

Direct measurements of atmospheric iron, cobalt, and aluminum-derived dust deposition at Kerguelen Islands

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[1] Atmospheric deposition is one of the major sources of nutrients bringing trace metals to remote marine biota. In this study, total atmospheric deposition and crustal aerosol concentrations were monitored at Kerguelen Islands (49°18'S; 70°07'E) in the Southern Ocean during a short campaign in early 2005 and then continuously for about 2 years (2009–2010). Results show very low levels of atmospheric dust and trace metals concentrations but higher deposition fluxes than expected. The averaged total dust deposition flux as derived from Al deposition measurements is $659 \mu\text{g m}^{-2} \text{d}^{-1}$. Simultaneously measured Fe and Co deposition fluxes are respectively $29 \mu\text{g m}^{-2} \text{d}^{-1}$ ($520 \text{ nmol m}^{-2} \text{d}^{-1}$) and $0.014 \mu\text{g m}^{-2} \text{d}^{-1}$ ($0.24 \text{ nmol m}^{-2} \text{d}^{-1}$), giving typically crustal elemental ratios to Al of 0.54 and $2.6 \cdot 10^{-4}$. Measured dust deposition is in relatively good agreement with those simulated by current atmospheric models, but suggest that previous indirect calculations from field experiments are too low by a factor of 20. Observations and model results show that dust is transported above the marine atmospheric boundary layer to Kerguelen Islands, and thus that surface concentrations are not representative of the total dust column. Indeed, using surface concentrations leads to very large computed wet scavenging ratios, and to the conclusion that it is not appropriate to derive deposition fluxes from surface concentrations at remote ocean sites.

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1. Introduction

[2] Atmospheric aerosols play an essential role in the global climate forcing: they affect marine biogeochemical cycles by supplying nutrients, as well the Earth's radiative budget through direct and indirect effects [Jickells *et al.*, 2005]. Crustal atmospheric particles are essentially produced by aeolian erosion in arid and semi-arid areas, and some of this dust is transported over long range distance and deposited to remote oceanic areas by dry and wet deposition processes [Prospero *et al.*, 2002; Mahowald *et al.*, 2005]. Dust is one of the major sources of metallic micronutrients to the open ocean surface [Buat-Ménard and Chesselet, 1979; Duce and Tindale, 1991; Fung *et al.*, 2000]. Trace metals are necessary for phytoplankton growth [Morel and Price, 2003]. Cassar

et al. [2007] argued that the distribution of primary productivity in the Southern Ocean is controlled by aeolian dissolved iron deposition.

[3] The Southern Ocean (between 40° and 65°S) is remote from continental dust sources and receives little atmospheric deposition [Fung *et al.*, 2000; Prospero *et al.*, 2002; Jickells *et al.*, 2005; Mahowald *et al.*, 2005, 2009], from South America, from Australia [Mahowald *et al.*, 2009], and probably from South Africa too [Bhattachan *et al.*, 2012]. It is a High-Nutrient-Low-Chlorophyll (HNLC) area [de Baar *et al.*, 1995], characterized by a lack of micronutrients, especially iron [Martin, 1990; Boyd *et al.*, 2000; Blain *et al.*, 2007]. In this area, available micronutrients depending on dust deposition could be a severe limiting factor for the primary production [Erickson *et al.*, 2003; Cassar *et al.*, 2007; Martinez-Garcia *et al.*, 2011]. Furthermore, this ocean seems to be the major sink of CO₂ on Earth [Sarmiento *et al.*, 1998; Caldeira and Duffy, 2000; Schlitzer, 2000]. The knowledge of biogeochemical cycles in the remote Southern Ocean is thus critical to a better understanding of the global primary production, essential to control climate [Chisholm, 2000; Denman *et al.*, 2007].

[4] The recent inventory of measurements of iron deposition to the world ocean of Mahowald *et al.* [2009] reveals the scarcity of deposition measurements between 30°S and 60°S. During the “Kerguelen: compared study of the Ocean and the Plateau in Surface water” (KEOPS) cruise [Blain *et al.*, 2007],

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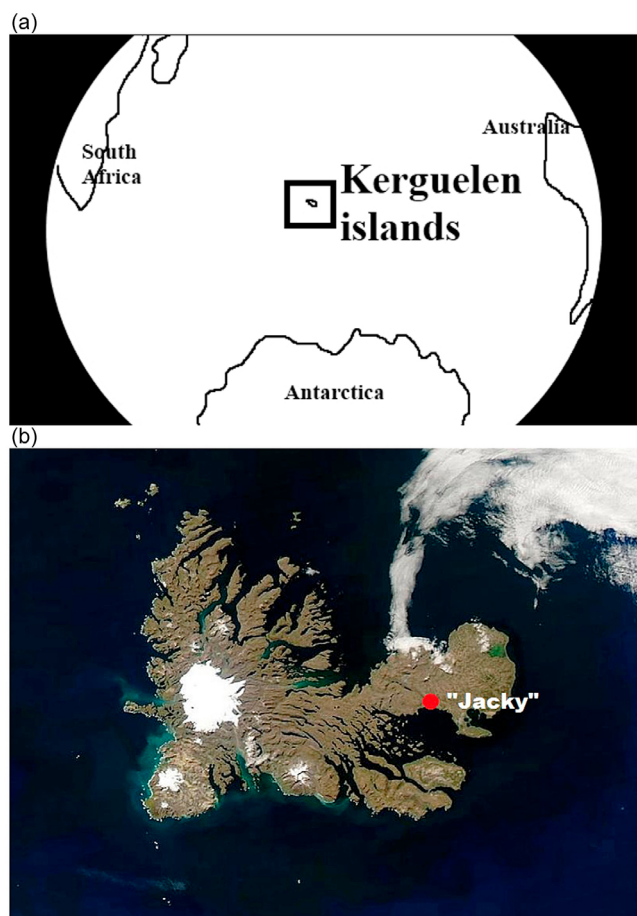


Figure 1. (a) Location of Kerguelen Islands ($49^{\circ}18'S$; $70^{\circ}07'E$) in the Southern Ocean; (b) location of the sampling site “Jacky” (J) where total atmospheric deposition and aerosol samples were collected. Credits: NASA (Figure 1b).

Wagner *et al.* [2008] estimated a dust deposition flux of $38 \pm 14 \mu\text{g m}^{-2} \text{d}^{-1}$ from aerosol sampling at sea level. This unique observation-derived data in literature on dust deposition in the Kerguelen Islands oceanic area is up to one order of magnitude lower than former predictions [Jickells *et al.*, 2005; Mahowald, 2007].

[5] In this work, we report results from total deposition and suspended aerosol sampling performed at Kerguelen Islands in early 2005 and during 2009–2010. We first detail the sampling methods and analytical techniques. Then we present results of both total deposition and surface aerosol concentrations of mineral dust. Finally, we compare dust deposition fluxes directly measured to those calculated from ground or sea level aerosol concentrations using scavenging ratios, and those modeled for the same time period [Luo *et al.*, 2003; Mahowald *et al.*, 2003].

2. Methodology

2.1. Study Area

[6] The research area was located in Kerguelen Islands ($48^{\circ}35'S$ to $49^{\circ}54'S$ and $68^{\circ}43'E$ to $70^{\circ}35'E$) situated in the Southern Ocean, approximately 4000 km southeast of South

Africa and 2000 km from Antarctic coasts (Figure 1a). The field campaign “Flux Atmosphérique d’Origine Continentale sur l’Ocean Austral” (FLATOCOA) supported by “Institut polaire française Paul Emile Victor” (IPEV) was carried out between 23 November 2008 and 10 December 2010. A previous field campaign “Kerguelen: Erosion and Fallout of Trace Elements and Nitrogen” (KEFREN) was carried out during one month from 25 January to 12 February 2005 at the same time as the KEOPS experiment [Blain *et al.*, 2007]. An atmospheric deposition sampling site named “Jacky” (J) ($49^{\circ}18'42.3''S$; $70^{\circ}07'47.6''E$; altitude 250 m) was installed 8 km northwest (upwind) of “Port aux Français” (PAF), the only permanently occupied basis of the archipelago (Figure 1b). Sampling was performed on a continuous basis since atmospheric deposition fluxes depend on variable meteorological phenomena (rain, wind speed, transport from continents) [Mahowald *et al.*, 2011]. Measured wind velocity at 2 m above ground level exhibit a lognormal distribution centered around 7 m s^{-1} on average for 80% of the time and less than 4 m s^{-1} during the remaining 20%. The permanent base PAF has a negligible influence on the air at station J: the southeast wind sector covering PAF had a 0.9% occurrence probability expressed as frequency and 0.5% considering the wind run (cumulated length of air passing across the station) during FLATOCOA sampling time.

2.2. Total Atmospheric Deposition Sampling and Measurements

2.2.1. Deposition Collector

[7] Total deposition (i.e., dry + wet depositions) was sampled using an open collector. The sampler is a 120 mm diameter PTFE Teflon[®] funnel (0.0113 m^2 collection aperture) machined on a circular base with a thread adapted to 1 L polypropylene (PP) Nalgene[®] bottle neck. All the funnels were manufactured by the “Société des Plastiques Nobles” company (Bobigny, France). Special attention was paid to the internal surface of the funnel to make it as smooth as possible (nothing detectable with a finger). Each funnel coupled to its bottle preloaded with nitric acid was deployed on a 100 mm diameter and 2 m high PVC pipe, vertically erected with Kevlar[®] shrouds (Figure 2). The height was controlled by a spirit level and using the 90° -machined end of the pipe to ensure that the funnel aperture was horizontally leveled. Kevlar[®] is used to prevent contamination by metals or/and fibers and its permanent tension also ensures geometric stability. A third 1 m high PVC pipe was installed as a bottle holder to help the sample change. Only one total deposition sampler was installed during KEFREN in 2005. Duplicate samplers (named A and B), which were $\sim 20 \text{ m}$ apart, were operated in parallel during most of FLATOCOA (2009–2010) as detailed later.

2.2.2. Washing Protocol and Sampling Preparation at Lab

[8] All the deposition sampling materials (Teflon[®]-PTFE capped funnels, 1 L and 60 mL Nalgene[®] PP bottles, and 60 mL PP boxes with a screwing cap for bottle’s corks) were thoroughly washed at the laboratory as described below. Equipment is (1) washed by common dish detergent in a ISO 8 controlled laboratory room, (2) soaked from 2 days to 2 weeks in a bath of 2% Decon[®] detergent diluted with reverse osmosis purified water, (3) soaked 1 week in 10% v/v Normapur[®] analytic grade nitric acid, and (4) soaked



Figure 2. (a) Deposition collectors with duplicate sampling and bottle holder pipes; (b) detail of the deposition device.

2 weeks in 10% v/v *Normapur*[®] analytic grade hydrochloric acid. Extensive rinsing is performed between each step with purified water. Afterward, the material is transferred in an ISO 5 clean room. All operations involving opening of a bottle or funnel internal surface exposition are carried out inside an ISO 1 horizontal laminar flow clean hood. The

material is (5) rinsed by *Elga*[™] *Purelab ultra*[®] pure water ($18 \text{ M}\Omega \text{ cm}^{-1}$), (6) soaked from 3 to 8 months in a high purity hydrochloric acid solution (5% *Merk*[™] *Suprapur*[®]), and (7) soaked again from 3 to 8 months in a 2% high purity hydrochloric acid solution after an intense rinse by ultra pure water. The total soaking time is not less than 10 months. At

the end of all the cleaning process, material is (8) individually rinsed at least 6 times with ultra pure water and (9) left in the ISO 1 laminar flow hood until dryness (2 to 4 h). Finally, funnels were closed by Teflon[®] cap and screwed on a dry cleaned bottle. One L and 60 mL bottles (used in the field for sample collection and collection funnel rinsing, respectively) are filled with weighted 50 mL and 60 mL, respectively, of 2% v/v *Romil-UpA*[™] ultra pure nitric acid in ultra pure water. All the equipment is triple bagged in sealed polyethylene (PE) bags until deployment on the field.

2.2.3. Field Sampling Protocol and Sample Preservation

[9] Total atmospheric deposition sampling begins by putting a device (funnel + 1 L PP bottle) on the top of its support. The cork of the first bottle is stored into a closed box intended for this purpose. The funnel cap is removed and no longer used. Just before collecting a sample after its sampling period, the internal surface of the funnel is rinsed with the nitric acid content of a 60 mL bottle, taking care to flush the entire surface. The rinsing solution is collected in the sample bottle to be removed. A new 1 L PP bottle is placed on the bottle holder. The sampling bottle is unscrewed from the funnel's bottom and closed by the cork of the new bottle. Then, the new bottle is screwed into the funnel's bottom and the used bottle is bagged. This operation is repeated each time when a sample is renewed, the funnel is changed after one year of sampling. Field blanks are performed at the funnel installation and removal, but also from time to time by repeating twice the sampling procedure. At PAF, each sample is triple bagged and stored to be shipped back. Because of the logistic difficulties to transport material from the sampling site to France by boat, the delay between bottle preparation and collected sample analysis is very long, up to 2 years in the case of FLATOCOA.

[10] Sampling was performed by experienced scientists during field summer campaigns of January–February 2005 (KEFREN) and November–December 2008, 2009, and 2010 (FLATOCOA). One permanent staff of the scientific station was carefully advised and trained during the 1 month duration of the summer campaigns to perform sampling during the rest of the FLATOCOA monitoring period.

[11] A dedicated clean area was installed at PAF in the scientific building to provide clean room facilities. A large PE film was deployed and attached forming a tent covering about 5 m². About 600 m³ h⁻¹ of air is pushed into this covered area through a 30 cm × 60 cm H14 filter. A 30 cm × 60 cm clean hood (AirC2) was placed inside the area to provide an ultra clean zone. The entry was controlled and people must wear clean room suits. Counting particles (Lighthouse Handheld 2016 laser particle counter) with diameters between 0.2 and 2 μm indicated an ISO 2 quality in the clean hood and ISO 6-ISO 7 in the rest of the covered area.

[12] Five total deposition samples were collected during KEFREN from 28 January to 12 February 2005. During FLATOCOA, deposition was collected approximately twice a month and a total of 47 successive deposition samples plus 36 additional duplicate samples was collected between 23 November 2008 and 10 December 2010 (Table 1). Duplicate B stopped running on 31 May 2009 and resumed on 4 December 2009 when a renewal of the volunteer changing the sampling bottle occurred.

2.2.4. Laboratory Analyses and Determination of Total Atmospheric Deposition

[13] In the laboratory, total atmospheric deposition sampled bottles were weighted. The amount of rainwater collected in the funnel was deduced by subtracting added acid solution (around 110 mL) to the sample total mass found in the bottle. Each sample was vigorously shaken and then 15 mL were immediately transferred into a PE sampling vial. Vials had followed the same clean protocol as the sampling material except step 3. The step 7 was replaced by filling with 2% of *Romil-UpA*[™] HCl and storage (filled) until being used. Samples from 2005 were filtered before analysis with acid washed (2% v/v *Romil-UpA*[™] HCl during at most 2 h) Nuclepore[®] polycarbonate (PC) filters (0.2 μm porosity). Filters were digested with *Romil-UpA*[™] ultra pure nitric acid attack during 14 h in an air oven at 130°C at 6 bar using Savilex[™] fluorinated ethylene propylene digestion vessel. Samples from FLATOCOA were not filtered to reduce possible contamination from the filtration protocol. Analyses were performed by both Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3000 or Spectro ARCOS) coupled with a CETAC ultrasonic nebulizer and by High Resolution–Inductively Coupled Plasma–Mass Spectrometry (HR-ICP-MS, *Thermo Fisher Scientific*[™] Element 2). Both analytical systems are installed in an ISO 5 clean room. They allow us to obtain elemental concentrations of as many trace metals as possible (altogether 45 elements are analyzed). Here, we will focus mainly on Al as a tracer of continental dust transport [Mahowald *et al.*, 2005] and of dust deposition to the ocean [Measures and Vink, 2000; Han *et al.*, 2008]. In addition, we consider Fe [Martin, 1990; Boyd *et al.*, 2000; Blain *et al.*, 2007] and Co [Saito *et al.*, 2002; Saito and Moffett, 2004] which are potential nutrients also associated to crustal dust particles, Na and Mg to track sea-salt contribution, and Ti as an indicator of possible contamination by local soils. Analytical blanks were made using 10 mL of 1% v/v *Romil-UpA*[™] HNO₃ to determine detection limits (DL) of the analytical method ($DL = t \cdot SD(C_{\text{blanks}})$, $t = 2.8$) for both ICP systems. Al, Fe and Ti were analyzed by ICP-AES, their DLs are 20 ng L⁻¹ (Al, Ti) and 100 ng L⁻¹ (Fe). Co was analyzed by HR-ICP-MS, its DL is 0.3 ng L⁻¹. For both analytical methods, repeatability and accuracy of measurements were checked by four measurements of the Canadian National Research Council SLRS-4 certified river water reference material for trace metals that we have diluted 10 times to reach elemental concentrations of the same order of magnitude than our samples. Multiplied by 10, median values obtained are (±standard deviation SD) 53.9 ± 0.1, 96.5 ± 0.3 and 0.035 ± 0.003 μg L⁻¹, respectively for Al, Fe, and Co, whereas respective certified values are 54 ± 4, 103 ± 5 and 0.033 ± 0.006 μg L⁻¹. The value is 1.30 ± 0.10 μg L⁻¹ for Ti with a recommended concentration of 1.46 ± 0.08 μg L⁻¹ [Yeghicheyan *et al.*, 2001]. The relative standard deviation (%RSD = SD/mean) associated to those measurements is 3% for Al, 3% for Fe and 7% for Ti and Co. Field blanks concentrations (corrected by analytical blanks) are 3.9 ± 1.4, 1.7 ± 0.35, 0.030 ± 0.014 and 0.0004 ± 0.0002 μg L⁻¹ for Al, Fe, Ti and Co, respectively. Field blank variabilities are used as DLs of the whole sampling and analytical procedure. Expressed as amounts, those DLs are always far less than

Table 1. Daily Al Fluxes at “Jacky” Station, Kerguelen Islands, During FLATOCOA Campaign

Sampling Begin	Sampling End	Al Deposition Flux Duplicat A ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Al Deposition Flux Duplicat B ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Fe Averaged Deposition Flux ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Co Averaged Deposition Flux ($\text{ng m}^{-2} \text{d}^{-1}$)	Volume of Rain (mm d^{-1})
23/11/08	28/11/08	10 ± 1	9.0 ± 0.8	2.8 ± 0.4	0.021 ± 0.003	0.73
28/11/08	03/12/08	15 ± 1	15 ± 1	5.7 ± 0.7	1.0 ± 0.1	1.09
03/12/08	12/12/08	56 ± 5	55 ± 5	27 ± 3	8.8 ± 1.1	4.50
12/12/08	31/12/08	60 ± 5	57 ± 5	31 ± 4	10 ± 1	4.97
31/12/08	14/01/09	51 ± 5	58 ± 5	28 ± 4	9.3 ± 1.2	5.31
14/01/09	02/02/09	32 ± 3	33 ± 3	17 ± 2	4.3 ± 0.6	3.99
02/02/09	17/02/09	39 ± 4	39 ± 4	22 ± 3	5.1 ± 0.7	3.16
17/02/09	03/03/09	29 ± 3	27 ± 2	15 ± 2	3.7 ± 0.5	1.82
03/03/09	13/03/09	35 ± 3	37 ± 3	19 ± 2	5.7 ± 0.7	1.93
13/03/09	28/03/09	31 ± 3	27 ± 2	18 ± 2	8.1 ± 1.1	4.41
28/03/09	15/04/09	53 ± 5	46 ± 4	24 ± 3	8.3 ± 1.1	5.95
15/04/09	29/04/09	20 ± 2	13 ± 1	9.1 ± 1.2	3.0 ± 0.4	1.59
29/04/09	14/05/09	17 ± 2	11 ± 1	7.7 ± 1.0	3.0 ± 0.4	1.77
14/05/09	31/05/09	28 ± 3	24 ± 2	14 ± 2	5.9 ± 0.8	3.28
31/05/09	17/06/09	63 ± 8		31 ± 4	14 ± 2	3.60
17/06/09	02/07/09	58 ± 8		31 ± 4	15 ± 2	4.89
02/07/09	13/07/09	17 ± 2		8.2 ± 1.1	3.3 ± 0.4	2.18
13/07/09	06/08/09	38 ± 5		20 ± 3	14 ± 2	1.86
06/08/09	21/08/09	23 ± 3		14 ± 2	7.3 ± 1.0	0.81
21/08/09	10/09/09	191 ± 25		92 ± 12	42 ± 5	0.84
10/09/09	06/10/09	69 ± 9		36 ± 5	24 ± 3	3.52
06/10/09	17/10/09	35 ± 4		18 ± 2	12 ± 2	2.15
17/10/09	04/11/09	108 ± 14		58 ± 8	29 ± 4	2.02
04/11/09	21/11/09	24 ± 3		14 ± 2	7.2 ± 0.9	1.83
21/11/09	04/12/09	73 ± 10		40 ± 5	19 ± 2	2.76
04/12/09	11/12/09	156 ± 14	220 ± 20	88 ± 11	41 ± 5	8.45
11/12/09	24/12/09	131 ± 12	150 ± 13	77 ± 10	35 ± 5	6.18
24/12/09	03/01/10	147 ± 13	162 ± 15	92 ± 12	47 ± 6	7.58
03/01/10	10/01/10	24 ± 2	32 ± 3	16 ± 2	7.6 ± 1.0	1.69
10/01/10	31/01/10	40 ± 4	40 ± 4	24 ± 3	11 ± 1	2.00
31/01/10	05/03/10	15 ± 1	15 ± 1	8.9 ± 1.2	5.7 ± 0.7	3.41
05/03/10	22/03/10	31 ± 3	37 ± 3	21 ± 3	8.7 ± 1.1	6.01
22/03/10	07/04/10	15 ± 1	18 ± 2	8.8 ± 1.1	4.6 ± 0.6	3.64
07/04/10	27/04/10	18 ± 2	18 ± 2	9.0 ± 1.2	4.0 ± 0.5	5.37
27/04/10	12/05/10	66 ± 6	83 ± 7	37 ± 5	24 ± 3	7.19
12/05/10	03/06/10	31 ± 3	34 ± 3	20 ± 3	9.6 ± 1.3	4.39
03/06/10	17/06/10	116 ± 10	139 ± 12	69 ± 9	34 ± 4	4.31
17/06/10	04/07/10	68 ± 6	58 ± 5	34 ± 4	20 ± 3	4.09
04/07/10	19/07/10	89 ± 8	66 ± 6	45 ± 6	27 ± 3	2.74
19/07/10	01/08/10	38 ± 3	36 ± 4	23 ± 3	12 ± 2	0.59
01/08/10	16/08/10	25 ± 2	55 ± 5	23 ± 3	13 ± 2	2.74
16/08/10	07/09/10	62 ± 6	56 ± 5	38 ± 5	26 ± 3	3.97
07/09/10	24/09/10	84 ± 8	156 ± 14	67 ± 9	34 ± 4	4.93
24/09/10	01/11/10	59 ± 5	95 ± 9	44 ± 6	27 ± 4	2.71
01/11/10	24/11/10	75 ± 7	111 ± 10	55 ± 7	33 ± 4	3.95
24/11/10	04/12/10	101 ± 9	135 ± 12	69 ± 9	33 ± 4	7.51
04/12/10	10/12/10	202 ± 18	148 ± 13	91 ± 12	44 ± 6	10.03
Mean ± SD		54 ± 42	48 ± 39	28 ± 22	14 ± 12	3.5 ± 2.0

10% of the measured quantities in samples and therefore neglected.

[14] Amounts of collected elements are calculated multiplying concentrations ($C_{tot.dep}$) by the total weights of water in the sampled bottle ($V_{tot.dep}$). We have subtracted to those amounts the measured quantities found in field blanks, which are never larger than 10% of the deposited quantities in any of the collected samples. The “field contamination” is certainly due to remaining metals on the walls of bottles: contamination is leached by acid (checked to be ultra pure) contained in samples or blanks during the long storage time, which is always more than one year. Finally, the daily elemental deposition fluxes (F) are calculated by dividing amounts corrected from field blanks by the aperture area of the funnel ($S_{funnel} = 0.0113 \text{ m}^2$) and by exposition times

($T_{exposure}$): $F = C_{tot.dep} V_{tot.dep} / S_{funnel} T_{exposure}$. Total dust deposition flux is derived from Al flux based on the Al average abundance in the Earth’s crust (8.1% following *Lutgens and Tarbuck* [2000]) assuming the common hypothesis that Al is an exclusive crustal dust indicator in atmospheric aerosols [e.g., *Mahowald et al.*, 2005]. It should be noted that there is some variability in the average Al crustal abundance that ranges in the literature between 7.74% [*Wedepohl*, 1995] and 8.23% [*Taylor*, 1964] with a common used standard value of 8.04% [*Taylor and McLennan*, 1985], whereas average Earth’s soil models even give a somewhat lower Al content of $\sim 7.10\%$ [*Vinogradov*, 1959; *Bowen*, 1966]. An uncertainty of about 10% in dust determination may result from such variability in Al abundance.

Table 2a. Aluminum Concentrations in Aerosols During the 1-Month KEFREN (2005)

Sample	Sampling Start	Sampling End	Al Concentration (ng m ⁻³)	Al Dry Deposition (μg m ⁻² d ⁻¹)
Kerj2	25/01/05	29/01/05	2.28 ± 0.11	2.56
Kerj3	29/01/05	02/02/05	0.68 ± 0.03	0.76
Kerj4	02/02/05	06/02/05	1.84 ± 0.09	2.07
Kerj6	06/02/05	08/02/05	1.54 ± 0.08	1.73
Kerj7	08/02/05	12/02/05	2.17 ± 0.11	2.44
Mean ± SD			1.84 ± 0.64	1.91 ± 0.72

2.3. Aerosol Sampling and Measurements

[15] Surface aerosol sampling was carried out at the same site than deposition during the 2005 KEFREN campaign and between 12 December 2008 and 13 July 2009 during FLATOCOA. During FLATOCOA, aerosol sampling was performed with the same time sampling as for the deposition. Aerosol particles were collected on Zefluor[®] filters (0.5 μm porosity, 47 mm diameter, Pall Corp.) using the NILU (Norwegian Institute for Air Research) open face filter holder system with a ~1 m³ h⁻¹ pumping rate. This device was hanging 2 m above the ground and housed inside a 80 cm diameter PVC bend pipe. The filter was facing downward and placed 2 cm from the end of the bend. Pumped volume was recorded with a *Schlumberger*[™] model Gallus 2000 volumetric counter connected at the pump exhaust and free at its other end. Power supply was insured by a 400 W wind generator (model Air-X-400) buffered by 4 × 40 A h lead battery and an inverter providing 230 V AC. Batteries were protected from deep discharge by an automatic electronic circuit breaker. This system was able to supply power over 70% of the time during one year of continuous sampling.

[16] Each caped filter holder is put in a PP box and has followed the same cleaning protocol than those of the deposition collecting system, except step 3. Zefluor[®] filters are also cleaned by the following procedure: the filter is (1) placed in an ultra clean filtering device (Nalgene[®]) connected to a vacuum pump, (2) washed by purified methanol prepared by subboiling quartz distillation with pure grade methanol (*Merk*[™], HPLC), to moist its pores, (3) washed immediately after by ultra pure diluted hydrochloric acid (1% v/v *Romil-UpA*[™] HCl in ultra pure water), (4) rinsed 5 times with 20 to 40 mL of ultra pure water (methanol can be poured again if necessary to wet the pores again), and (5) deposited in a *Pall*[™] Analyslide[®] filter box previously cleaned as filter holders. After drying in the ISO 1 laminar flow (30 to 60 min), filter boxes are closed and double bagged.

[17] During the KEFREN campaign, size segregated aerosol were also sampled using a EGA 80 cascade impactor with Nuclepore[®] PC filters (47 mm in diameter, 0.2 μm porosity). This custom made impactor has 6 stages including a terminal filter and was operated at low flow rate (~1 m³ h⁻¹) [*Bergametti et al.*, 1982]. Its entrance was 1.5 m high above ground and oriented downward. Three samples were performed from the beginning to the end of the campaign, with a time step of one week. The size distribution was recovered from analyses of final filter and impactor stages using a retro-fitting method as described in *Gomes et al.* [1990].

[18] All the total aerosol and cascade impactor filters are analyzed by X-ray fluorescence spectrometry (*PANalytical*[™]

2400) for Al, Na and Mg as in *Wagener et al.* [2008]. Detection limit is 5 ng per filter for Al and accuracy is 16% for those three elements. Fe and Co values are under DLs. Five aerosol samples are available from the KEFREN campaign (25 January to 12 February 2005), and 13 from the beginning of the FLATOCOA campaign (from 12 December 2008 to 13 July 2009). Samples are listed in Table 2a, 2b. The total atmospheric particulate dust concentration is derived from the Al aerosol concentration as explained above for dust deposition.

2.4. Determination of Dry Deposition Flux of Dust From Aerosol Concentrations

[19] Total deposition is the sum of wet and dry deposition (i.e., with and without precipitation, respectively): $F_{\text{total}} = F_{\text{dry}} + F_{\text{wet}}$. We derived dry deposition flux of Al using our data on atmospheric particulate aerosol concentrations (C_{aerosols}) and a dry deposition velocity ($V_{\text{deposition}}$): $F_{\text{dry}} = C_{\text{aerosols}} V_{\text{deposition}}$. Following *Ezat and Dulac* [1995], we used a dry deposition velocity $V_{\text{deposition}} = 1.3 \text{ cm s}^{-1}$. These authors computed velocity based on the dry deposition model of *Slinn and Slinn* [1980] and following the “100-step method” to take into account dust particle lognormal size distribution, as proposed by *Arimoto et al.* [1985]. Dry dust deposition flux was computed for each sample during the period from December 2008 to July 2009, when aerosol concentrations were measured with the same time step than total deposition. Wet only dust deposition flux is deduced by subtracting computed dry deposition to observed total deposition.

2.5. Dust Emission Transport and Deposition Modeling

[20] Estimates of dust transport and deposition at Kerguelen Islands were conducted using a dust emission and deposition module [*Zender et al.*, 2003] inside a chemical transport model based on reanalysis winds [*Mahowald et al.*, 1997], which matches observations fairly well for mean and variability [*Luo et al.*, 2003; *Mahowald et al.*, 2003]. The model includes a dependence of the dust emission on wind speed, soil moisture and soil erodibility [*Luo et al.*, 2003], transports the dust following the winds for a particular day, as diagnosed by the National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis data [*Kalnay et al.*, 1996], and includes wet and dry deposition of desert dust as described in *Luo et al.* [2003]. The simulations

Table 2b. Aluminum Concentrations in Aerosols During FLATOCOA Campaign (2009)

Sample	Sampling Start	Sampling End	Al Concentration (ng m ⁻³)	Al Dry Deposition (μg m ⁻² d ⁻¹)
Z1	12/12/08	31/12/08	2.20 ± 0.11	2.47
Z2	31/12/08	14/01/09	5.41 ± 0.27	6.08
Z3	14/01/09	02/02/09	0.90 ± 0.05	1.02
Z4	02/02/09	17/02/09	2.12 ± 0.11	2.39
Z5	17/02/09	03/03/09	0.50 ± 0.03	0.56
Z6	03/03/09	13/03/09	0.96 ± 0.05	1.08
Z7	13/03/09	28/03/09	0.32 ± 0.02	0.36
Z8	28/03/09	15/04/09	0.44 ± 0.02	0.50
Z9	15/04/09	29/04/09	1.07 ± 0.05	1.20
Z20	29/04/09	14/05/09	2.70 ± 0.14	3.03
Z21	14/05/09	31/05/09	4.98 ± 0.25	5.60
Z23	17/06/09	02/07/09	4.29 ± 0.22	4.82
Z24	02/07/09	13/07/09	1.96 ± 0.09	2.09
Mean ± SD			1.86 ± 1.75	2.40 ± 1.97

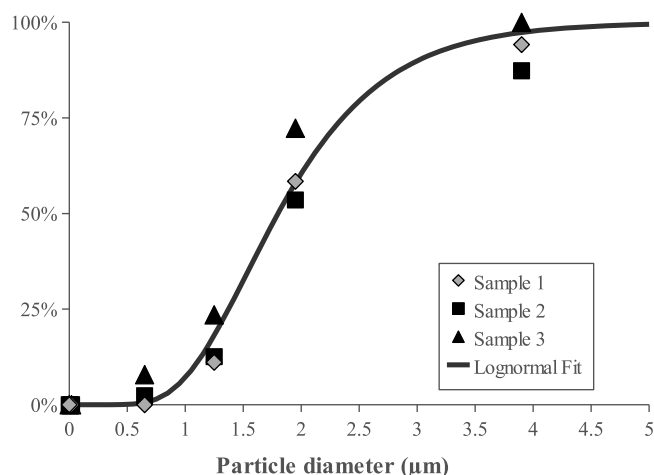


Figure 3. Cumulative mass size distribution measured using 6 stages cascade impactors. Solid line represents a lognormal fitting with a mean value of $1.8 \mu\text{m}$ and a standard deviation of 0.4.

shown here are for the time period 2008–2010, at the location of Kerguelen Islands observational site. More details on the behavior of the model and comparisons to observations, especially in remote regions, are available in previous papers [Luo *et al.*, 2003; Mahowald *et al.*, 2003, 2009; Hand *et al.*, 2004].

2.6. Soil Sample Analyses

[21] To check possible contamination issues for deposition sampling, 32 potentially erodible soils were collected over a 500 km^2 windward area around J site. Back to the laboratory, those soils were (1) sieved on a 1 mm mesh nylon sieve, (2) 10 g were ground during 3 min in a tungsten carbide ball electrical mill, (3) 5 g were used to press pellets with 1% wax which (4) were analyzed by Energy Dispersive X-Ray Fluorescence (Panalytical MiniPal). Al and Ti soil elemental composition was obtained using the provided “Omnian” software and calibration. Geostandards (NIM-G,

NIM-L, NIM-P, BE-N, DT-N, GS-N) were analyzed to estimate accuracy of the analytical method: recovery rates are from 105 to 120% for Al and from 90 to 100% for Ti, with a reproducibility better than 1% for the both elements.

3. Results

3.1. Atmospheric Particulate Aluminum and Size Distribution

[22] Average Al concentrations from the KEFREN 2005 and the FLATOCOA 2009 data sets (Table 2a, 2b) are similar (mean \pm SD = 1.84 ± 0.64 and $1.86 \pm 1.75 \text{ ng m}^{-3}$, respectively) with a higher variability during the longer FLATOCOA period. These Al concentrations are not significantly different from those measured offshore in January–February 2005 during the KEOPS cruise close to Kerguelen Islands ($1.00 \pm 0.49 \text{ ng m}^{-3}$ [Wagner *et al.*, 2008]); they are among the lowest measured concentrations in oceanic areas as reported in Witt *et al.* [2010, Table 3].

[23] Size distribution in mass derived from cascade impactors shows a stable and narrow lognormal mode centered at $1.8 \mu\text{m}$ in diameter with a 40% geometric standard deviation (Figure 3). It is in good agreement with result from Wagner *et al.* [2008] for the same area but obtained by Transmission Electronic Microscopy observations on a total filter collected offshore during KEOPS.

3.2. Al and Dust Measured Deposition Fluxes

[24] Results of Al fluxes (F_{Al}) from FLATOCOA are represented in Figure 4 and reported in Table 1. During the period in which both duplicates (A and B) were collected simultaneously, we observe a good correlation between them for both concentrations and fluxes (Figure 5) and for all the samples. The only exceptions are the last five sample pairs collected from 7 September to 10 December and the sample (D on Figure 4) collected between 4 December and 11 December 2009, which are not considered in the following discussion and tables. Those differences between A and B were caused by the funnel apertures not being perfectly horizontal for both devices yielding biased vertical

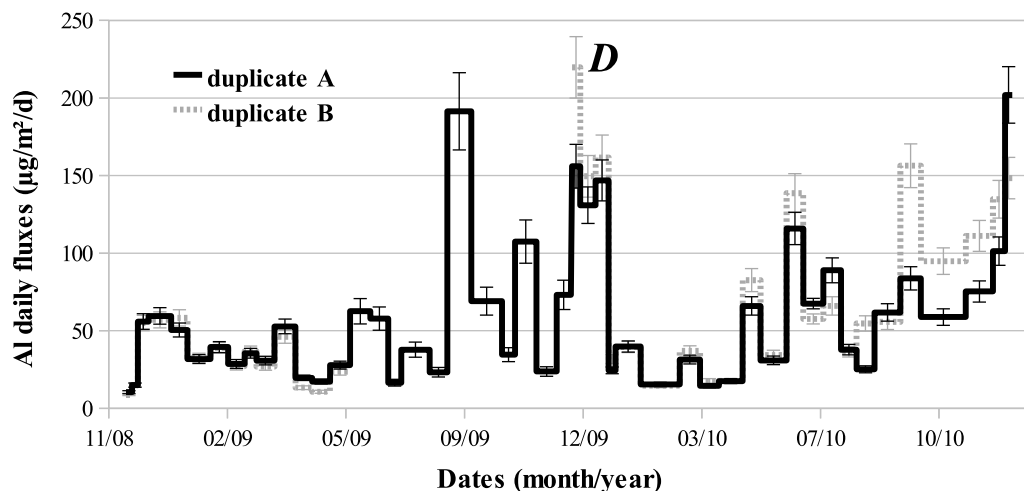


Figure 4. Al daily fluxes ($\mu\text{g m}^{-2} \text{ d}^{-1}$) at Kerguelen during FLATOCOA for both A and B duplicates. Duplicates are well fitted except for point D and the last five samples when horizontality of the funnel aperture was not insured.

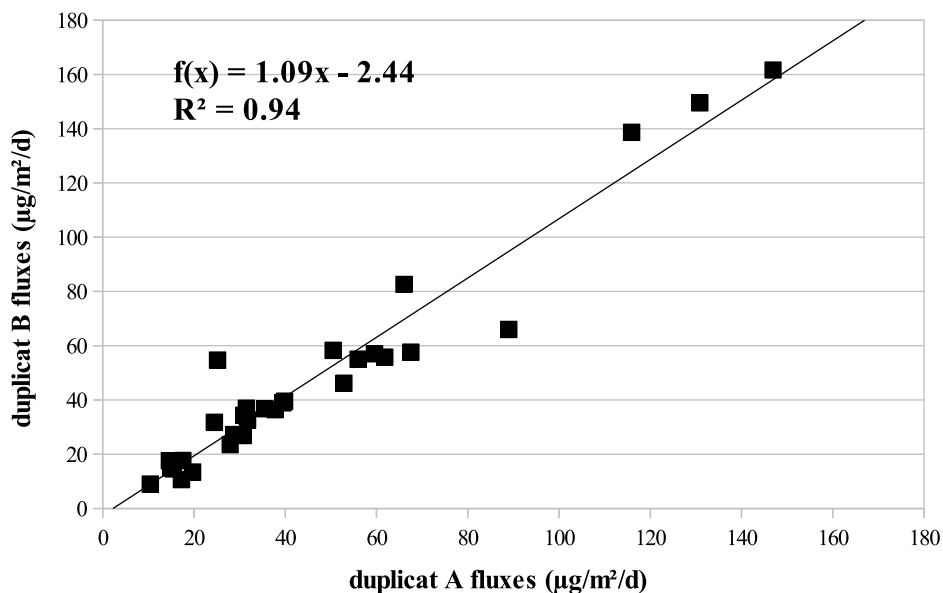


Figure 5. Correlation between the duplicated Al deposition flux measurements ($N = 30$), excluding the 6 sample pairs (sample D and the five last duplicates) that do not match. Deposition fluxes match from low to high values.

deposition. In these cases, weights of collected rainwater are significantly different between both duplicates and therefore deposition fluxes not properly measured.

[25] When otherwise available, A and B fluxes were averaged together. The median relative difference between both duplicates is 13% and can be considered as an uncertainty associated with both experimentation and sample analysis. Sampling duration weighted averages of Al fluxes allow us to derive a mean Al flux over the campaign periods. It is estimated at $52 \mu\text{g m}^{-2} \text{d}^{-1}$ during the 1-month 2005 campaign and $53 \mu\text{g m}^{-2} \text{d}^{-1}$ for the FLATOCOA sampling time, with a sample to sample variability of a factor 20 (range from 10 to $200 \mu\text{g m}^{-2} \text{d}^{-1}$). Integrating all available samples over 3 month periods reduces the variability (range of 40 to $100 \mu\text{g m}^{-2} \text{d}^{-1}$) and suggests some seasonality with larger

fluxes during local winter and spring (Figure 6). Modeled deposition tends to be lower than observed, especially for the October–November–December time period of 2009.

[26] The total dust deposition flux derived from Al is on average $642 \mu\text{g m}^{-2} \text{d}^{-1}$ from 2005 samples and $659 \mu\text{g m}^{-2} \text{d}^{-1}$ from 2009 to 2010 samples, with no noticeable change between 2009 and 2010. Those values are a bit larger than the highest modeled estimations based on composites of dust models [Jickells *et al.*, 2005], that give annual dust fluxes from 0 to $550 \mu\text{g m}^{-2} \text{d}^{-1}$ in Kerguelen area, but in good agreement with the dust deposition model from Mahowald [2007] (dust fluxes from 550 to $1400 \mu\text{g m}^{-2} \text{d}^{-1}$).

[27] Wagener *et al.* [2008] provides the only other dust deposition flux estimates available in literature and from

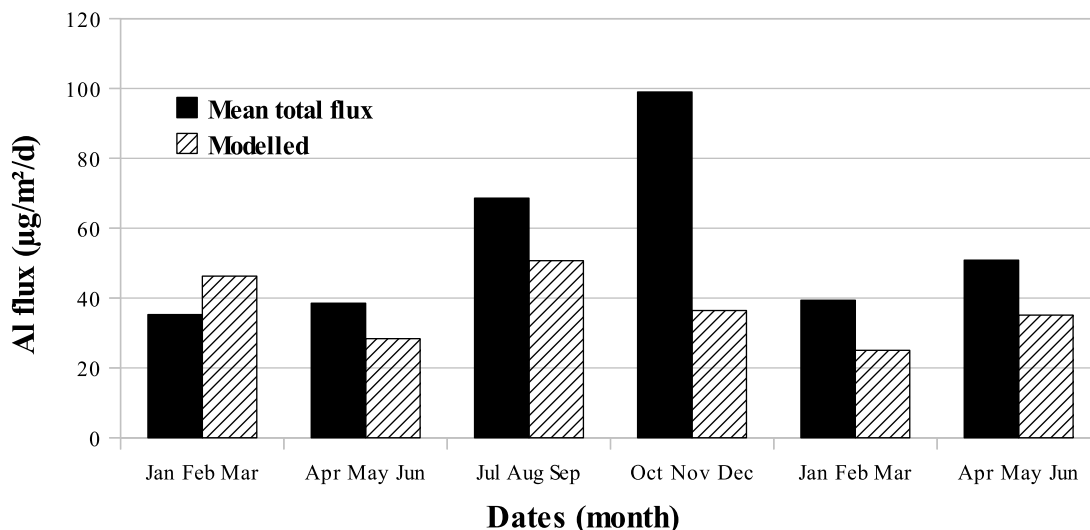


Figure 6. Three-month sampling time weighted average (full) of total deposition fluxes of Al for the years 2009–2010 and corresponding modeled outputs (hatched).

in situ offshore aerosol sampling performed during KEOPS cruise taking place southeast of Kerguelen Islands (approximately between 48°S and 54°S, 65°E and 80°E). Their indirect measurement of the total dust deposition flux using an assumed scavenging ratio and observed surface aerosol concentrations is of $38 \pm 14 \mu\text{g m}^{-2} \text{d}^{-1}$ on average, i.e., one order of magnitude less than dust fluxes we directly measured in the same area during the same period than KEOPS in 2005 (KEFREN measurements) and during the 2 years of FLATOCOA measurements in 2009–2010. This discrepancy is discussed in section 4.

3.3. Iron and Cobalt Deposition Fluxes

[28] We computed Fe and Co total deposition fluxes (Table 1) using the same method as to determine Al flux from total atmospheric deposition samples. Averaged over all the measurement period (KEFREN + FLATOCOA) with a weighting by sampling duration, Fe and Co fluxes are respectively $29 \mu\text{g m}^{-2} \text{d}^{-1}$ ($520 \text{ nmol m}^{-2} \text{d}^{-1}$) and $0.014 \mu\text{g m}^{-2} \text{d}^{-1}$ ($0.24 \text{ nmol m}^{-2} \text{d}^{-1}$). Flux variabilities of both elements are strongly correlated with those of Al flux ($r^2 > 0.9$); averaged fluxes exhibit an elemental ratio to Al of $2.6 \cdot 10^{-4}$ for Co and 0.54 for Fe, compatible with a purely crustal origin [Taylor, 1964; Wedepohl, 1995].

3.4. Titanium as an Indicator of Local Contamination

[29] Ti/Al elemental ratios were computed for both soils and atmospheric total deposition samples. Their values are on average 0.04 ± 0.01 (mean \pm SD) for deposition and 0.15 ± 0.05 for soils. Because Ti/Al mean ratio for soils is more than three times higher than the one observed in deposition, we can exclude a significant contribution of locally emitted soils in our atmospheric deposition samples.

3.5. Dry and Wet Dust Deposition Fluxes

[30] Although uncertainties in dry deposition velocity are relatively large [Ezat and Dulac, 1995; Wagener et al., 2008], dry deposition (shown in Table 2a, 2b using the dry deposition velocity from Ezat and Dulac [1995]) has a very low contribution to the total flux (Figure 7a): dust deposition is controlled by wet deposition over Kerguelen Islands. This result is consistent with the dominant role of wet deposition predicted by models (see Figure 7b) [Duce and Tindale, 1991; Gao et al., 2003; Moxim et al., 2011] and observed previously over remote oceanic sites [Arimoto et al., 1985, 1987] (see also the review in Mahowald et al. [2011]). Average dry dust deposition flux is $30 \mu\text{g m}^{-2} \text{d}^{-1}$, i.e., of the same order of magnitude as previously estimated by Wagener et al. [2008] during the 1-month KEOPS campaign ($31 \pm 11 \mu\text{g m}^{-2} \text{d}^{-1}$) and the one predicted by the model (62 ± 74 (mean \pm SD) $\mu\text{g m}^{-2} \text{d}^{-1}$).

4. Scavenging Ratios and Vertical Dust Distribution

[31] Wet deposition can be computed from aerosol concentration based on precipitation rate (RR) and an aerosol scavenging ratio (SR):

$$F_{\text{wet}} = C_{\text{aerosols}} SR RR \quad (1)$$

with

$$SR = \rho_{\text{air}} C_{\text{rain}} / \rho_{\text{water}} C_{\text{aerosols}} \quad (2)$$

where ρ_{air} and ρ_{water} are the volume mass of air and water, and C_{aerosols} is atmospheric particulate concentration of mineral dust or of a given element of interest.

[32] We computed scavenging ratios (Figure 8) for Al, Na and Mg using rain volumes collected in each deposition sample and concentrations in rain as deduced from wet deposition fluxes, computed by subtracting dry deposition to total deposition. Results on scavenging ratios are high and variable: from 1000 to 46000 for Al (dust proxy) and from 50 to 48000 for both Na and Mg (originating from sea-salt). There are two types of scavenging ratio values generally considered in the literature: (1) those relating surface aerosol concentration to aerosol wet deposition from observations [e.g., Jickells and Spokes, 2001] and (2) those which use a scavenging ratio relating modeled concentration and precipitation at different vertical heights, and wet deposition generated at the same level. Those values are $SR = 200$ which has been suggested for a typical oceanic atmosphere [Jickells and Spokes, 2001] and $SR = 750$ which is used in dust models [Tegen et al., 2002; Luo et al., 2003], respectively. Discrepancies between our observed SR and SR in literature explain discrepancy between our total deposition flux ($642 \mu\text{g m}^{-2} \text{d}^{-1}$ for 2005; $659 \mu\text{g m}^{-2} \text{d}^{-1}$ for 2009–2010) and the one proposed by Wagener et al. [2008] ($38 \pm 14 \mu\text{g m}^{-2} \text{d}^{-1}$), who used SR from Jickells and Spokes [2001] to compute his flux. This suggests that concentrations of aerosols we measured close to the surface are either (1) not well collected or (2) not representative of the column-averaged aerosol concentration effectively scavenged by rain, as discussed hereafter.

[33] (1) High wind conditions encountered at Kerguelen might be an issue for representative aerosol sampling using a low-volume aerosol filtration system. We performed laboratory experiments in a wind tunnel [Alfaro et al., 1997] to test the ambient aerosol collection efficiency of our sampling system. The filter holder was installed in the wind tunnel under the same geometry as in the field and we used a 6-channel (0.5–0.7, 0.7–1, 1–2, 2–5, and $>5 \mu\text{m}$ particle optical diameter) laser particle counter (MetOne 237B) downstream the filter holder to measure variations in particle size distribution under different wind conditions. Wind speeds could be varied from 1.9 to 8.3 m s^{-1} . For each air-flow speed, the experiment was performed 3 times. Relative to a reference quiet air conditions (2 m s^{-1}), we observed variations of the collected particle numbers from 0.8 to 1.3 for particles smaller than $5 \mu\text{m}$ in diameter and from 0.8 to 1.1 for the largest channel ($>5 \mu\text{m}$). On the field, our low volume aerosol collection system has also been reported to give results comparable to other filtration samplers in a similar environment to our study (François et al., 1995): the maximal discrepancy between high and low volume systems is a factor 2 for Al and a factor 3 for sea salts. It is suggested that coarse particles could be responsible for this discrepancy and especially for sea-salt component. In case where large particles would be present at Kerguelen Islands, our scavenging ratio values might therefore be overestimated by a factor of 2 for Al and 3 for sea salts. The magnitude of these uncertainties do not explain

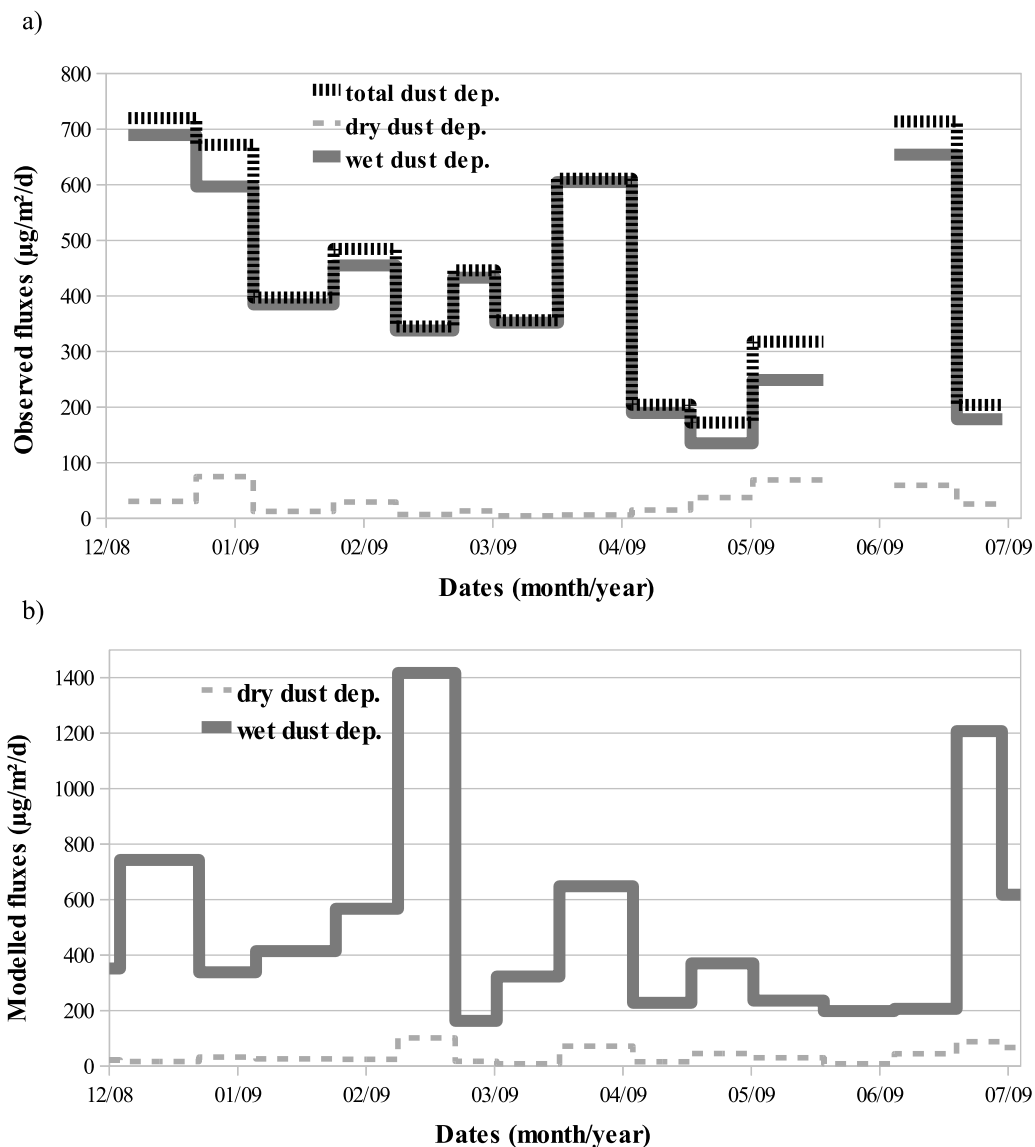


Figure 7. Total, dry, and wet dust deposition flux over Kerguelen Islands from December 2008 to July 2009, when aerosol and total deposition were sampled simultaneously. (a) Wet deposition is well correlated to total deposition, suggesting that wet deposition controls the total dust deposition flux. (b) Modeled wet and dry depositions.

large differences found between our computed SRs and those commonly admitted in literature.

[34] (2) Because the concentration at the surface is quite different from the concentration aloft, where precipitation forms, the SRs are difficult to define from such surface observations, although *Jickells and Spokes* [2001] argue that $\text{SR} = 200$ is valid for a typical oceanic atmosphere. Some chemical transport models use a similar, although slightly larger value ($\text{SR} = 750$; e.g., in *Tegen et al.* [2002], *Luo et al.* [2003]), although models include more physically based parameterizations to calculate the wet deposition, based on the vertical distribution of dust concentration and precipitation formation [e.g., *Rasch et al.*, 2001]. The large discrepancy between our observed values (1000–45000) and those

suggested by *Jickells and Spokes* [2001] as representative, highlight the difficulty in relating surface aerosol concentrations to aerosols scavenged by rain. The very low ground (this work) or sea [*Wagner et al.*, 2008] level observed aerosol concentrations may be due to a frequent and purging washout of the boundary layer.

[35] If we consider that literature values of SR reported above are representative of aerosol wet scavenging processes, aerosol concentrations at high altitude can be deduced from wet deposition using equation 2. Applying a SR of 750 to rainwater AI concentrations, we find AI particle concentrations between 9 and 36 ng m^{-3} with a median value of 18 ng m^{-3} . Based on this calculation, average dust particle concentrations in the column scavenged by rain are a factor

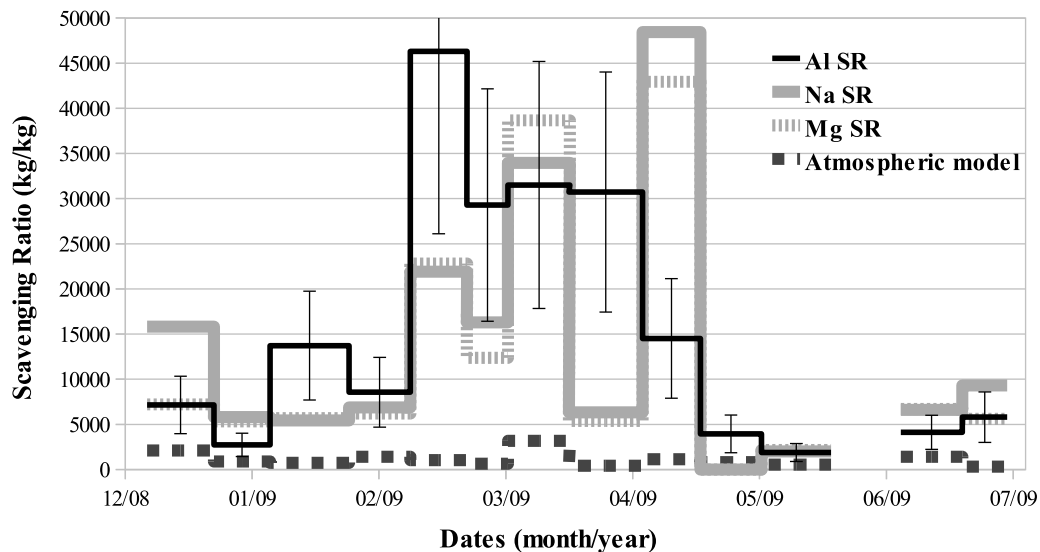


Figure 8. Scavenging ratio (SR) computed for Al, Na, and Mg and comparison with SR of atmospheric model based on indirect total deposition measurements.

ten higher than those at ground level (1.9 ng m^{-3} ; Table 2a, 2b). A strong dust positive gradient from ground or sea level to higher altitude should exist. It is likely that crustal aerosols that reach Kerguelen Islands are exported from the continent within continental air masses that travel above the shallow marine atmospheric boundary layer of the Southern Ocean, resulting in a significant maximum concentration of aerosol particles of continental origin in altitude. This is also simulated by models [Moxim *et al.*, 2011] and observed over other oceanic areas, e.g., North Pacific [Kritz *et al.*, 1990], tropical [Dulac *et al.*, 2001], and subtropical [Chazette *et al.*, 2001] Atlantic Ocean.

[36] Observed large variations of SR (Figure 8) further suggest that there is no correlation between surface aerosol concentrations and fluxes. We can therefore assume no correlation between high altitude and surface aerosol. This has been suggested to occur over large areas of the remote ocean in model studies [Mahowald *et al.*, 2003, Figure 8]. Using aerosol lidar remote sensing and surface in situ observations in the coastal environment of Goa on the western coast of India, Chazette *et al.* [2005] has shown such a significant decorrelation between aerosol measurements at the surface and as low as 100 m above.

[37] We can argue that indirect total deposition estimates based on surface aerosol concentration measurements are inappropriate over the Southern Ocean located around Kerguelen Islands, and probably over all the sub-Antarctic region, and must be checked for other regions of the open ocean (for example in Bowie *et al.* [2009]). We can assume that the following conceptual transport and deposition mechanism for continental dust over oceanic areas applies in the Southern Ocean: dust aerosols are transported above rain clouds over long distances to reach the remote Southern Ocean; the marine boundary layer is continuously entraining dust from the free troposphere and is subject to a significant and effective scavenging. For the constituents with strong sea-salt sources (Na and Mg) it should be noted that their SR

are usually lower, but they too can result from medium- to long-range transport of sea-salts to this site, 30 km downwind from the shore line and 250 m above sea level.

[38] Modeled behavior of dust aerosol (Figure 9a) also exhibits a vertical positive gradient, with a maximum in dust at 600 to 700 hPa. The model predicts that most of the removed dust comes from the upper levels (about 600 hPa), as suggested above (Figure 9b). The modeled concentrations at the midpoint of the bottom layer of the model are estimated to be between 130 and 260 ng m^{-3} and are almost ten times higher than measured at the surface. Moreover, although the standard deviation relative to the magnitude of the observations is about right, suggesting the model is capturing the amount of variability at this site well, the correlation coefficient between modeled and observed concentrations is 0.05 suggesting it has no skill in capturing the seasonal cycle or events. Because modeled dust deposition flux fits well with observed, discrepancy between measured and modeled aerosol concentrations is likely due to the model errors in simulated the entrainment of aerosols into the boundary layer and subsequent transport to the bottom layer. Here we compared observations to one model, but models have a wide variability in their simulation of surface concentration and deposition [Huneus *et al.*, 2011].

5. Conclusion

[39] Dust deposition derived from Al measurements and its abundance of 8.1% in the Earth's crust is $659 \mu\text{g m}^{-2} \text{ d}^{-1}$ at Kerguelen Islands. Fe and Co elemental ratios to Al are respectively 0.54 and $2.6 \cdot 10^{-4}$, corresponding to crustal ratios. Early studies hypothesized that atmospheric deposition is the main source of trace elements and nutrients to the open ocean [Buat-Ménard and Chesselet, 1979; Duce *et al.*, 1991; Duce *et al.*, 1991; Fung *et al.*, 2000]. In situ indirect estimates of atmospheric dust deposition flux based on surface aerosol concentration measurements have

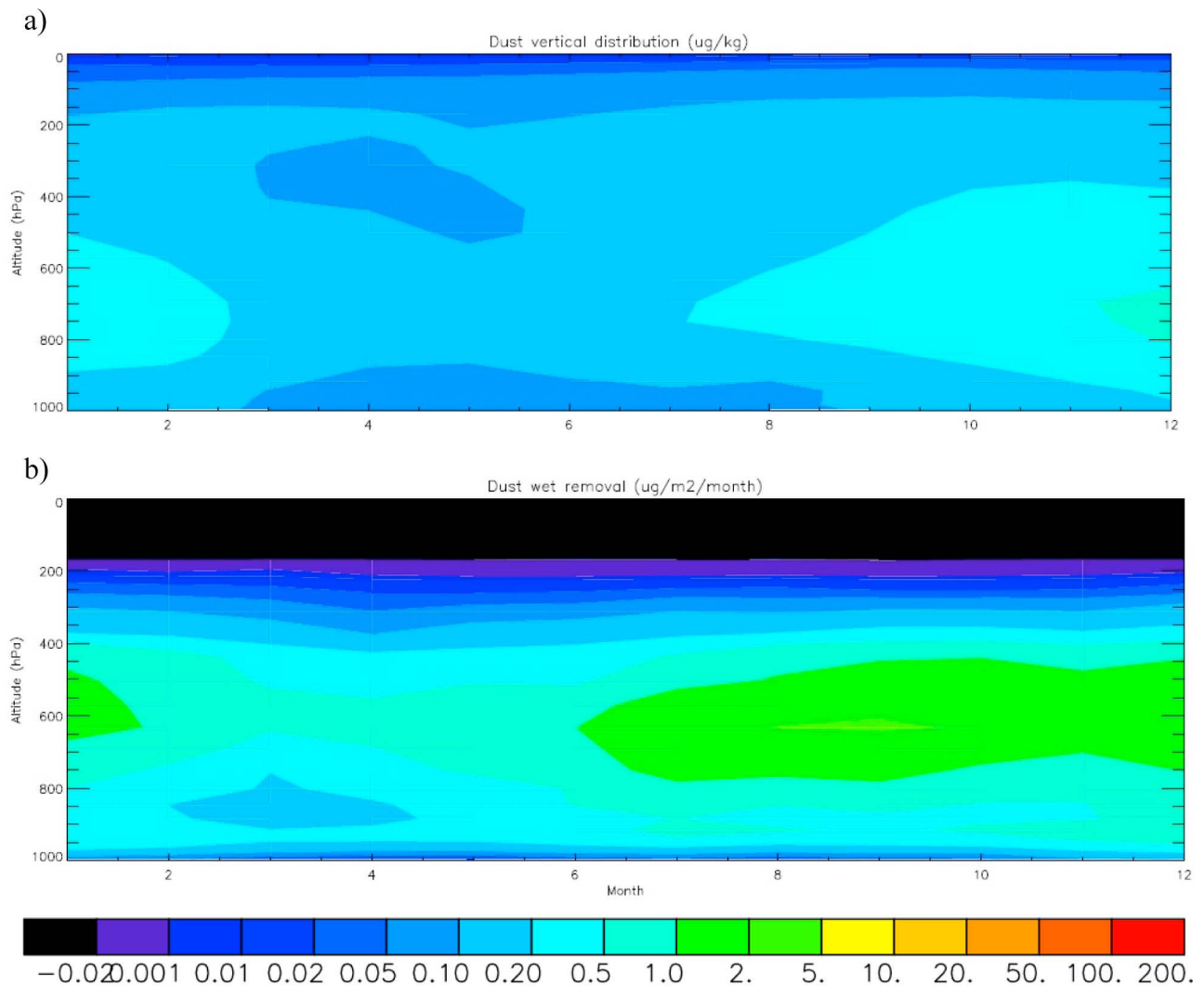


Figure 9. Seasonal cycle of modeled (a) dust vertical distribution and (b) dust wet removal at Jacky location during the years 2008, 2009, and 2010. At ground level dust vary from 130 (March–September) to 260 (October–February) ng m^{-3} .

lead to revise downward this hypothesis in the Southern Indian Ocean [Wagner *et al.*, 2008]. By performing unprecedented direct deposition measurements of aluminum at Kerguelen Islands, we have shown in this study that deposition flux computed from surface aerosol concentration measurements using assumptions based on deposition velocities or scavenging ratios leads to atmospheric fluxes 20 times lower than those directly measured. This result reopens the debate on the importance of the atmospheric deposition flux over the Southern Ocean. Additional direct measurements of atmospheric deposition over this oceanic area and more generally over oceanic areas are needed in order to properly assess the atmospheric dust deposition flux and know its actual contribution to the regional marine biogeochemical cycles.

[40] **Acknowledgments.** We would like to thank the IPEV institute and its staff, which supported our work (KEFREN and FLATOCOA programs) and has enabled us to perform field campaigns by taking over transportation of all the material deployed on the field by ship from France to Kerguelen Islands, as well as transportation and accommodation on site of

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