Analysis of an Antarctic ice core by ion chromatography (Mg²⁺, Na⁺, Cl⁻, and SO₄²⁻ content)

Magdalena de Mello Marques[1,2,3]*
Maria do Carmo Ruaro Peralba[1]
Jefferson Cardia Simões[2]
Ronaldo Torma Bernardo[2]
Sharon B. Sneed[4]
Gino Casassa[5]

[1]Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS) – Porto Alegre (RS) Brazil.

[2]Centro Polar e Climático, Instituto de Geociências, UFRGS – Porto Alegre (RS) Brazil.

[3]Centro de Estudos Gerais, Instituto de Química, Universidade Federal Fluminense (UFF) – Niterói (RJ) Brazil.

[4]Climate Change Institute, University of Maine – EUA.

[5]Presently at Geoestudios – Santiago, Chile.

*Corresponding author:
magdalena.marques@gmail.com

Abstract

This study presents the ion chromatography analysis of an Antarctic ice core (IC-3; 85°59'S, 81°35'W) and discusses Mg^{2+}, Na^+, Cl^-, and SO_4^{2-} concentration data. The Mg^{2+}, Na^+ and Cl^- concentration peaks, are environmentally interpreted as winter layers and lower concentrations are considered as summer ones and can be directly associated to sea spray. The higher concentrations in winter are probably caused by transport of marine air masses over the Antarctic ice sheet, which are stronger in this season. There are probably additional sources for Cl^- in the IC-3 core region, which could have originated from gaseous HCl adsorption processes, essentially as a result of acid–base reactions between NaCl and HNO_3 or H_2SO_4 in aerosol particles or directly over the snow surface.
Key-words: glaciochemistry, ice core, ion chromatography.

Resumo

Este artigo apresenta resultados da análise por cromatografia iônica, de um testemunho de gelo antártico (IC-3; 85° 59'S, 81° 35'W) e discute os dados de concentração dos íons Mg^{2+}, Na^+, Cl^-, e SO_4^{2-}. Os íons Mg^{2+}, Na^+ e Cl^-, apresentam picos de concentração que podem ser ambientalmente interpretados como camadas de neve depositadas no inverno. As concentrações mais elevadas no inverno são provavelmente causadas por transporte de massas de ar marinhas sobre o continente antártico, que são mais fortes nesta estação. Existem, provavelmente, fontes adicionais de Cl^- na região do testemunho de gelo IC-3, que pode ser originado em processos de adsorção gasosa de HCl, essencialmente, como resultado de reações ácido-base entre o NaCl e HNO_3 ou H_2SO_4 em partículas de aerossol ou diretamente sobre a superfície da neve.
Palavras-chave: *glacioquímica, cromatografia iônica, testemunhos de gelo.*

1. INTRODUCTION

The study of chemical species carried out by snow fall from the atmosphere and accumulated in polar snow and ice layers through the last millenniums provides a unique tool for obtaining information about the chemical composition of the preindustrial atmosphere and its natural variability in the past (Legrand & Delmas 1988)(Legrand & Mayewski 1997)(Delmas 1994)(Wolff *et al.* 2010). Glaciochemistry is the branch of glaciology dedicated to the chemical analysis of snow and ice (Simões 2004).

Due to their geographical position and meteorological conditions, Polar Regions are of interest for a variety of environmental studies. Located far away from the continents (where local sources of dust, biogenic emissions from soil or vegetation, and anthropogenic emissions are dominant) Antarctica and, in a smaller degree, the Arctic Region provide a clean atmospheric environment in their respective hemispheres (Legrand & Mayewski 1997).

The Antarctic ice sheet keeps a unique archive on the chemical composition of Earth atmosphere that can be reached by analyzing ice cores (ICs) (Legrand *et al.* 1993). The environmental record contained in these cores provide valuable information for the reconstruction of the past climate and can be used to validate models for future conditions (Curran & Palmer 2001) (Steig *et al.* 2005). Soluble impurities stored in snow and ice layers reflect changes in the chemical composition of polar aerosols over time (Legrand *et al.* 1984)(Sakurai *et al.* 2011).

Analysis of ionic chemical species is an essential tool for the study of ICs. The ions of interest are: Cl$^-$, NO$_3^-$, SO$_4^{2-}$, MS$^-$ (methanesulfonate, CH$_3$SO$_3^-$), Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+} (Legrand *et al.* 1993)(Curran & Palmer 2001)(Bolius *et al.* 2006). Obtaining high-resolution data for these ions, with each sample corresponding to a short time interval in the IC, poses several challenges like: very low concentrations (in the order of mg/L), limited sample volumes, preparation in a clean room, and processing of a large number of samples (Curran & Palmer 2001). The ion chromatography technique is widely employed in analyzing snow and ice, and can provide results within the required low detection level (Legrand & Mayewski 1997)(Osterberg *et al.* 2006)(Wolff *et al.* 2010).

In general, chemical compounds found in ice and snow samples from the Antarctic Region are transported through the atmosphere by primary aerosols (sea salt and continental dust) and secondary ones (produced by gaseous emissions from biogenic and/or anthropogenic sources) (Delmas 1994)(Simões 2004).

The relative proportion of the marine ionic species, obtained by IC analyses, can show differences from those found in the average composition of sea water, indicating contributions from other sources (Legrand & Mayewski 1997)(Mulvaney *et al.* 1993).

This work aims to discuss the concentrations of the ions Mg^{2+}, Na$^+$, Cl$^-$, and SO$_4^{2-}$, in order to examine the existence of other sources for these ions, besides the sea salt, in the sampling region of an IC from the interior of the Antarctic Continent.

2. MATERIALS AND METHODS

2.1. Studied region

Since the beginning of this century Brazil has participated in the *International Trans-Antarctic Scientific Expedition* (*ITASE*; http://www2.umaine.edu/itase/), a program started in the 1990s which now includes 22 countries. The main *ITASE* goal is to investigate how the present atmospheric environment is represented in the superficial layers of the Antarctic ice sheet and measuring spatial and temporal variations of several chemical parameters (Mayewski *et al.* 2005)(Steig *et al.* 2005)(Bertler *et al.* 2005). Actions are centered in collecting representative samples of the last 200 years, obtained from ICs spaced by 100 km. This period of time was chosen due to the facility in recovering shallow ICs (100–200 m depth), allowing a significant study to be developed. Furthermore, it also comprises the beginning of the greatest anthropic influence over the atmospheric composition and the end of the Little Ice Age (from 1550 to 1850 AD when the atmospheric temperature fell below the last 2000-year average) (Bernardo & Simões 2006).

This work discusses ion chromatography data of the IC-3 (85°59'S, 81°35'W), 43.48 m depth, collected by J.C. Simões during the Chilean–Brazilian traverse of Antarctica in the summer of 2004/2005, from the Geographic South Pole (90°S) to the Parodi Chilean Station (80°10'S, 81°26'W).

The sampling site of the IC-3 in the West Antarctic ice sheet is 1620 m above sea level. Figure 1 shows the traverse path and the IC-3 location. Temperature in the drilling site was -36°C, determined by measuring the snow pack temperature 12 m below the surface.

The drilling was carried out during the expedition return trip, leaving the Geographic South Pole and heading to Patriot Hills. In this traverse, six shallow firn[1] cores were collected.

These cores were stored in sealed identified plastic tubes, placed in specific boxes. The boxes containing the cores were then transported by air to New York (USA), by truck to Bangor (Maine) and placed in a cold storage room at -20°C. Afterwards, the boxes were transported to the Climate Change Institute (CCI – University of Maine, EUA) for sampling.

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[1]*Firn is the intermediary stage of the snow metamorphism to ice. The ice core used in this investigation is in fact a firn core, and no section has reached the density that marks the passage from firn to glacial ice (0.83 g cm^{-3}).*
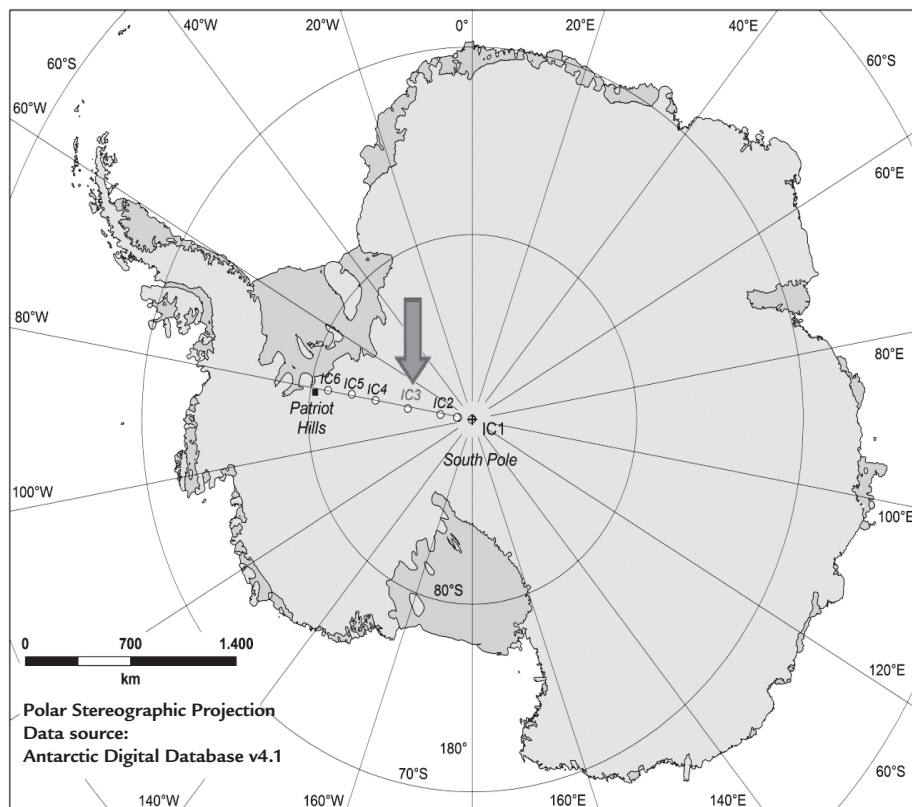
Figure 1
Geographical localization of IC-3 core (85°59'S, 81°35'W) in the Antarctica ice sheet, note the other core sites in the traverse from South Pole (IC-1) to Patriot Hills.

2.2. Sampling preparation

A continuous melting system developed by the CCI researchers was employed to subsample this core, which allows firn length intervals in the order of centimeters (Osterberg *et al.* 2006). This automated system separates samples automatically for various analyses to determine, for example: trace elements by inductively coupled plasma mass spectrometry, ionic content by ion chromatography, and oxygen and hydrogen isotopes ratios in water by isotope ratio mass spectrometry (Osterberg *et al.* 2006).

Ice, firn, and snow cores require restricted subsampling and decontamination protocols because the analytes to be studied are in very low concentrations (mg/L or less) (Hammes & Simões 2009).

The decontamination process begins in a cold storage room (at -20°C) with the physical removal of the outer layer using a ceramic saw. Polypropylene masks and gloves are worn during the decontamination procedure. The firn/ice section is placed into acrylic cylinders, avoiding any contact with the decontaminated surface. The acrylic recipient is cleaned with deionized water between each fusion sections (Osterberg *et al.* 2006).

The acrylic cylinder is then transported to a clean room (class 100, containing a maximum of 100 airborne particles larger than 0.5 μm by cubic feet) (Torreira 1996) and submitted to the continuous melting system. Before this procedure, the vials for storing the ion chromatography sample fractions are submitted to a cleaning protocol (triple rinse with ultra-pure water, soaking for 24 hours and another triple rinse with ultra-pure water).

The melting system, kept in a freezer at -20°C, consists of a Ni disc (>99.99% Ni) and a cone (Ni) mounted over an aluminum base. The core is vertically positioned maintaining the stratigraphic sequence, essential for paleoenvironmental interpretation (Osterberg *et al.* 2006). This system melts and the resulting liquid is physically separated in two channels. An outer ring channel, containing the external potentially contaminated part of the core, is intended to stable isotopes ratio analysis ($\delta^{18}O$) by mass spectroscopy. The internal channel, free of contamination and originated from the centre of the core, is directed to major ions and trace elements. The melt water is then conducted by tubes to a dripping system which conveys the sample directly to the vials. Immediately after the melting, the discrete ion chromatography samples were frozen.

2.3. Analytical procedures

Analysis was carried out at the CCI laboratories using a Dionex DX-500 Ion Chromatograph equipped with a conductivity detector CD-20 (Dionex) and an automatic injector (Gilson, 215 Liquid Handler, USA), which drives the samples for cation and anion analyses simultaneously. Anion separation was obtained using a KOH eluent generator in the gradient mode with concentration varying from 1 mM to 8 mM, guard column AG-11 (Dionex), analytic column AS-11 (Dionex), and suppressor ASRS-300 (4 mm) (Dionex). Cation separation was obtained using methane-sulfonic acid as eluent at 20 mM (Fluka) isocratic mode, analytic column CS-12A (Dionex), and suppressor column CSRS-300 (4 mm) (Dionex).

Helium gas was used to pressurize the deionized water and eluent flasks. The equipment was configured with a flow of 1 mL/min and loop of 500 µL for cations and anions. The software Chromeleon 6.8 (Dionex) was employed for data acquisition and equipment control. This analytical method was based on the method 300.1—*Determination of inorganic anions in drinking water by ion chromatography*, U.S. Environmental Protection Agency (EPA) (Pfaff *et al*. 1997).

2.4. Instrumental analysis and quantification

Stock solutions were prepared using ion chromatography standards for Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}, 1000 µg. mL^{-1} (Ultra Scientific, North Kingstown, Rhode Island, USA).

A solution of ION-92, a water reference standard (acquired from *National Water Research Institute*, Canada) and methanesulfonic acid were used to verify calibration results. All solutions were kept under refrigeration until use.

The calibration curve was prepared from the stock solutions using a micropipette (Eppendorf Research, Germany) and ultra-pure water (Milli-Q System, Millipore, MA, USA). According to the process established by the CCI laboratory, the detection limit (DL) was calculated by the EPA-300.1 Method (Pfaff *et al*. 1997).

Blanks were generated during sampling/melting of the IC to establish the analytes detection limits, as indicated by the EPA-300.1 Method (Pfaff *et al*. 1997). Seven blank samples were processed and analyzed in the same way as the IC samples. DL was calculated from:

Where "t" is the Student's test value for a confidence level of 99% and a standard deviation estimated with (n–1) degrees of freedom (t=3.14 for seven replicated analyses) and S is the standard deviation for the analysis of the seven blank samples (Pfaff *et al*. 1997). The DLs for the studied ions are presented in Table 1.

Samples were kept frozen until two hours before beginning the analysis. After verifying the ion chromatograph calibration parameters, the vials were placed, in numerical order, in the automatic sampler using polypropylene gloves to avoid sample contamination.

	DL	Blanks average concentration
Cl^-	1.88	2.64
SO_4^{2-}	0.85	1.10
Na^+	0.88	1.27
Mg^{2+}	0.28	0.38

Table 1

Detection limits (DLs) and blanks average concentration of ions determined by ion chromatography in mg/L.

3. RESULTS AND DISCUSSION

The IC-3 core provided 2002 samples but this study discuss results only from the upper 1049 samples, i.e., from the snow surface to 25.07 m depth (or 15.80 m in water equivalent). The IC depth was converted from snow/firn meters to water equivalent meters, eliminating density differences along the core.

Counting the annual layers based on the seasonal variation of concentration of the ionic species Na^+ and SO_4^{-2} allowed dating the IC-3 core (Figure 2). In the interior of the Antarctic continent, the ions Cl^-, Na^+, and Mg^{+2}, marine tracers, present concentration peaks during winter and lower ones during summer. Marine air masses over the ice sheet are stronger in the winter, increasing the concentration of ions generated from sea salt (Legrand & Mayewski 1997). On the other hand, the excess sulfate profile (non-sea salt sulfate, *nss*-SO_4^{2-}) originated from sources other than the sea salt, behaves in an opposite manner, presenting higher concentrations in the summer and lower ones during the winter (Udisti 1996) (Dixon *et al*. 2004)(Pruett *et al*. 2004). The nss-SO_4^{2-} fraction was calculated using the total Na^+ as a marine spray marker according to the equation:

$$nss\text{-}SO_4^{2-} = SO_4^{2-} - 0.253\ Na^+$$

where SO_4^{2-} corresponds to the total sulfate concentration and 0.253 is the (SO_4^{2-}/Na^+) mass ratio (w/w) in sea water (Becagli *et al.*, 2005).

At a depth of 25.05 m, the core is estimated to be 48±3 years old, or in other words, the deepest snow layer of this core was deposited in 1956. As a result of different counting, an error of ±3 years is estimated for the dating process.
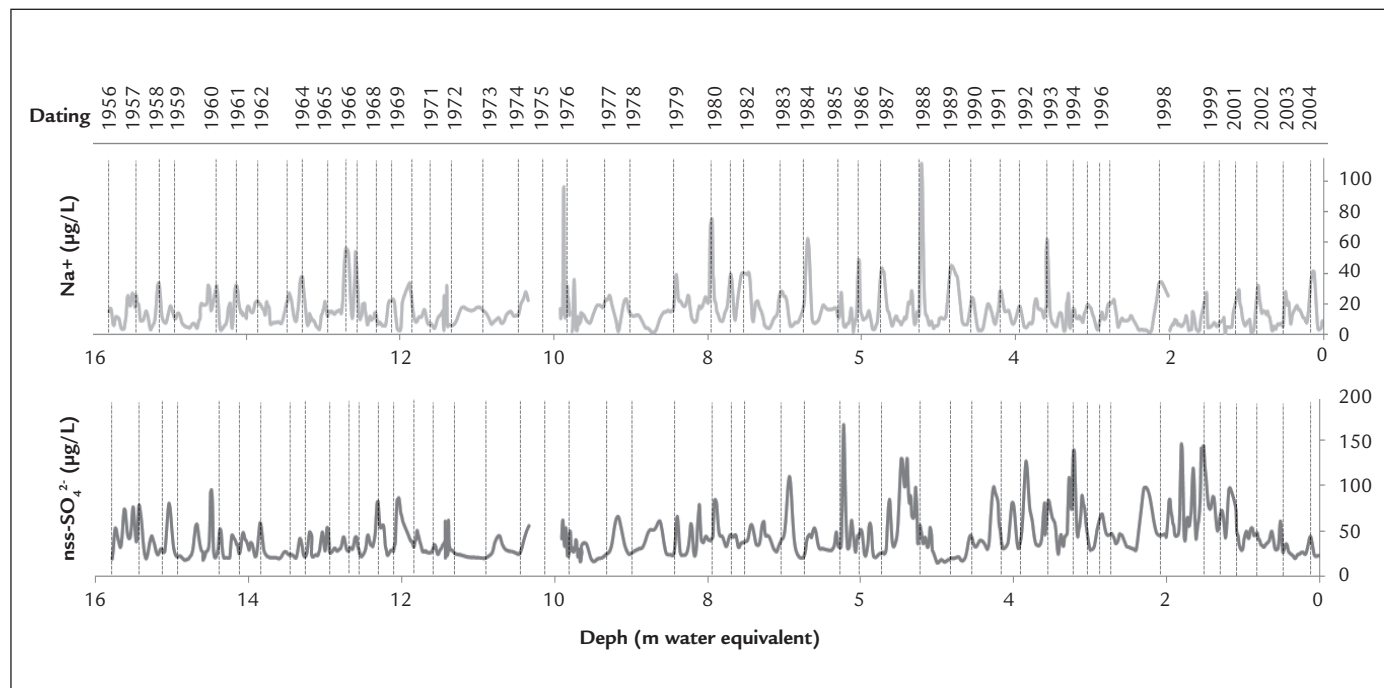

Figure 2

Dating of IC-3 core by counting annual layers based on seasonal variations in Na+ ions and non-sea salt sulfate (nss-SO_4^{2-}) (µg/L). A filter (three samples moving average) has been used to draw these graphics in order to eliminate small data noise. Dotted lines indicate the layer dating. Dating of IC-3 was estimated in 48±3 years at its bottom layer.

3.1. Relations between Na⁺, Mg²⁺, and Cl⁻

The ion ratios can be significantly modified when compared to the average composition of the sea water, as demonstrated by ionic measurements of Antarctic aerosol, snow, and ice (Dixon *et al.* 2004)(Benassai *et al.* 2005). Such fractionation processes can occur in the atmosphere or on the snow surface layers by the interaction between sea spray particles and the acid species HNO_3 and H_2SO_4, mainly in the gas phase or in the aerosol submicrometric particles (Benassai *et al.* 2005). The reaction leading to the formation of gaseous HCl follows different routes from the sea spray particles. Other possible fractionation effects, mainly involving sulfate, can result in the selective precipitation of

mirabilite ($Na_2SO_4.10H_2O$) over the snow surface under particular conditions of temperature and humidity, and also from the formation of frost flowers (fragile structures of ice rich in sea salt, grown during the process of sea water evaporation/condensation at the moment of the sea ice formation) (Rankin 2002)(Benassai *et al.* 2005).

Figure 3 shows the Mg^{2+}, Na^+, and Cl^- content, the ionic ratios Mg^{2+}/Na^+, Cl^-/Na^+, as a function of Na^+ concentration, and Mg^{2+}/Cl^- ratios as a function of Cl^- concentration. These graphs can be used to investigate the existence of other Mg^{2+} and Cl^- sources, and the sea spray fractioning effect during the atmospheric transport to the IC-3 core region.
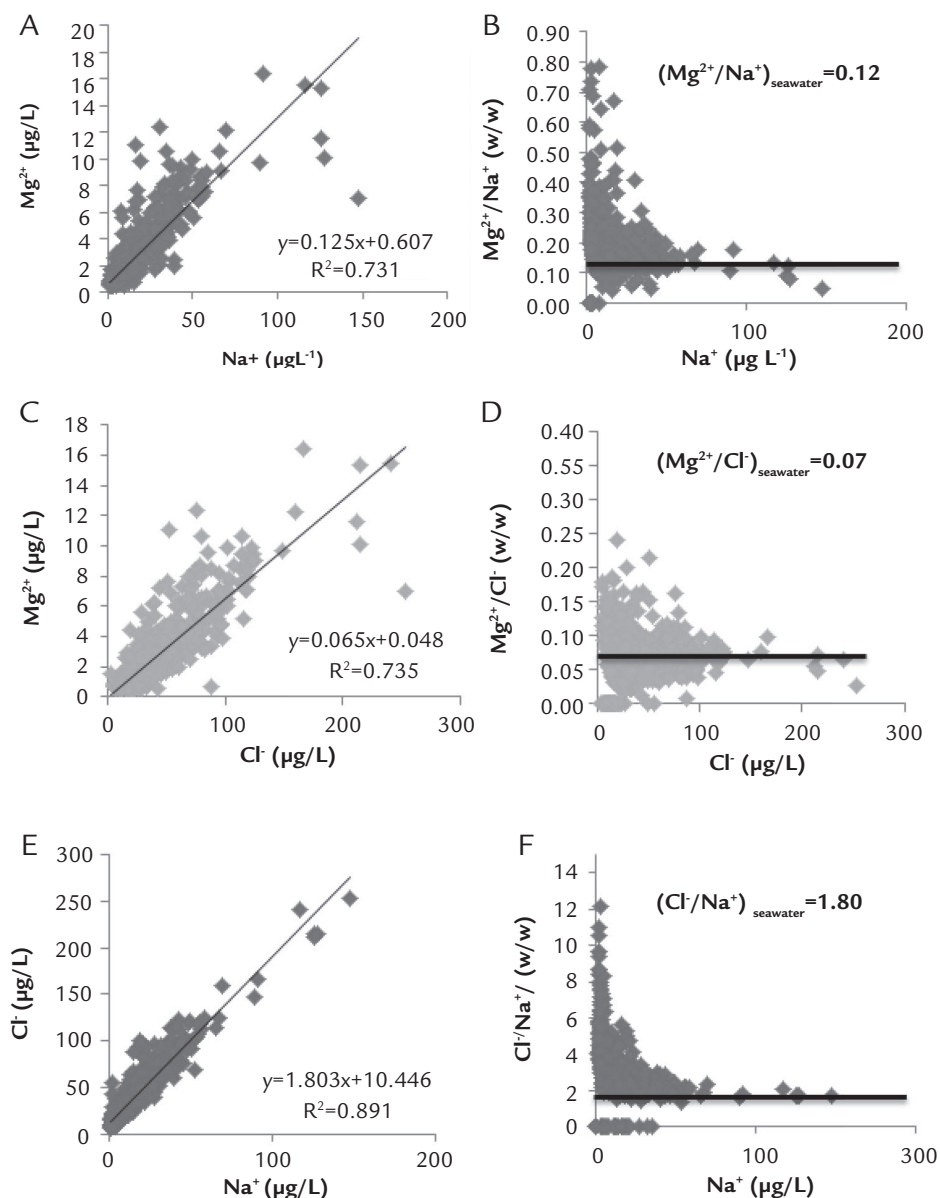
Figure 3

(A) Linear regression between Mg^{2+} and Na^+; (B) Mg^{2+}/Na^+ ratio as a function of Na^+; (C) Linear regression between Mg^{2+} and Cl^-; (D) Mg^{2+}/Cl^- ratio as a function of Cl^-; (E) Linear regression between Cl^- and Na^+; (F) Cl^-/Na^+ ratio as a function of Na^+. Horizontal lines in the graphs b, d, and f represent sea water ionic ratios.

Figure 3A, 3C, and 3E make evident a strong correlation between ions $Mg^{2+} \times Na^+$, $Mg^{2+} \times Cl^-$, and $Cl^- \times Na^+$ ($r = 0.73$; $r = 0.73$; $r = 0.89$, respectively). The linear regression slope for these ions (0.12 for $Mg^{2+} \times Na^+$, 0.07 for $Mg^{2+} \times Cl^-$, and 1.80 for $Cl^- \times Na^+$) are characteristic of marine contributions, confirming the sea spray as the main source of these ions in the IC-3 core.

In Figures 3B and 3D, the dispersion cloud of dots near the indicative value for marine contributions (0.12 for Mg^{2+}/Na^+

and 0.07 for Mg^{2+}/Cl^-) is well distributed confirming the higher influence of the sea spray in both cases.

On the other hand, in Figure 3F, in spite of having a great influence of the sea spray, in addition to the dispersion near to 1.8 (reference value Cl^-/Na^+ for marine contributions), one can observe a large number of dots above this value. In these cases the concentration of Cl^- is greater than that of Na^+, indicating additional source for Cl^- at the IC-3 site.

4. CONCLUSION

The Na^+, Cl^-, and Mg^{2+} concentration peaks are environmentally interpreted as winter layers and the lower concentrations considered as summer ones. The ions Na^+, Cl^-, and Mg^{2+} can

be directly associated to the sea spray. The highest concentrations in winter are probably a response to a strong transport of marine air masses over the ice sheet, which are stronger in this season.

There are probably additional sources for Cl⁻ in the IC-3 region. This additional Cl⁻ can be originated from gaseous HCl adsorption processes, essentially as the result of acid–base reactions between NaCl and HNO_3 or H_2SO_4, in aerosol particles or directly over the snow surface.

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