov 14th</td>
</tr>
<tr>
<td>2004&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2IJ</td>
</tr>
<tr>
<td>2GH</td>
<td>Feb 16th</td>
</tr>
<tr>
<td>2EF</td>
<td>Feb 21st</td>
</tr>
<tr>
<td>2CD</td>
<td>Mar 4th</td>
</tr>
<tr>
<td>2AB</td>
<td>Mar 6th</td>
</tr>
<tr>
<td>2005&lt;sup&gt;c&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>M</td>
<td>Oct 22nd</td>
</tr>
<tr>
<td>N</td>
<td>Oct 23rd</td>
</tr>
<tr>
<td>O</td>
<td>Oct 26th</td>
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<tr>
<td>P</td>
<td>Oct 27th</td>
</tr>
<tr>
<td>Q</td>
<td>Oct 28th</td>
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<tr>
<td>R</td>
<td>Oct 29th</td>
</tr>
<tr>
<td>S</td>
<td>Nov 1st</td>
</tr>
<tr>
<td>T</td>
<td>Nov 4th</td>
</tr>
</tbody>
</table>

<sup>a</sup> Trajectory: from Brazil to Antarctica.
<sup>b</sup> Trajectory: from Antarctica to Brazil.
<sup>c</sup> Time GMT.
<sup>d</sup> ID: Identification of sampling step.
In samples collected in 2003 campaign, total atmospheric Fe showed a decrease towards higher latitudes. Concentrations in the fine mode were 7–12.7 times higher than in coarse mode from latitude ~22°S to ~55°S (an exception was a ratio of 2.3 found near King George Island). In general, total Fe concentrations can be distinguished in three concentration levels: (1) a major peak at latitudes associated to the Patagonian semi-desert, the imprint of the marine spray activity acting along the transport near sea level. At “1 EF” we observed ~20% of AlSi/Na2CO3. In contrast, “1 GH” exhibited dust particles with abundance of only ~3%. It also corresponds to the farthest sampling site from the coast line. Although Fe concentrations were relatively low (4.75–9.59 ng m⁻³) at latitudes associated to the Patagonian semi-desert, the imprint of dust was measurable at that site, including the presence of AlSi–Fe oxides.

Concerning the microanalyses by EPMA, the dust imprint in the 6 latitudinal bands was somewhat comparable to the Fe concentration profile; this is, Fe peak at sampling ID “1AB” coincided with a high dust abundance of ~38% (obtained from the sum of dust particles defined by their elemental composition in Table 4) and Fe-rich particles of ~3.5%; at “1CD” we observed particles relative abundance of ~27.2% for NaCl + FeO, ~1% for SiO and ~3 for dust. The presence of FeO–NaCl structures at lower latitudes (25–31°S) indicates the sea salt attachment over terrigenous particles, probably due to the marine spray activity acting along the transport near sea level. At “1 EF” we observed ~20% of AlSi/Na2CO3. In contrast, “1 GH” exhibited dust particles with abundance of only ~3%. It also corresponds to the farthest sampling site from the coast line. Although Fe concentrations were relatively low (4.75–9.59 ng m⁻³) at latitudes associated to the Patagonian semi-desert, the imprint of dust was measurable at that site, including the presence of AlSi–Fe oxides.
and dust-organic particles. Observed organic structures were identified in regions of high marine biological activity and probably are associated to surface adsorption of micro-algae fragments or suspended dissolved organic matter.

CaCO$_3$ was detected in total aerosol particles in the latitudinal band $\sim 32-42^\circ$S. A potential source-term of it is the presence of coccolithophorid micro-algae, whose shells are composed basically by calcite. CaCO$_3$ in the atmosphere, near the sea surface, could be the result of the mechanical action of winds. Blooms of these organisms have been reported in the same region by Brown and Podesta (1997). The detection of CaCO$_3$ in the atmosphere of that region coincides with reported data of suspended PIC (Particulate Inorganic Carbon or calcite), obtained from MODIS/Terra database for the Southern Ocean (Balch et al., 2005). According to Signorini et al. (2006), peaks of calcite may occur predominantly in the period December to February. Another characteristic that reinforces the marine origin of CaCO$_3$ structures is the simultaneous occurrence of 2 particles types of NaCl-organic structure (relative abundance of $\sim 13\%$) and NaSO$_4$ ($\sim 27\%$). Coccolithophorid species are mostly very small organisms ($<5$ $\mu$m) that are covered with ‘scales’ of calcite, called coccoliths. The organisms normally occur in the top 30 m of the water column, including the very surface, which allow them to be detected by ocean color satellite sensors. The ‘scales’ (approx. 2 $\mu$m) are shed by the live cells during growth and also at the end of a bloom.

Comparing modeled air mass trajectories and Fe concentrations, one can observe that the higher concentrations, corresponding to “1AB”, “1CD” and “1 EF” can not be explained by a direct association to a single HYSPLIT air mass back-trajectory that apparently brings to the sampling site a marine influence, due to easterly winds near the coastal region. Nevertheless, a better description of the continental influence over the air mass can be achieved by the use of the ensemble model, also provided by the HYSPLIT, Fig. 1. Air masses associated to “1AB” clearly have migrated across coastal region, where the samplings took place at the nearest position from land ($\sim 150$ km). Sampling ID “1CD” and “1EF” are also marked by terrigenous influence, contrasting to “1GH”, “1IJ” and “1LM” that were under the influence of the tip of South America. Differently from 2003, in campaign of 2004 we have not observed a stepwise decrease in Fe concentrations from tropical to sub-polar latitudes, but it was characterized by an abrupt episode of Fe increase associated to a air mass that has previously advected across a considerable land extension of the Patagonian semi-desert. Increases of Fe in fine and coarse aerosol modes occurred at latitudes 25–32°S (“2CD” in Fig. 2).

Fig. 1. Five-days air mass back-trajectories associated for the 2004 campaign in the Southwest Atlantic and altitude profile of the trajectories in meters above sea level.
between ~30°S and 37.5°S (sampling ID “N”). In contrast, the other
sampling locations were basically influenced by marine air masses,
with restricted migration over the continent. This may explain the
relatively low terrigenous concentrations (Fe concentrations were
lower than 5 ng m⁻³) along the campaign.

Considering the air mass trajectories prevailing during 2004 and
2005 cruises (and to a lesser extent 2003), dust/Fe tended to be
transported from Patagonia to lower latitudes around 22°–40°S. The
episodic events observed here constitute a different scenario of
continental shelf at early winds, blowing from the Patagonian desert to the Argentinean
models (e.g. Erickson et al., 2003) that assume the dominant west-
erly winds influenced by marine air masses, related to Zn, Mn, Pb, Ni and S (Castanho and Artaxo, 2001). In an
important industrial district of Rio de Janeiro (Santa Cruz),
aerosols containing Fe were associated with Ca, Mo, Mn, Zn, Cu and Ni (Quiterio et al., 2004). In general, the steel industries are
expected to emit Ca, Mn, Cu and Fe. To clarify this, during the 2004
campaign we measured Fe, Pb, Cu, Zn and BC simultaneously. The

4.2. Potential anthropogenic source of atmospheric Fe

Another important point to consider is that the high values of Fe
between ~22°S and ~38°S, may include contributions of anthropo-
getic sources due the proximity to large urban domains like the
Cities of Rio de Janeiro and São Paulo located at ~22.5°S and ~23–24°S; and probably Buenos Aires/Argentina.
These metropolises together comprise approximately 40 million
people and several industrial sites where Fe are largely emitted.
A detailed study of aerosol elemental composition conducted in São
Paulo indicated that Fe could be associated either with the
fine mode soil dust, related to Ca, Si, Ti and K, or to industry emissions
associated with Zn, Mn, Pb, Ni and S (Castanho and Artaxo, 2001). In a
detailed study of aerosol elemental composition conducted in São
Paulo indicated that Fe could be associated either with the

Table 5
Particle relative abundance obtained by EPMA technique (fine + coarse modes) for the 2004 oceanographic campaign at the Western South Atlantic. (The two highest relative abundances are in bold).

<table>
<thead>
<tr>
<th>Identification</th>
<th>Particulate type</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td>2AB</td>
<td></td>
<td></td>
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<tr>
<td>No. particles</td>
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<tr>
<td>Abund.(%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major Elements</td>
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<td></td>
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<tr>
<td>2CD</td>
<td></td>
<td></td>
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<tr>
<td>No. particles</td>
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<tr>
<td>Abund.(%)</td>
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<td>Major Elements</td>
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<tr>
<td>2EF</td>
<td></td>
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<tr>
<td>No. particles</td>
<td></td>
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<tr>
<td>Abund.(%)</td>
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<tr>
<td>Major Elements</td>
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<tr>
<td>2GH</td>
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<tr>
<td>No. particles</td>
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<tr>
<td>Abund.(%)</td>
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<tr>
<td>Major Elements</td>
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<td>2II</td>
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<td>Abund.(%)</td>
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<tr>
<td>Major Elements</td>
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</tbody>
</table>
latter is carbonaceous particle produced by the incomplete combustion of fossil fuel (also by biomass burning), commonly employed as a tracer of anthropogenic activities, (Evangelista et al., 2007). The on board results indicated that Fe and the set of heavy metals presented different latitudinal profiles; this is, Pb, Cu and Zn exhibited higher concentrations at the boundaries of the urban regions, ~22–25°S, Fig. 3, followed by a sharp decrease southwards, reflecting an atmospheric dilution of the urban/industrial emissions. BC also decreases at about the same latitudes but it remains at relatively high values to finally drop at ~45°S. At the coast of tropical South American at ~32–45°S, Argentine and Uruguay constitute important additional sources of BC (Evangelista et al., 2007; Pereira et al., 2006), while differences exist in their industrial activities. This difference can also be attributed to different aging and removal process among BC, soil dust and particles of urban/industrial sources. For these anthropogenic tracers, the major contribution to the total elemental concentration comprised the fine mode fraction: Cu (89%), Zn (85%) and Pb (62%). By contrast, Fe presented a distinct peak South of 25°S, extending to ~32°S, indicating a decoupling from anthropogenic sources. In order to distinguish the sources of atmospheric Fe, if primarily derived from soil dust or urban emissions, we have compared the ratios BC/Fe obtained on board (cruises of 2003 and 2004) with ratios reported for urban environments (e.g.: the City of São Paulo). We postulated that aerosols containing Fe from Patagonian semi-desert are depleted of BC, while from urban sites they would be internally or externally mixtures (Jacobson, 2001) with BC.

Table 6 summarizes the BC/Fe inventory for the campaigns of 2003 and 2004.

Since the 2003 campaign was conducted in October–November, a more adequate comparison with data of BC/Fe in Table 6 is the interval defined by Equation 1b. In this case, higher Fe concentrations obtained at 22–40°S (“1AB”, “1CD”and “1EF”) could not, unequivocally, be interpreted as derived from long-range atmospheric transport, although ratios obtained on board were very close to the minimum expected values of the urban environment. In contrast, ratios in latitudes higher than 55°S were far from the interval limits. The 2004 campaign was conducted in February–March and the interval of Equation 1a is adequate. In this case, Fe concentrations corresponding to the peak at ~25°S and 30°S (sampling ID “2CD”), could not be explained by the regional urban sources and corroborate the long-range atmospheric transport as also suggested by the air mass back-trajectory analyses.
4.3. Fe deposition flux to the sea surface

4.3.1. Dry deposition

Gravimetric deposition velocities of particles (∇) onto the ocean generally differ from continental land, due to the distinct surface characteristics and the adhesion of water to the aerosol surface during their transit over the sea, causing them to increase in size. Therefore, the Fe flux derived from dry deposition is better estimated from methods that allow aerosol size distribution. We have estimated the dry flux by two methods: one employing a six-stage cascade impactor during the 2002 campaign, in which one set of filters was used to accumulate a large amount of dust integrated from 25°S to 55°S; a second employing a two-filter holder to collected aerosols in fine and coarse modes. For the first method, the dry deposition flux was calculated by Equation (2):

\[ \Phi_{Fe,dry} = \sum_{i=1}^{k} v_i C_{Fe,air,i} \]  

where \( \Phi_{Fe,dry} \) is the total Fe flux, expressed in nmolFe m\(^{-2}\) day\(^{-1}\); \( v_i \) is the dry deposition velocities for the \( i \)-th diameter of the cascade (according to Slinn and Slinn, 1980), considering a mean wind velocity of 5 m s\(^{-1}\) measured on board; \( C_{Fe,air,i} \) is the \( i \)-th Fe concentration; and \( k \) is the number of stages used to separate the total sampled aerosol. Fig. 4 shows the results of Fe concentrations and corresponding \( v_i \). For the experiment, the mean Fe deposition flux integrated at 25°–55°S was 113 nmolFe m\(^{-2}\) day\(^{-1}\). Additionally, we estimated the Fe Mass Median Aerodynamic Diameter (MMAD) to be 0.9 μm.

For the 2003, 2004 and 2005 campaigns, the mean dry deposition was inferred from the two-stage filter unit which associated deposition velocities are 0.001 m s\(^{-1}\) for fine mode and 0.02 m s\(^{-1}\) for coarse mode, Du (1991). Based on these considerations, we found 219 nmolFe m\(^{-2}\) day\(^{-1}\) for 2003 campaign, 127 nmolFe m\(^{-2}\) day\(^{-1}\) for 2004 and 16 nmolFe m\(^{-2}\) day\(^{-1}\) for 2005.

4.3.2. Wet deposition

Along the cruise tracks, very few precipitation events have occurred, preventing measurable Fe in rain water (\( C_{Fe,rain} \)). Nevertheless, it does not mean that regionally it has not occurred. Since the wet deposition estimation requires \( C_{Fe,rain} \) values, concentrations in precipitation were alternatively estimated, using the dimensionless below-cloud scavenging ratio, \( S_t \) (Jickells and Spokes, 2001) as follows:

\[ \Phi_{Fe,wet} = PC_{Fe,rain} \rho_{air} \]

where \( \Phi_{Fe,wet} \) is in nmolFe m\(^{-2}\) day\(^{-1}\), \( P \) is the precipitation rate (mm day\(^{-1}\)); \( \rho_{air} \) is the rain water density (10^3 g m\(^{-3}\)) and \( C_{Fe,rain} \) is the Fe concentration in rain (g g\(^{-1}\)) which can be expressed as a function of \( S_t \), as:

\[ C_{Fe,rain} = C_{Fe,air} \frac{s_r}{\rho_{air}} \]

where \( \rho_{air} \) is the air density (1290 g m\(^{-3}\)) at 20 °C and at 1013 hPa, \( S_t \) consists in an important part of the uncertainty of the modeled wet deposition component, since \( S_t \) is highly dependent on the aerosol size, its hygroscopic characteristics, chemical speciation, atmospheric life history and precipitation intensity (Encinas et al., 2004). Precipitation data employed here (Fig. 5) refers to the period of sampling as described in Section 3. We assumed \( S_t \) to be 200, according to Du (1991), Gao et al. (2003), Sarthou et al. (2003) (for the South Atlantic).

4.3.3. Total deposition

Table 7 presents Fe fluxes in the WSA. Our results clearly identify two concentration levels for total Fe flux with the transition being near latitude 40° S. Two main factors contributed to this difference: (1) during the campaigns, the latitudinal band ~22–40° S received air mass that advected across larger land portions of the Patagonia semi-desert, of Southwest direction, in low altitudes before reaching the sampling sites. Therefore, air masses along there continental migration could be enriched with dust particles.

Fig. 4. Measured Fe concentrations (●) and corresponding dry deposition velocities (×) (based on Slinn and Slinn, 1980).

Fig. 5. Precipitation rates (from CDC/NASA) corresponding to the periods of 2003, 2004 and 2005 oceanographic cruises in the Western South Atlantic.
5. Summary and conclusions

In this work, we present results of measurements of atmospheric Fe at the coastal region of the WSA. Aerosol samplings were carried out underway, during four oceanographic cruises from the Southeastern Brazil (22°S) to King George Island (62°S), during spring and summer periods from 2002 to 2005. Data was analyzed in conjunction with modeled air mass back-trajectories attempting to identify potential dust/Fe source region. Shipboard measurements exhibited important episodically high atmospheric Fe concentrations during 2004 and 2005 cruises, varying from 38 ng m\(^{-3}\) to 1256 ng m\(^{-3}\) at sea and from 691 to 63.9 ng m\(^{-3}\) at land. These relatively high values were explained by the back-trajectory analysis of regional air masses that apparently transport Fe enriched aerosols from the Patagonian desert to lower latitudes in the South Atlantic Ocean. These results suggest that Fe from the Patagonian desert can travel long distances and be deposited over ocean areas very far from the source. Particularly in summer 2004, calcium carbonate was measurable in the atmosphere between 32°S and 42°S, a vicinity where coccolithophorids have been previously detected by remote sensing techniques. Fe fluxes calculated for the WSA margin varied from 4.73 nmolFe m\(^{-2}\) day\(^{-1}\) to 1688 nmolFe m\(^{-2}\) day\(^{-1}\).

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References


