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# Chemical characterization of aerosols in the equatorial atmosphere over the Indian Ocean

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# ABSTRACT

The region of the Indian Ocean and adjacent countries has received increased attention in recent years in the context of particulate air pollution. Aerosol samples were collected over the equatorial Indian Ocean during a one-year-long sailing cruise that covered the northeast and southwest monsoons, and an intermonsoon period. The concentrations of airborne particulate matter (PM), selected metals and watersoluble ions were measured. In general, the PM concentrations were influenced by the proximity of sampling locations to land and air mass origins. The enrichment of metals in PM relative to those in the crustal material was very high (up to 40,000). The metal concentrations were significantly higher in PM samples which were influenced by volcanic emissions from the land masses of Indonesia. Volcanic plumes were traced using backward air mass trajectory and chemical tracers, and identified as a major particulate pollution source to the otherwise pristine air of the southern hemisphere of the Indian Ocean.  $NO_3^-$ ,  $NH_4^+$  and  $SO_4^{2-}$  were low in aerosols collected over the open ocean, but a linear relationship between  $NH_4^+$  and  $SO_4^{2-}$  indicates their importance in the formation of cloud condensation nuclei.

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# 1. Introduction

Air pollution in the region of the Indian Ocean and adjacent countries, especially those in South and Southeast Asia, has been of considerable interest from both scientific and regulatory perspectives due to its impact on global atmospheric chemistry and climate (Fishman et al., 1991; Lelieveld et al., 2001) and rapid population growth and urbanization in these regions (Lawrence and Lelieveld, 2010). Aerosols are unique among air contaminants because of their potential complexity in terms of both chemical composition and physical properties (Balasubramanian et al., 2003). By acting as cloud condensation nuclei (CCN) or ice nuclei, aerosols can modify cloud optical and physical properties, and therefore affect the climate system, giving rise to the so-called aerosol indirect effect.

Marine aerosols play an important role as a transport vector for the cycling of trace metals and nutrients between the atmosphere and the ocean through wet and dry deposition (Baker et al., 2007).

Some trace metals, such as Fe, are known to affect biogeochemical cycles in the ocean as limiting micronutrients (Abram et al., 2003; Baker et al., 2007). Natural emission sources of aerosols are windborne dust (Savoie et al., 1987), volcanic activities (Mather et al., 2003) and sea spray (Nair et al., 2005). Major anthropogenic sources of aerosols include metal processing, waste incineration, and fossil fuel and biomass combustion (Nriagu and Pacyna, 1988).

The impact of gaseous and particulate emissions from forest and peat fires in Indonesia on the regional air quality of Southeast Asia has been of great concern during recent years (Balasubramanian et al., 1999, 2003). Another phenomenon of much concern is the spread of an aerosol layer of 3 km thickness from China to Southeast Asia and the northern part of the Indian Ocean known as the Atmospheric Brown Cloud (Ramanathan et al., 2002; Wu et al., 2005).

The northern Indian Ocean and Arabian Sea have been extensively studied on aerosols and their chemical characterization during the INDOEX (Ramanathan et al., 2002; Nair et al., 2004) and Joint Global Ocean Flux Study (JGOFS) (Johansen and Hoffmann, 2003, 2004) projects. The atmospheric system over the Indian Ocean is dynamically and chemically very active due to differential heating between the continents and ocean, high humidity and precipitation, and the large and increasing anthropogenic emissions. However, the knowledge of the atmospheric chemistry over





ATMOSPHERIC ENVIRONMENT

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the Indian Ocean is still limited, in particular for the southern hemisphere and during inter-monsoon periods. The INDOEX and JGOFS studies focused on the northern Indian Ocean with the rationale that the pollution levels are highest in this region due to the proximity to the Indian subcontinent. However, recent modeling has showed that the pollution level can be relative high south of 10°S compared to the northern Indian Ocean (Kunhikrishnan and Lawrence, 2004) during inter-monsoon periods, when zonal winds dominate the circulation.

The present study focuses on the characterization of atmospheric trace elements and soluble ions in aerosols over the Indian Ocean. The key objective is to study the particulate air pollution levels in the supposedly pristine southern Indian Ocean by collecting total suspended particulate matter (TSP) and measuring the concentrations of trace metals and water-soluble ions in TSP. To achieve this objective, a year-long sailing cruise was conducted across the Indian Ocean under different monsoon seasons.

# 2. Experimental

# 2.1. Sampling

In contrast to other similar studies conducted on research vessels, the sample collection was conducted on an 18 m long fiberglass sailing vessel named Jocara. PM samples were collected under sail to reduce possible contamination from combustion sources to an absolute minimum. In total, 16 aerosol samples were collected between September 2004 and August 2005 during a cruise which circumnavigated the Indian Ocean from Singapore to Sumatra, Cocos Keeling, Madagascar, Seychelles, Chagos Archipelago, Maldives, and back to Singapore – a distance of approximately 8000 nautical miles (Fig. 1a–c). PM samples were collected in an opportunistic manner as part of broad research activities of the Jocara Indian Ocean Quest (i.e. Wurl et al., 2006a; Wurl et al. 2006b). Nevertheless, the sampling distribution and frequency covered important environmental features in this region such as monsoon seasons and events of major volcanic eruptions.

Samples were categorized in three distinct groups according to sampling date and locations: Group I (S1–S6), Group II (S7–S9) and Group III (S10–S16). Particulate samples during anchorage were collected in proximity to the islands Anak Krakatau (13 September 04), Peucang (17 September 04), Cocos Keeling (25 September 04), Cargados Carajos (27 November 04), Dzaudzi (22 December 04), Takamaka Island (6 June 05), Boddam (11 June 04), Isle de la Passe (14 June 04) and Gan (10 July 04). The remaining PM samples were collected during transects while sailing.

Ambient aerosol samples were collected with a pre-calibrated Air Metrics sampler (Air Metrics, USA). The aerosol sampler was operated for 21–45 h at 5 L min<sup>-1</sup> to collect the sufficient mass for chemical characterization. The aerosol samples collected in this study represented the total suspended particulate matter (TSP) in the air. Pre-weighed Teflon filters (Pall Life Sciences) were used for sample collection, which were stored individually in an air-tight plastic container at ambient temperature prior to sampling. After sampling, the filters were stored in the plastic container at -18 °C prior to analysis.

#### 2.2. Chemical analysis

For the preparation of reagents and standards, ultrapure water (18.2 M $\Omega$ ) from Maxima Ultra Pure Water system (ELGALABWATER, UK) was used. HNO<sub>3</sub> (TraceSelect for trace analysis, Fluka,), H<sub>2</sub>O<sub>2</sub> (Merck), and HF (Merck) were used for the digestion of filters. A multi-element standard from Merck was used for calibration of the analytical equipment.



**Fig. 1.** a) Group I: S1 and S2 (13–17 Sept 2004), S3 (18–20 September 2004), S4 (25–27 September 2004), S5 (11–13 October 2004) and S6 (17–19 October 2004). b) Group II: S7 (27–29 November 2004), S8 (9–11 December 2004) and S9 (22–24 December 2004). c) Group III: S10 (16–18 May 2005), S11–S13 (6–15 June 2005), S14 (10–11 July 2005), S15 (15–17 August 2005) and S16 (22–23 August 2005). Lines represent 5-days backward air trajectory and different styles are used for better illustration only. Sampling locations are indicated by black dots on the dotted line representing the sailing route.

### 2.2.1. TSP analysis

The filters were weighed before and after the sampling using a calibrated microbalance (Sartorius, Model MC 3) with 1  $\mu$ g sensitivity to obtain the TSP mass. The filters were pre-equilibrated in a dry box with stabilized temperature (22–23 °C) and relative humidity (30–33%) for at least 24 h before the actual weighing.

#### 2.2.2. Trace metal analysis

One half of each filter was digested according to a quality assured microwave assisted digestion procedure reported previously (Karthikeyan et al., 2006). Briefly, the filters were digested in an acid mixture (HNO<sub>3</sub> (4 mL); H<sub>2</sub>O<sub>2</sub> (2 mL); HF (0.2 mL)) for 12 min with increasing temperature from 95 °C to 130 °C. The filtered extracts (through 0.2  $\mu$ m PTFE syringe filters) were stored in acid-cleaned HDPE vials at 4 °C prior analysis. The extracts were analyzed with a Perkin–Elmer Elan 6100 ICP-MS (Perkin–Elmer Inc., USA) on following metals (Karthikeyan et al., 2006): Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn. Quality assurance is presented as Supplementary information.

## 2.2.3. Water-soluble ion analysis

The second half of each filter was extracted with 20 mL ultrapure water in a sonicator for 1 h at 60 °C. The extract was subsequently filtered through a 0.45-(PTFE) membrane filter (Whatman plc) and analyzed on following inorganic anions and cations by ion chromatography (Dionex Corporation): F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>.

## 2.3. Air mass trajectory

Air mass back trajectories were constructed to assess the origin of air masses collected at each station and to evaluate their travel time over the open ocean using the HYSPLIT model accessed via NOAA Air Resource Laboratory READY website (Draxler and Rolph, 2003). Backward trajectories (BTs) were traced for 5 and 10 days at altitudes of 125, 1500, 4000 m above sea level including vertical motion calculations. The BTs are presented for 5-day trajectories at an altitude of 125 m (Fig. 1a–c). The trajectory analysis at different altitudes was used to assess the degree of vertical mixing.

## 3. Results and discussion

## 3.1. Air mass origins

The air circulation over the Indian Ocean is characterized by a seasonal monsoon system, the southwest (SW) and northeast (NE) monsoons. The SW monsoon lasts typically from June through September with winds blowing from the SW direction over the equator into the northern hemisphere. The northeast monsoon is developed in late November and persists until February. During the NE monsoon, northeasterly winds are persistent from the Indian subcontinent while pristine air from the remote Southern Indian Ocean prevails. The period from late September to November is the inter-monsoon period with westerly zonal winds dominating the air circulation.

The typical atmospheric residence time of aerosols is one to two weeks (Papastefanou and Bondietti, 1991; Poet et al., 1972). Air mass back trajectories (5 days) are shown in Fig. 1a-c. Air masses sampled adjacent to the coast of the northern tip of Java (S1 and S2) were partly continental and partly oceanic, but crossing the highly urbanized area of Jakarta located in proximity to the sample locations. For most of the remaining air samples, the collected air masses originated from oceanic region. In particular, the samples S5-S7 and S10-S14 represented aerosol samples from pristine regions of the Southern Indian Ocean (5-days trajectory) and Southern Ocean (10-days trajectory, altitude <1500 m). The sample S9 had appeared to originate from the north along the African coastline. A 10-day trajectory analysis showed that the air flow originated from as north as the Arabian Sea. Air masses collected for samples S3-S7 and S11-S14 experienced partially strong vertical mixing from altitudes up to 4000 m within 5–10 days before they reached the air sampler.

## 3.2. Variations of trace metal concentrations

The aerosol samples were divided into three groups (Fig. 1a–c) according to the sampling period and the region. As the samples were collected over a period of 12 months, analysis of the concentration of the PM components in terms of spatial distributions is not possible, but grouping the concentration data provides some rough estimates as to what extent the different regions of the Indian Ocean are polluted under different seasons. Samples belonging to Group I were collected during the inter-monsoon period (September to October). Group II represents aerosol samples collected during the course of the NE monsoon (late November to December), whereas the samples belonging to Group III were collected during the SW monsoon (May to August).

TSP and selected metal concentrations measured on the cruise at individual stations and within the grouped regions are shown in Tables 1 and 2, respectively. Concentrations of most of the metals are higher than those reported from previous studies from the Indian Ocean, although this comparison is not so straight forward because of changes in the seasonal air circulation. As expected, the TSP and metal concentrations were highest in locations that are in close proximity to the land masses of Indonesia (S1, S2, S16), the Maldives (S14) and East Africa (S9) with maximum TSP and Zn concentration being 45  $\mu$ g m<sup>-3</sup> for TSP and 179 ng m<sup>-3</sup> for Zn.

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Table 1
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Concentration of total suspended particulate ( $\mu g \ m^-$	$^{3}$ ), trace elements (ng m $^{-3}$ ) and i	ions ( $\mu g \ m^{-3}$ ). Locations of stations are	e given in Fig. 1

Station	Group	Date	Anchored or Transect (A/T)	TSP	Al	As	Cd	Cr	Cu	Pb	V	Zn	$nss-SO_4^{2-}$	nss-K <sup>+</sup>	$\mathrm{NH}_4^+$	$NO_3^-$
S1	Group I	13-14 Sept 2004	А	45.4	89.7	2.40	0.79	6.15	145	14.3	7.77	54.3	3.75	0.60	1.03	2.40
S2		15-17 Sept 2004	A	27.2	5.10	0.87	0.33	1.88	2.14	2.47	3.48	6.86	1.88	0.40	0.34	0.69
S3		18-20 Sept 2004	Т	28.9	23.1	1.77	0.69	6.92	6.10	0.27	5.57	86.9	<0.1	0.11	0.08	0.08
S4		25–27 Sept 2004	A	29.9	7.47	1.01	0.18	4.17	6.21	1.25	4.44	6.72	0.06	0.15	0.09	0.07
S5		11-13 Oct 2004	Т	26.0	57.5	0.87	0.73	3.31	18.3	7.90	3.68	142	0.51	0.10	0.25	0.15
S6		17-19 Oct 2004	Т	13.4	13.3	0.27	0.34	1.69	1.06	0.89	2.67	9.54	<0.1	< 0.06	0.05	< 0.04
S7	Group II	27-29 Nov 2004	Α	12.8	1568	0.23	0.55	21.7	76.2	22.3	0.08	40.8	0.39	< 0.06	0.10	< 0.04
S8		9-11 Nov 2004	Т	9.40	166	0.33	0.27	32.8	30.1	46.0	0.10	26.5	0.72	0.30	0.16	< 0.04
S9		22-24 Dec 2004	A	21.8	1911	0.97	0.31	15.9	17.5	0.14	0.48	21.2	0.74	0.08	0.23	0.05
S10	Group III	16–18 May 2005	Т	6.57	92.6	0.20	0.39	15.4	14.1	2.94	0.55	68.0	0.30	0.18	< 0.02	0.05
S11		6–7 June 2005	A	6.00	189	0.44	0.54	22.9	19.6	7.63	0.74	93.8	<0.1	0.21	< 0.02	< 0.04
S12		11–12 June 2005	Α	20.1	233	0.24	0.24	35.7	19.0	0.84	0.05	247	<0.1	0.10	0.04	< 0.04
S13		14–15 June 2005	Α	6.95	373	0.03	0.67	21.3	36.3	4.34	0.17	199	0.36	0.17	0.06	< 0.04
S14		10-11 July 2005	Α	22.0	75.4	0.12	0.21	13.9	16.1	12.0	0.29	33.9	0.12	0.10	< 0.02	0.05
S15		15-17 Aug 2005	Т	22.9	389	0.25	0.21	23.8	11.7	1.71	0.68	18.6	0.30	0.75	0.13	0.05
S16		22-23 Aug 2005	Т	37.9	452	0.44	0.37	23.7	140	30.9	2.02	88.5	0.33	0.08	< 0.02	< 0.04

Table 2
Mean metal concentrations and ranges in ng $m^{-3}$ in aerosols from this study and the literature.

	CIO (Group I), This study	CIO (Group II), This study	CIO (Group III), This study	CIO, Chester et al. (1991)	AS, Chester et al. (1991)	AS, Johansen and Hoffmann (2003)	SIO, Witt et al. (2006)
Al	32.7 (5.1-89.7)	1214 (165–1911)	257 (75.4–452)	13 (4.3–159)	1227 (317–5148)	390 (119–970)	
As	1.2 (0.27-2.4)	0.51 (0.23-0.97)	0.24 (0.03-0.44)				
Cd	0.51 (0.18-0.79)	0.38 (0.27-0.55)	0.38 (0.21-0.67)	0.005 (0.0002-0.053)	0.045 (0.024-0.099)		0.01 (0.004-0.02)
Со	0.25 (0.01-0.52)	0.28 (0.01-0.73)	0.15 (0.01-0.49)	0.026 (0.004-0.17)	0.38 (0.037-1.9)		
Cr	4.0 (1.7-6.9)	23.4 (15.9-32.8)	22.4 (13.9-35.7)	0.085 (0.01-0.44)	3.0 (0.77-14)		
Cu	29.8 (1.1-145)	4.3 (17.5-76.2)	36.7 (11.7-140)	0.12 (0.018-0.86)	2.6 (0.96-12)		3.9 (0.51-16.3)
Fe	105 (4.8-412)	273 (186-404)	222 (82.3-368)	11 (3.1–109)	790 (317-3074)	720 (230-1590)	
Mn	3.0 (0.91-5.5)	6.5 (2.8-9.9)	2.7 (0.45-6.4)	0.19 (0.04-3.9)	17 (6.3–59)	10.8 (3.7-19.9)	
Ni	7.9 (0.51-24.6)	10.2 (7.7-11.9)	9.7 (5.1-21.6)	0.061 (0.018-0.58)	2.0 (0.39-9.4)		2.8 (0.01-3.2)
Pb	4.5 (0.27-14.3)	22.8 (0.14-46.0)	8.6 (0.84-30.9)	0.18 (0.017-1.1)	4.3 (1.1-12)	5.7 (1.3-11.5)	0.8 (0.08-4.6)
Ti	66.2 (2.6-122)	58.8 (30.2-84.2)	87.7 (19.4-264)			39.3 (15.9–97.2)	
V	4.6 (2.7-7.8)	0.22 (0.08-0.48)	0.64 (0.05-2.0)			1.4 (0.68-3.9)	
Zn	51.1 (6.7–142)	29.5 (21.2-40.8)	106 (18.7-247)	0.17 (0.018–1.1)	10 (4.2–29)	7.8 (1.9–19.9)	5.2 (0.37-20.1)

CIO: Central Indian Ocean (55°E–95°E, 5°N–25°S); AS: Arabian Sea (40°E–75°E, 5°N–25°N); SIO: Southern Indian Ocean (55°E–95°E, 25°S–35°S).

However, high concentrations of TSP (30  $\mu$ g m<sup>-3</sup>) and metals (e.g. Zn, 142 ng  $m^{-3}$ ) were found at oceanic regions south of the equator (S3-S5) at levels that are typical for the Arabian Sea influenced by polluted air masses from the Indian subcontinent (Table 2). During inter-hemispheric transect measurements, it was observed that the Intertropical Convergence Zone (ITCZ) acts as an isolator in blocking the transport of pollutants from the Indian subcontinent to the southern hemisphere (Gabriel et al., 2002). It was reported that inter-hemispheric transport of air masses across the ITCZ may occur during the northeast monsoon (Verver et al., 2001; Williams et al., 2002), and such a process may have affected the levels of trace elements and TSP collected at stations S1-S6 during the northeast monsoon season. However, it is not clear if the inter-hemispheric transport processes were the single source causing the high pollution levels observed in this study. The influence of volcanic activities on the Indonesian land masses on air quality was therefore examined as a possible source.

Previous studies using satellite observations and computer models showed that the Central Indian Ocean (CIO,  $55^{\circ}E-95^{\circ}E$ ,  $5^{\circ}N-25^{\circ}S$ ) in the southern hemisphere is not always as pristine as found earlier during the NE monsoon period, and could be polluted during the inter-monsoon periods by pollution plumes from Africa and Southeast Asia (Kunhikrishnan and Lawrence, 2004; Kunhikrishnan et al., 2004) through pronounced anti-cyclonic circulations and weak maritime convection over the CIO. Evidence in favor of major contributions of volcanic emission plumes to high pollution levels over the CIO is presented and discussed in Section 3.5.

We found several significant correlations (p < 0.05) between different trace elements (Table 3). A positive correlation was observed between V and Al and As whereas the correlation with Cr

was negative. Furthermore, Al correlated significantly with Cr, Cu, Fe and Mn. Zn correlated with other anthropogenic metals including Cd, Co, Cu, Ni and Ti, but not with Pb. Pb correlated only with Cu.

No significant differences in metal concentrations were observed between Group I (S1–S6), II (S7–S9) and III (S10–S16), except for Al, Cr, V and As. Cr was only significantly lower (p = 0.007and 0.027 respectively) in Group I compared to the other groups. Al was significantly higher in Group II compared to Groups I and III. As was significantly higher (p = 0.027) in Group I compared to group III. V is the only element which was significantly higher in Group I compared to both other groups (p = 0.002 for group II and III). TSP concentrations were significantly higher (p = 0.046) in Group I compared to Group II, probably due to the influences of emissions from the land masses of Southeast Asia.

The average contribution of individual elements to their total mass is shown in Fig. 2. The major components of aerosols were Al, Fe, Cu, Ti and Zn. High concentration of Al at S9 (Group II) may originate from deserts in the Middle East as revealed by air mass trajectory. A similar contribution of Al at S7 cannot be easily explained with air masses originating from the Southern Indian Ocean, but is consistent with the finding of relatively high concentration of metals from anthropogenic sources at this station (Table 1). Overall, the high contribution of Al and Fe may indicate that the aerosols were of crustal origin (dust and soil).

### 3.3. Enrichment factors of metals in aerosols

Enrichment factors (EF<sub>crust</sub>) of metals in the marine aerosols were calculated according to Duce et al. (1983). The EF<sub>crust</sub> for the metal X relative to the earth crust with reference to Al is defined by EF<sub>crust, x</sub> = (X/Al)<sub>Air</sub>/(X/Al)<sub>crust</sub>. Average elemental composition of

**Table 3** Correlation matrix with Spearman coefficient and p values (gray-shaded) on nss- $SO_4^{2^-}$  and trace element data. Significant correlation in bold (i.e. p < 0.05).

	nss-SO <sub>4</sub>	Al	Со	Cr	Cu	Fe	Mn	Pb	Zn	Cd	Ni	Ti	V	As
nss-SO <sub>4</sub>		0.210	0.345	-0.032	0.440	0.128	0.427	0.418	-0.118	0.223	0.178	0.059	-0.013	0.209
Al	0.434		0.252	0.768	0.626	0.553	0.568	0.182	0.341	0.013	0.456	0.156	<b>-0.629</b>	-0.345
Со	0.191	0.346		-0.028	0.325	-0.078	0.363	-0.260	0.511	0.601	0.292	0.840	0.202	0.396
C.	0.005	0.001	0.010		0 530	0.405	0.215	0.225	0.204	0 2 4 0	0 200	0.070	0 700	0 200

Cr	0.905	0.001	0.918		0.529	0.485	0.215	0.235	0.394	-0.249	0.368	0.076	<b>-0.700</b>	-0.398
Cu	0.088	0.009	0.220	0.035		0.297	0.485	0.691	0.556	0.394	0.400	0.359	-0.315	-0.110
e	0.637	0.026	0.773	0.057	0.264		0.444	0.144	-0.121	-0.406	0.094	0.018	-0.247	-0.031
Лn	0.099	0.022	0.167	0.425	0.057	0.085		0.256	0.026	0.369	0.362	0.194	0.147	0.402
Ъ	0.107	0.499	0.331	0.380	0.003	0.594	0.339		0.182	0.247	0.276	-0.244	-0.153	-0.208
2n	0.664	0.196	0.043	0.131	0.025	0.656	0.922	0.499		0.543	0.544	0.579	-0.235	-0.243
Cd	0.406	0.961	0.014	0.353	0.131	0.118	0.159	0.356	0.030		0.397	0.512	0.334	0.212
Ni	0.509	0.076	0.272	0.161	0.125	0.729	0.169	0.300	0.029	0.128		0.182	-0.294	-0.200
ï	0.829	0.564	<0.001	0.778	0.172	0.948	0.471	0.362	0.019	0.043	0.499		0.159	0.297
/	0.961	0.009	0.453	0.003	0.235	0.356	0.587	0.572	0.380	0.206	0.269	0.557		0.778
As	0.437	0.191	0.129	0.127	0.684	0.909	0.123	0.440	0.364	0.430	0.457	0.263	<0.001	



Fig. 2. Average contribution of a) trace metals and b) ions to their total mass.

the earth crust was taken from Krauskopf (1986). Given local variations in crustal composition, if  $\text{EF}_{\text{crust}, x} > 10$  the element X in marine aerosols may have a primary contribution originating from non-crustal sources.  $\text{EF}_{\text{crust}}$  values for the Group I are 10–120-fold higher compared to those reported in the literature for the Indian Ocean (Table 4 and Fig. 3). Fig. 3 shows that a specific group of metals (e.g. As, Co, Fe, Mn, Ti and V) was only enriched at stations represented by Group I whereas the remaining metals were enriched throughout the CIO. For example, the metals, Cu and Pb, were not significantly different in their  $\text{EF}_{\text{crust}}$  among the Groups I–III. It indicates that the region of Group I received a unique source of trace metal inputs enriched with As, Co, Fe, Mn, Ti and V.  $\text{EF}_{\text{crust}}$  values calculated from the data of Groups II and III are comparable to those reported by Chester et al. (1991) and Siefert et al. (1999) (Table 4).

Overall, high contributions from non-crustal sources to pollution levels over the CIO are evident including the regions at the south of the equator (Group I + II). However, the unique enrichment pattern observed for Group I indicated the influence of

different sources compared to those for Groups II and III. We further discuss potential inputs from volcanic emissions to the region represented by Group I.

## 3.4. Characterization of soluble ions

Anion and cation concentrations measured during the cruise are summarized in Table 5. Concentrations of  $NO_2^-$ ,  $F^-$ ,  $PO_4^{3-}$  and Li<sup>+</sup> were below detection limits for all samples. Based on the Na<sup>+</sup> concentrations and the seawater composition, the non-sea-salt (nss) fractions of Cl<sup>-</sup>,  $SO_4^{2-}$ , K<sup>+</sup> and Ca<sup>2+</sup> were calculated according to Savoie et al. (1987). The presence of sea-salt fractions in aerosols was further investigated by the mass ratio of Cl/Na, which is about 1.8 in seawater. Aerosols samples, S3–S7, S9, S10, S12 and S14, showed a ratio in a range of 1.5–2.2 indicating an oceanic origin. In the remaining aerosols, the ratio varied between 0.34 (S1) and 1.3 (S15). However, depletion of Cl<sup>-</sup> was reported in the presence of elevated levels of  $SO_4^{2-}$  and  $NO_3^-$  (Johansen and Hoffmann, 2004; Xie et al., 2005). Negative values for nss-Cl<sup>-</sup> observed during this

Table 4

Mean enrichment values (range in bracket) for the Central Indian Ocean (CIO) and Arabian Sea (AS) from this study and the literature.

		,		•				
	CIO (Group I)	CIO (Group II)	CIO (Group III)	CIO	AS	CIO	AS	
	This study	This study	This study	Chester et a	al. (1991)	Siefert et al. (1999)		
As	3342 (682-7700)	39 (7-88)	56 (4-104)					
Cd	14918 (4757-39839)	386 (87-880)	1088 (296-2291)	542	18			
Со	37 (1.9–83)	0.6 (0.2–1.4)	2.3 (0.5-4.8)	8.7	2.1			
Cr	200 (47-452)	59 (6.7–160)	92 (42–149)	8.5	2.4	101	6.5	
Cu	953 (129-2618)	129 (15–295)	228 (49-502)	16	7.2	96	23	
Fe	16 (0.5-83)	0.9 (0.2-2.1)	1.6 (0.5-2.9)	1.3	1.0	1.4	2.2	
Mn	14 (4.9–30)	0.7 (0.3-1.4)	1.0 (0.2–2.3)	1.3	1.4	0.9	1.4	
Ni	295 (42-778)	28 (4.4-72)	49 (26-101)	6.0	2.3			
Pb	1110 (75-3135)	630 (0.5-1798)	296 (23-1035)	146	27			
Ti	63 (3.1–144)	1.4 (0.6-3.0)	6.3 (1.4–11)			8.4	1.2	
V	230 (47-530)	0.2 (0.04-0.4)	2.2 (0.2-4.4)	1.9	6.3	1.0	1.8	
Zn	1892 (701-4356)	76 (13–185)	581 (55-1224)	24	18	80		

CIO: Central Indian Ocean (55°E-95°E, 5°N-25°S); AS: Arabian Sea (40°E-75°E, 5°N-25°N).



**Fig. 3.** EF<sub>crust</sub> values for atmospheric trace metals over the Central Indian Ocean (CIO) at stations represented in group 1 (white bars), groups 2 (light gray bars) and group 3 (dark gray bars). The horizontal bars represent the average  $\text{EF}_{crust}$ , and the vertical bars represent the minimum and maximum  $\text{EF}_{crust}$  observed.

study indicate depletion processes in all aerosol samples, except in the oceanic aerosol samples S5 and S6 (Table 5). Enrichment of Cl can be explained through thermodynamically favorable displacement reaction of mineral acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) with sea-salt particles leading to the formation of HCl (Johansen and Hoffmann, 2004). Moreover, reactive chlorine gases (Cl<sub>2</sub>, HOCl, ClNO<sub>3</sub> and BrCl) can volatilize from sea-salt particles (Vogt et al., 1996; Sander and Crutzen, 1996). The concentrations of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and nss-SO<sub>4</sub><sup>2-</sup> of Group I were about 2-fold lower compared to data from the Arabian Sea, but 2–10 fold higher compared to the Groups II and III. It further indicates that the southern region of the Indian Ocean was more polluted than the northern regions during the course of this study.

 $Nss-SO_4^{2-}$  can originate from anthropogenic (homogeneous gasphase or heterogeneous in-cloud oxidation of the primary gaseous pollutant  $SO_2$ ), biogenic (dimethyl sulfide as a source of oceanic sulfate aerosols) and crustal sources.  $Nss-SO_4^{2-}$  did not correlate with any of the trace metals (Table 3). Sulfate-containing particles are hygroscopic in nature and therefore grow rapidly in size under tropical conditions with high humidity (Langmann and Graf, 2003). Consequently, such particles tend to fall out from the atmosphere via dry deposition, or removed by clouds and rainfall i.e. wet deposition. In contrast, trace metals are rather conservative and typically bound to smaller particles i.e. chemically unreactive with longer atmospheric residence times as compared to that of the hygroscopic sulfate particles (Balasubramanian and Qian, 2004). The average fraction of nss-SO<sub>4</sub><sup>2-</sup> was around 58% and was highest in aerosols collected in locations that are in close proximity to land masses (S1, S2, S8 and S9). Dimethyl sulfide as a source of nss-SO<sub>4</sub><sup>2-</sup> has been reported to account for <20% during the northeast monsoon (Krishnamurti et al., 1998) and up to 75% during the intermonsoon period and southwest monsoon (Johansen et al., 1999) over the Arabian Sea.

Considering an oceanic background concentration for nss-SO<sub>4</sub><sup>2–</sup> of 0.3–0.7  $\mu$ g m<sup>-3</sup> (Savoie, 1989), the concentrations observed during this study are at a low range, except for samples collected along the Indonesian coastline (S1 and S2). The latter two samples were under the influence of air masses which were in contact with land masses of Java (including Jakarta). Our observation is consistent with that of Pfeffer et al. (2006) who reported dry and wet deposition of SO<sub>4</sub><sup>2-</sup> containing particles over the land masses of Java and Sumatra after emission from volcanic emissions. It was found that  $nss-SO_4^{2-}$  was strongly correlated with  $NH_4^+$  in the aerosols (Fig. 4;  $r^2 = 0.9121$ , p = 0.0001). A similar correlation between nss- $SO_4^{2-}$  and  $NH_4^+$  was found in aerosol samples collected over the South China Sea (Hsu et al., 2007) and the Yellow Sea (Lee et al., 2002). The high correlation suggests the formation of  $(NH_4)_2SO_4/$ NH<sub>4</sub>HSO<sub>4</sub> in the aerosol samples collected, which was identified to be a major component in marine aerosols over the South China Sea (Hsu et al., 2007) and the Pacific (Ooki et al., 2007). A cloud formation pathway was recently reported involving heterogeneous ice nucleation by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solid aerosols (Abbatt et al., 2006) indicating an important role of such aerosols in climate feedbacks. The ratio of  $NH_4^+$  to nss- $SO_4^{2-}$  is generally below 0.5 indicating that  $NH_{4}^{+}$  cannot completely neutralize nss-SO<sub>4</sub><sup>2-</sup> and the remaining amount may be present as sulfuric acid reacting with dust and seasalt particles (Hsu et al., 2007).

The concentrations of  $NH_4^+$  and  $nss-SO_4^{2-}$  were highest during the inter-monsoon season with the respective mean concentrations of 0.31 and 1.6 µg m<sup>-3</sup> (Group I) compared to those observed during the NE monsoon (Group II, mean concentrations of 0.16 and 0.61 µg m<sup>-3</sup>, respectively) and the SW monsoon (Group III, mean concentrations of 0.04 and 0.28 µg m<sup>-3</sup>, respectively). However, the differences were insignificant (p > 0.140) and were mainly caused by their elevated levels observed in proximity to the southern tip of Sumatra (Indonesia) (S1 and S2, collected on 13–17 Sept 2004).

Concentrations of  $NO_3^-$  were low in the aerosol samples and close to the background concentration of 0.1 µg m<sup>-3</sup> (Savoie, 1989), except for samples S1 and S2. Higher concentrations have been reported for the Arabian Sea, in particular, during high dust loads from the Middle East (Savoie et al., 1987) or the Indian subcontinent (Johansen and Hoffmann, 2004). However, in this study, the air

Table 5

Mean concentrations and	d ranges of soluble	ions in µg m <sup>-3</sup> ir	n aerosols from this stud	y and the literature.
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	CIO (Group I), This study <sup>a</sup>	CIO (Group II), This study <sup>a</sup>	CIO (Group III), This study <sup>a</sup>	CIO, Savoie et al. (1987) <sup>,b</sup>	AS, Johansen and Hoffmann (2004) <sup>,a</sup>
Na <sup>+</sup>	4.0 (2.2–5.6)	1.7 (1.4–2.0)	3.3 (1.4–5.9)	2.9 (1.0)	0.84 (0.33-1.7)
$K^+$	0.37 (0.11-0.68)	0.16 (<0.06-0.36)	0.35 (0.23-0.90)		0.20 (0.06-0.45)
nss-K <sup>+</sup>	0.23 (<0.06-0.60)	0.19 (0.08-0.30)	0.23 (0.09-0.75)		0.16 (0.04-0.37)
Ca <sup>2+</sup>	0.76 (0.40-1.23)	0.33 (0.20-0.40)	0.30 (0.20-0.41)		0.39 (0.11-1.1)
nss-Ca <sup>2+</sup>	0.61 (0.25-1.0)	0.26 (0.13-0.34)	0.18 (<0.08-0.30)	0.01 (0.03)	0.36 (0.09-0.96)
$Mg^{2+}$	0.37 (<0.07-0.56)	0.21 (<0.07-0.45)	0.36 (0.15-0.56)		0.12 (0.05-0.21)
$NH_4^+$	0.31 (0.05-1.0)	0.16 (0.10-0.22)	0.05 (<0.02-0.13)		0.75 (0.24-1.5)
Cl <sup>-</sup>	6.4 (0.74-9.9)	2.2 (1.5-2.9)	4.5 (2.0-7.2)		0.66 (0.16-2.0)
nss-Cl <sup>-</sup>	0.54 (0.28-0.8)	all < 0	all < 0		all < 0
$NO_3^-$	0.57 (<0.04-2.4)	0.05 (<0.04-0.05)	0.05 (<0.04-0.05)	0.16 (0.05)	0.97 (0.39-1.7)
$SO_4^{2-}$	1.9 (0.21-4.3)	1.0 (0.89-1.16)	1.0 (0.38-1.8)		2.37 (1.6-5.7)
nss-SO <sub>4</sub> <sup>2-</sup>	1.6 (<0.10-3.8)	0.62 (0.4-0.74)	0.28 (0.12-0.36)	0.50 (0.17)	3.2 (1.4–5.4)

CIO: Central Indian Ocean (55°E–95°E, 5°N–25°S); AS: Arabian Sea (40°E–75°E, 5°N–25°N); SIO: Southern Indian Ocean (55°E–95°E, 25°S–35°S).

<sup>a</sup> Values in bracket are ranges.

<sup>b</sup> Values in brackets are standard deviations.



**Fig. 4.** Correlation between nss-SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> concentrations (in  $\mu$ g m<sup>-3</sup>). The line represents the best fit for data with an equation of NH<sub>4</sub><sup>+</sup> = 0.241 nss-SO<sub>4</sub><sup>2-</sup> + 0.031 ( $R^2$  = 0.9121, n = 16).

mass trajectory showed that air masses were derived primarily from oceanic regions traveling for 5 days without contact with land masses prior to collection (Fig. 1a-c).

The average contribution of ions to their total mass is shown in Fig. 2. The mean ion composition of aerosols is similar among the Groups I to III indicating similar physical and chemical processes during the course of the transport of air masses. Sea salt as NaCl contributed the majority of the mass of the aerosols with a contribution of about 73%. Among other ions, sulfate was the major contributor to the total mass of ions without significant differences between the groups. Nitrate was the only ion being significantly higher in Group I compared to Groups II and III, probably due to the influence of anthropogenic sources in Indonesia. We detected high  $NO_3^-$  concentrations in samples collected at S1 and S2 which were presumably affected by land masses originating from Indonesia.

#### 3.5. Sources of aerosols over the Indian Ocean

### 3.5.1. Anthropogenic sources

As expected, aerosols collected in proximity to land masses were more contaminated compared to those collected over pristine oceanic regions. However, aerosol concentration levels over small islands were remarkably high. Island-influenced stations include S4 (Cocos Keeling, Australia), S7 (Cargadoc Carajos, Mauritius), S9 (Dzaudzi, Mayotte), S11-S13 (Seychelles) and S14 (Gan, Maldives). Aerosols collected at the Seychelles were high in Zn whereas those over the island of Carjadoc Carajos seem to have contained high levels of Pb and Cu (Table 1). In comparison with concentration levels found at S1 in proximity to the Indonesian land masses and literature values on urban aerosols, those levels measured at S7, S11–S13 and S14 are very high. However, it has been shown that the Atmospheric brown cloud (ABC) from central Asia and Southeast Asia can pollute pristine sites in the Indian Ocean (Ramanathan et al., 2007), including the Maldives (Stone et al., 2007). Such pollution phenomenon may also explain the high concentrations of Zn, Pb, Cu and Cd observed at S5 and S15 during transects several hundred kilometers away from any land masses, and air masses collected were of maritime origin. The air mass trajectory constructed in this study in general does not support the influence of the ABC as a source of pollution in our study, as the collected air masses mainly originated from the Southern hemisphere. However, the air circulation and vertical mixing over the Indian Ocean can be very complex, and the upper troposphere of the CIO can be influenced by emissions from China due to outflows from the summer monsoon deep convection (Kunhikrishnan et al., 2004; Lawrence and Lelieveld, 2010). For this reason, we cannot entirely exclude the ABC as a potential source of the extreme high concentration levels and enrichment factors observed over the CIO. Nevertheless, local and regional sources could probably provide significant inputs of trace metals. For example, aerosol samples S10-S13 were collected within the Chagos Archipelagos and in proximity to a large joint US/UK naval support and refueling facility on Diego Garcia with 1500 military personal and 2000 contractors. Military activities can be a source for a wide range of contaminants including trace metals (Clausen et al., 2004; Clausen and Korte, 2009).

In addition, jet fuel combustion can also lead to air pollution similar to that in urban areas including Pb, Zn and Cd (Tesseraux, 2004). Industrial organic compounds were found at elevated levels close to Diego Garcia (Wurl et al., 2006a). Air masses traveled five days over the open ocean prior collection on the Chagos Archipelagos, and therefore activities on Diego Garcia were likely to be a local source of metal emissions. Furthermore, boat building, fishery (canning of fish) and construction industry on the Maldives (Chowdhury, 2008) were the likely additional local sources to the elevated concentrations of trace metals found at S14.

High concentrations of Al, an indicator for crustal origin of aerosols, at S7 (Cargadoc Carajos, Mauritius) suggest dust contribution from the island as air masses traveled at least five days over the open ocean prior to collection. Major volcanic activities of Piton de la Fournaise on Reunion, located 600 km south of S7, dispersed volcanic plumes in a cyclonic pattern to distances of up to 1000 km until 16 October 2004, but continual degassing might have contributed to trace metals on a regional scale up to the location S7. The importance of volcanic inputs from the Indonesia is further discussed in the following section.

# 3.5.2. Impact of volcanic activities on regional air pollution levels

Volcanoes constitute one of the most important natural sources of trace gases and heavy metals to the atmosphere (Mather et al., 2003) by passive degassing and eruptions. During the Jocara cruise, several violent volcanic eruptions occurred in the region of the Indian Ocean and it is likely that emissions from the eruptions of Mt Egon and Mt Rinjani between July and October 2004 had affected the aerosol concentrations and its chemical composition in the CIO as suggested by the air mass forward trajectory analysis (Fig. 5). Details on the volcanic activities of Mt Egon and Mt Rinjani are presented in Table 6. Air masses originating from Mt Egon and Mt Rinjani experienced strong vertical mixing from altitudes up to 5500 m within 5–10 days reaching low altitudes (<500 m). The remaining volcanic activities in the region had probably little or no impact on the concentration levels and composition of aerosols collected in this study. The aerosol samples collected at S1-S5 were likely influenced by volcanic plumes drifting westwards over the CIO (Fig. 5). These aerosol samples had a distinct chemical composition. The TSP concentrations in the oceanic aerosol samples S3–S5 were two-fold higher to the reported background concentration of 10  $\mu g\ m^{-3}$  in Japan (Lee et al., 2002). Typical atmospheric residence time of aerosols is one to two weeks (Papastefanou and Bondietti, 1991; Poet et al., 1972), and therefore aerosols emitted from Mt Egon and Mt Rinjani could have been collected during the course of sampling (S3-S5). Shorter atmospheric residence time for reactive sulfate-containing particles undergoing hygroscopic growth and relatively a long distance between sampling sites and the location of volcanic eruptions may explain our observation of low nss-SO<sub>4</sub><sup>2-</sup> concentrations in air masses impacted by the volcanic eruptions. Pfeffer et al. (2006) reported rapid wet deposition of  $SO_4^{2-}$  from volcanic emissions in Indonesia. Trace metals are relatively chemically unreactive and usually associated with smaller particles leading to long residence times in the atmosphere (see Section 3.4). However, some trace element minerals such as PbCl<sub>2</sub> are highly soluble and subjected to



**Fig. 5.** 10-day air mass forward trajectory for Mt Egon and Mt Rinjani during major volcanic activities and eruptions in 2004. Lines and areas represent typical transport of air masses. Mt Egon: 25 July (——), 3 Sept (………), 4 September (———), 6 September (hatched area I), 11 September (— … —). Mt Rinjani: 1–5 October (hatched area II).

rapid wet deposition (Pfeffer et al., 2006). For this reason, not all trace elements may undergo long range transport.

Interestingly, we found consistently elevated concentrations of V at stations S1–S6 impacted by major volcanic eruptions (Fig. 5). The concentrations of V in the aerosol samples S1-S5 were significantly higher (p = 0.004) compared to the samples S6–S16. In ash samples from Mt Copahue (Argentina) V was the highest in concentrations among 11 metals (Smichowski et al., 2003) whereas As were found in relatively higher concentrations compared to other anthropogenic metals. Although the chemical composition of volcanic ashes may vary with location and geological features, Kavalieris (1994) reported high V contents in fumarolic deposits at Merapi volcano, central Java indicating that volcanic eruptions in Indonesia are likely to be a source of high V emissions. In a global context, volcanic emission of vanadium account for approximately 25% of its total natural emission (Duce and Hoffman, 1976). Boström and Fisher (1971) reported high vanadium concentrations in sediments of the Indian Ocean with highest concentrations found in active ridge sediments closed to land masses. They suggested that submarine volcanism is an important source of vanadium in the

#### Table 6

Details on volcanic activities for Mt Egon and Mt Rinjani between July and Oct 2004.

Date	Description of volcanic activities
Mt Egon (Location: 122	.45°E 8.67°S, Summit: 1703 m)
25 July 2004	Eruption for 2.5 h. Ejected thick black plume about
	1000–1500 m above summit
27 Aug 2004	Increased volcano activity with plumes ejected about
	300 m above summit
3 Sept 2004	Strong eruptions with ash plumes ejected about
	1000 m above summit
4 Sept 2004	Strong eruptions with ash plumes ejected about
	3000 m above summit
6 Sept 2004	Strong explosion released ash plumes to about
	2500 m above summit
11 Sept 2004	Major eruptions with ash plumes ejected about
	5000 m above summit
13 Sept 2004	Continue eruptions with release of ash plumes
Mt Rinjani (Location: 1	16.47°E 8.42°S, Summit: 3726 m)
18 Aug 2004	Start of increased number of tectonic earthquakes
Since Sept 2004	Increased volcanic activities
23–26 Sept 2004	Registration of tremors with amplitudes of 12
	-13.5 mm for 90-290 s
1 Oct 2004	Major eruption
2-5 Oct 2004	Continued eruptions ejected ash plumes to about 300
	-800 m above summit

Indian Ocean, and it generally supports our suggestion of high V emissions from terrestrial volcanic activities in Indonesia. Furthermore, V and As were below 0.25 and 0.15 ng m<sup>-3</sup> respectively over the Indonesian land masses (Maenhaut et al., 2002), and with comparison of concentrations levels detected at S1-S6 we can exclude anthropogenic emissions (e.g. oil combustion) from Indonesia as a major contamination source. V was also a minor component in aerosols detected in the urban areas of Jakarta (Kondo et al., 2007). Smichowski et al. (2003) reported that Cr was depleted in volcanic ash samples. Aerosol samples S1-S5 had significantly lower concentrations of Cr (p = 0.0001) compared to the samples S6-S16 (Table 1). Mukai and Suzuki (1996) used V as a tracer to investigate the impacts of volcanic plumes from Mt Sakurajima to air pollution levels over the Japan Sea. Overall, it is suggested that air pollution levels over the CIO could be affected greatly by volcanic emissions from the Indonesian land masses, at least during the inter-monsoon periods when westerly zonal winds dominate air circulations.

# 4. Conclusions

Air masses collected from August 2004 to August 2005 over the equatorial Central Indian Ocean contained aerosols that vary in their chemical characteristics. Overall, the air masses collected south of the equator were found to be polluted, in contrast to previous studies suggesting a high level of air pollution in the northern hemisphere of the Indian Ocean. All aerosol samples show a signature of influences from metal emissions reflected in large enrichments of typical anthropogenic and natural tracers. The natural contribution of metal sources is highly pronounced in the first 5 samples. Volcanic eruptions occurring before and during sample collection had a great influence on the atmospheric pollution levels of the CIO, south of the equator. The concentrations of nss-K<sup>+</sup>, a typical tracer for biomass burning, were in general low as for the nitrogenous (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and sulfurous (SO<sub>4</sub><sup>2-</sup>) ions. No significant differences were observed in the concentrations of anions, cations and metals between the NE and SW monsoons, and the inter-monsoon period.

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### Appendix. Supplementary information

Supplementary information related to this article can be found online at doi:10.1016/j.atmosenv.2011.10.066.

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