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Particulate Matter and Associated Metal Levels in a Conservation Area in the Remaining Tropical Forest of Mata Atlântica, Brazil

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Ilha Grande is located in the south east of the State of Rio de Janeiro. The nearest point from the Brazilian coast is three kilometer away. The island is a conservation area in the remaining forest of Mata Atlântica, in the Brazilian South East coast and is part of the Biosphere Reserve of the UNESCO. The island covers an area of 193 km^2 and has a total population of 5,000 people. The main characteristic of the area is the lack of industrial and vehicular emissions. The only economic activities are fishing and ecological tourism. The population is concentrated in the north coast, in the villages of Abrão, Araçatiba, Bananal, Enseada das Estrelas, Saco do Céu, Sítio Forte, Enseada de Palmas, Vermelha e Itaguaçú (IG 2006).

The samples were collected at Dois Rios (Figure 1) in the south oceanic coast, at about 30 km from the populated region. In the north region no vehicles are used except for the police and the fire brigade cars. In the sampling area a small vehicle, fueled by diesel, is used five times in the week to transport goods and people to and from the Environmental Research Center (CEADS). This base is home to about 40 scientists and support personned of the Oceanographic Department of Rio de Janeiro State University (UERJ 2006).

MATERIALS AND METHODS

The monitoring campaign was performed in the period March to June 2005. Total suspended particulate matter (TSP) and particulate matter with diameter less than 10 μm (PM10) samples were taken in the period. Samplings were carried out during 24h, using two high volume sampler (Sibata, Model HVC 500) with a flow rate of aspiration of 500 L min^{-1} and a teflon filter (Gelman) with a porosity of 0.8 μm and a diameter of 100 mm. The samplers were located two meters above the ground, in two different locations approximately 20 m apart.

TSP and PM10 were determined gravimetrically, by drying and weighing the filters to constant weight. For analysis of trace metals, the filters were extracted by adding 5mL of nitric acid (Merck Suprapur 65%), 2 mL of hydrochloric acid (Merck Suprapur 36%) and 10 mL of ultrapure water (18MΩ cm^{-1} of specific resistivity) in a pyrex tube and standing for two hours at 95^0C.

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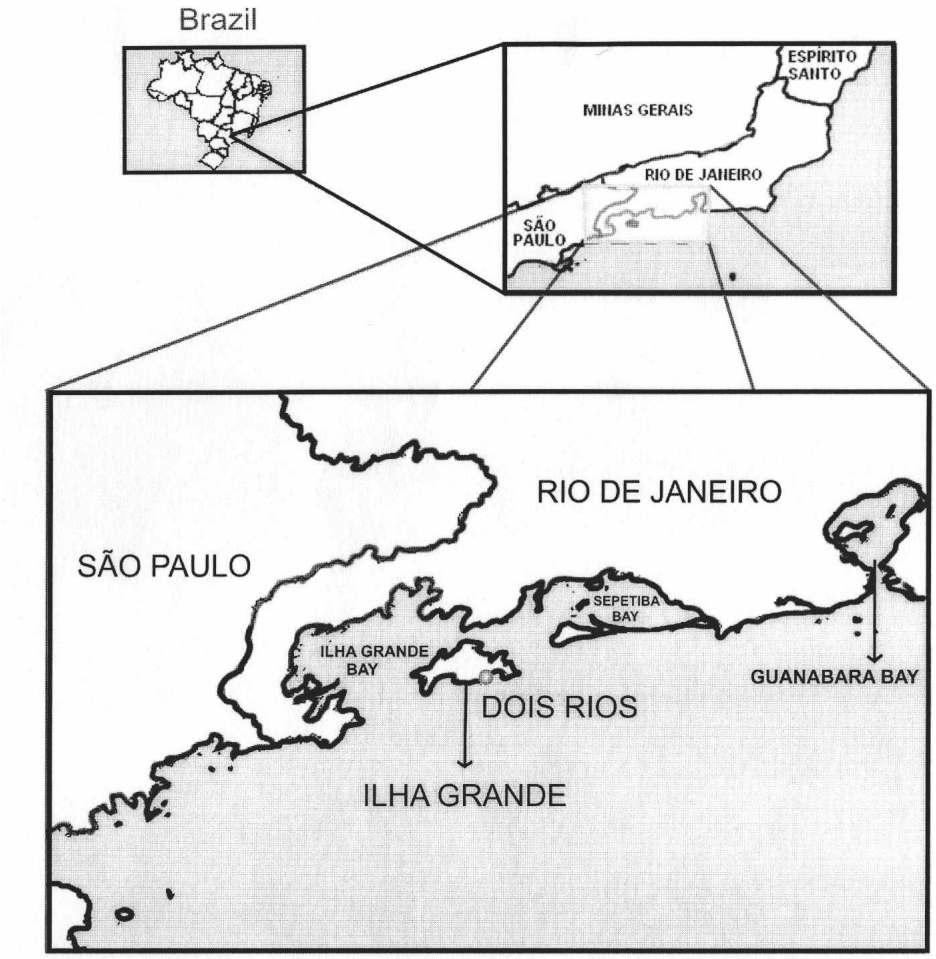

Figure 1. Location of the sampling site (Ilha Grande, Brazil).

The extracted solution was filtered, made to 50mL with ultrapure water and kept in pre-cleaned polyethylene bottles in the refrigerator until analysed (Beceiro Gonzalez et al. 1997; Quiterio et al., 2004a,b, 2005a; Serrano et al. 1996). Trace metal analysis was performed by Inductively Coupled Plasma Atomic Emission, Optima 3000 Perkin Elmer, with an atomic absorption spectrophotometer (ICP–OES), following Method IO–3.4 (1999).

Detection limits were computed as three times the standard deviation of the distribution of outputs for ten repeated measurements of the standard, which contained no metals (Boss and Fredeen 1999). These limits were calculated as 0.5 ng m^{-3} for Zn, Cu and Pb, 1 ng m^{-3} for Mn, 3 ng m^{-3} for Fe, Co, Cr and Al, 5 ng m^{-3} for Ni and Cd. The accuracy of the method was evaluated using a standard reference material (111355 ICP multi element Standard Solution IV from Merck)

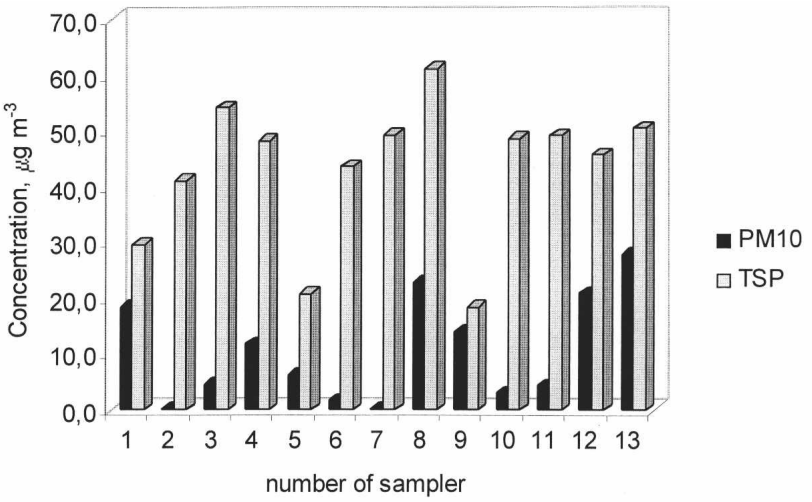

Figure 2. Levels of TSP and PM10 for Ilha Grande, Brazil (24h sampling).

(Merck, 2006). The obtained results were in the range of the reference material.

RESULTS AND DISCUSSION

Measured levels of TSP and PM10 for the 28 samples are shown in Figure 2. Primary national standards, for 24h samplings, are 240 and 150 μg m^{-3} for TSP and PM10, respectively. The secondary national standards are 150 μg m^{-3}, for both TSP and PM10 (CONAMA 1990).

Mean monthly values are (in units of μg m^{-3}): 29.7 (March), 42.8 (April), 44.6 (May) and 50.4 (June) for TSP and 18.4 (March), 4.1 (April), 13.1 (May) and 27.9 (June) for PM10. For TSP, the primary and secondary national standards (annual geometrical mean) are 80 and 60 μg m^{-3}, respectively (CONAMA 1990). For PM10, the annual arithmetic mean is 50 μg m^{-3} for both, primary and secondary national standards. Since data in this study were taken in a limited period of four months and were not collected every six days, these results are not directly comparable to the standards.

Mean TSP concentration for the period is 2.6 times the mean PM10 level. As known, geological material, as soil dust, is predominantly in the coarse particle size range and consists of oxides of aluminium, silicon, calcium, titanium, iron, depending of the geological area and anthropogenic activities. About 50% is in the PM10 fraction (Chow and Watson 1992). PM10 values at Mc Murdo Station, Antarctica, were reported by Mazzera et al. (2001) for the austral summers of 1995-1996 and 1996-1997. Average PM10 concentrations at Hut Point (downwind) and Radar Sat (upwind) were 3.4 and 4.1μg m^{-3}, respectively. Also

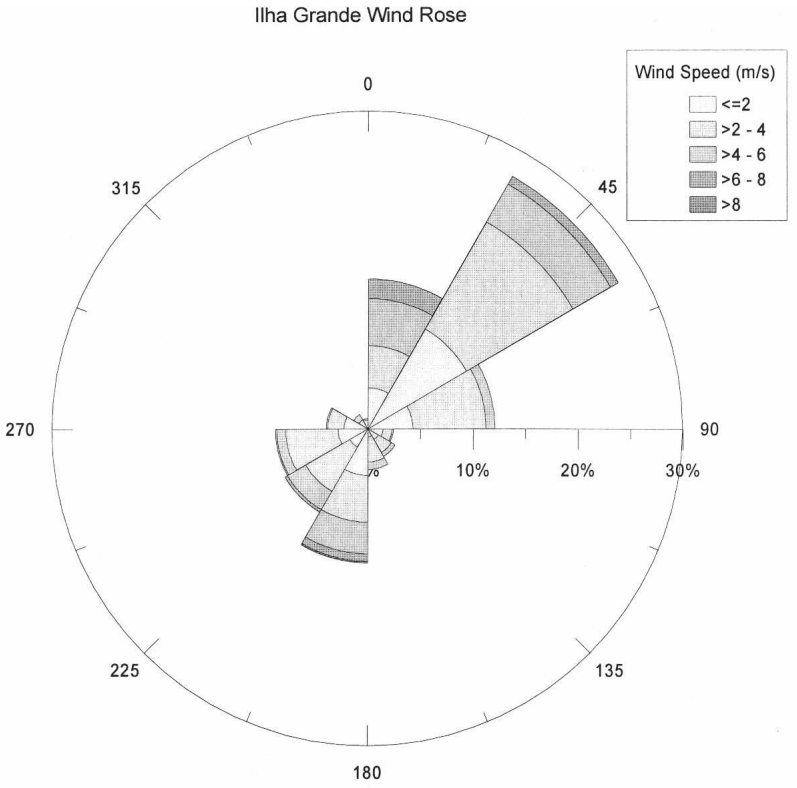

Figure 3. Mean wind frequencies over the studied period (March – June 2005).

Chow et al. (1996) reported a value of 7.3 μg m^{-3} for Pt. Reyes, CA, a remote coastal site, during summer 1990.

Values for Ilha Grande are in the range 0.1 – 27.9 μg m^{-3} (the mean value for the period being 15.9 μg m^{-3}). For comparision, Mazzera et al. (2001) reported that the highest values for PM10 were 10.4 and 16.6 μg m^{-3} for the Hut Point and Radar Sat, respectively. Values in Ilha Grande are, in general, higher than in Antarctica, due to ressuspension of soils and the contribution of airflow from the continent.

The prevailing surface wind direction over the island is from the continent, mainly from the industrial area of Santa Cruz, in the west region of the Metropolitan Region of Rio de Janeiro. The average surface wind speed and temperature in the sampling period were 3.0 m s^{-1} and 24.0 ^{0}C, respectively.

Mean wind frequencies over the studied period are shown in Figure 3.

Mean values for the concentrations of metals in TSP and PM10 are presented in

Table 1. Mean values for the concentrations of metals in TSP and PM10, in Ilha Grande, Brazil, for the period March – June 2005. Typical values for remote areas and EPA and WHO standards are shown for comparision.

	Concentrations (ng m^{-3})											
Local / TSP	**Ca**	**Mg**	**Mn**	**Fe**	**Zn**	**Cu**	**Cr**	**Co**	**Ni**	**Al**	**Cd**	**Pb**
This study[1]	134	230	2.6	101	12.1	1.6	<dl	<dl	<dl	61.2	<dl	0.7
EPA[2]	nd	nd	500	nd	nd	nd	100	nd	0.24	10	6.37	1500
WHO[3]	nd	nd	150	nd	nd	nd	11-130	nd	0.38	nd	5	500
Gipps Ice Rise[4]	nd	nd	nd	nd	0.0061	0.001	nd	nd	nd	0.194	0.00006	0.0047
Beethoven Peninsula[5]	nd	nd	nd	nd	0.0068	0.0058	nd	nd	nd	nd	0.0004	<0.0072
Crescent Scarp[5]	nd	nd	nd	nd	0.0122	0.0095	nd	nd	nd	nd	0.0003	<0.0099
South Pole[6]	nd	nd	nd	0.63	nd	nd	nd	0.39	nd	1.18	nd	nd
South Pole[7]	nd	nd	0.18	0.25	0.077	0.0790	0.011	0.0004	nd	0.32	<0.2	nd
King Sejong Antarctic[8]	nd	nd	nd	nd	0.133	0.143	0.114	0.0018	8.26	1.88	0.0014	0.041
Local / PM10	**Ca**	**Mg**	**Mn**	**Fe**	**Zn**	**Cu**	**Cr**	**Co**	**Ni**	**Al**	**Cd**	**Pb**
This study[1]	14.6	25.6	0.6	46.1	0.8	0.3	<dl	<dl	<dl	4.4	<dl	<dl
Mc Murdo Station (Hut Point)[9]	125	239	2.5	130	1.5	0.19	0.28	0.07	nd	181	nd	0.85
Mc Murdo Station Radar Sat Dome)[9]	128	254	3.5	164	0.86	0.20	0.4	0.12	nd	254	nd	0.47

Notes:

References (Rf): 1-This study; 2-ATSDR 2002, 3-WHO 2002 4-Dick et al. 1991; 5- Dick & Peel 1985; 6-Tuncel et al 1989; 7- Cunningham & Zoller 1981; 8-Mishra et al. 2004; 9-Mazzera et al. 2001

dl: detection limit

Table 1. For comparision, results for remote regions as well as USA national standards and WHO guidelines are included. As commonly found concentrations of metals of crustal origin (Ca, Mg, Fe, Al) exhibit enhanced values relative to anthropogenic elements (Cheng et al. 2005). For these metals, concentrations in TSP are 2.2 – 9.1 times the levels in the PM10 fraction. Mishra et al. (2004) suggested the division in three broad categories: high (above 0.1 ng m^{-3}), intermediate (0.01 – 0.1 ng m^{-3}) and low (below 0.01 ng m^{-3}). According to this classification, Ca, Mg, Mn, Fe, Zn, Cu, Al and Pb are in high concentrations in comparision to remote areas.

Concentrations in this study are higher than those found at the King Sejong Station, Antarctica Peninsula (Mishra et al. 2004) in TSP. In general, levels of metals in PM10 are lower than those determined by Mazzera et al. (2001) at Mc Murdo Station, Antarctica, except for Zn and Cu which have similar concentrations.

As previously determined for Mc Murdo Station, these values cannot be explained without considering local contamination and transport from the industrial and urban regions of the continent.

Enrichment factors (EF) were calculated, using Mg as reference (Caroli et al. 1996, Wedepohl 1995), as 13 and 10 for Zn and Cu, respectively, suggesting a possibly important role of anthropogenic process in this site. Both local (fuel burning for power generation, ships, police, fire brigade and Research Center's cars) and distant (from the continent) sources may be considered.

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