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# Lead adsorption in the clay fraction of two soil profiles from Fildes Peninsula, King George Island

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**Abstract:** Antarctica is considered the most isolated continent, but it is not free of pollution, which arrives at specific localities mainly as a result of tourism and research activities. Among environmentally harmful substances, heavy metals are especially important because of their high toxicity to organisms. The aim of this study was to estimate the maximum adsorption of lead (Pb) onto the clay fraction of samples from two soil profiles from the Fildes Peninsula, King George Island, South Shetland Islands. Experimental data were fitted to the Langmuir isotherm, and the adsorption parameters were correlated to mineralogical attributes of this soil fraction characterized by chemical extractions and X-ray diffraction. Values of maximum adsorption of Pb in the clay fraction were extremely high (maximum value: 322 581 mg kg$^{-1}$) when compared to those of soil samples from other regions of the world. Adsorption occurred in two stages: first stage in which a high percentage of Pb was adsorbed, and second stage in which adsorption was lower. From an environmental point of view, soils with high contents of clay and amorphous minerals, ones usually associated with ornithogenic activity in Antarctica, should have greater efficiency in filtering Pb, thus reducing risks of leaching and groundwater contamination.

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**Key words:** allophone, amorphous minerals, chemisorptions, imogolite, Langmuir isotherm, Maritime Antarctic, ornithogenic activity

## Introduction

Although it is the most isolated continent on Earth, Antarctica is not free of pollution. Fishing, tourism and research activities bring thousands of people, boats and various environmental impacts to specific sites and coastal areas of the continent every year. Antarctica also receives continuous continent-wide deposition of windborne pollutant-containing particles (Sheppard *et al*. 2000). Among substances harmful to the environment, heavy metals merit special attention because of their high toxicity to organisms.

Some researchers have already documented contamination sources related to hydrocarbons (Ferguson *et al*. 2003) and heavy metals (Sheppard *et al*. 2000, Santos *et al*. 2005, Townsend *et al*. 2009), introduced by human activity. Sheppard *et al*. (2000) analysed some areas near Scott Base, Antarctica, and at least one sample in each area had Pb levels above the background levels of the site. This was attributed to battery leaks and paint waste containing the metal. Santos *et al*. (2005) studied soils and coastal sediments of Admiralty Bay, King George Island, and found that house paint and oil were the main sources of heavy metals in sediments. Soils collected near the Commandante Ferraz station on King George Island had low Pb levels (11.5 mg kg$^{-1}$). In the sub-Antarctic, soils from Atlas Cove, Heard Island, showed contamination by heavy metals around the old station but not at levels likely to produce a significant potential toxic impact on local ecosystems (Stark *et al*. 2003). At Casey Station Cunningham *et al*. (2005) found a strong relationship between metal concentrations in soil and water and the composition of diatom communities. The Polar Regions are different to other parts of the world, for example, toxicology data using local species, are not available for the Antarctic and setting of triggers and targets are particularly significant in remote regions, where the costs of site clean-up may be orders of magnitude greater than in more populated parts of the world (Snape *et al*. 2003).

No studies to date have examined the relationship between the composition of Antarctic soils and their adsorption of heavy metals. Studies focusing on adsorption of pollutants in different soil constituents can provide information about their interactions with soil colloids and their partition among various soil constituents (Appel *et al*. 2008). Such data can

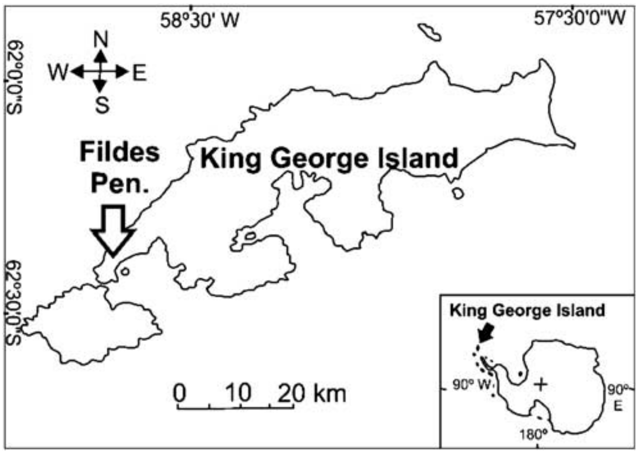

**Fig. 1.** Location of the study site on the Fildes Peninsula of King George Island (large map) and its location in Antarctica (inset).

help to predict the degree of vulnerability of Antarctic soil in response to the growing human occupation.

The vulnerability of the environment is directly proportional to the capacity of a soil for retaining pollutants. Environmental risks become greater when the amount of heavy metals exceeds the adsorptive capacity of the soil, which leads to leaching and groundwater contamination. Among the tools used to evaluate the adsorption of heavy metals in soils are the Langmuir and Freundlich isotherms (Sinegani & Araki 2010). Adhikari & Singh (2003) studied the Pb and Cd adsorption capacity of different Indian soils and found maximum adsorption ranging from 62.5–123.4 mg kg$^{-1}$ from the Langmuir equation. The authors suggested that the most important factors related to sorptive capacity of soils were cation exchange capacity, pH, organic matter, clay and $CaCO_3$ content, presenting positive statistical correlations between these parameters and adsorption data.

Sinegani & Araki (2010) evaluated Pb adsorption in soils from temperate and semi-arid regions of Iran and observed a good fit of the experimental data to the Langmuir and Freundlich isotherms. The concentrations added to the soils ranged from 2–150 mg l$^{-1}$, and the values of maximum adsorption estimated by the Langmuir equation ranged from 23.8–39.4 mmol kg$^{-1}$. Higher levels of adsorption were observed in temperate than in semi-arid soils, as result of high clay content, cation exchange capacity, organic matter and Fe and Al crystalline and Al amorphous minerals in this environment (Sinegani & Araki 2010).

Because of the adverse formation conditions, which include low temperatures and low availability of liquid water, Antarctic soils are rich in poorly crystalline minerals (Simas *et al.* 2006) such as allophane and imogolite. These minerals have high specific surface area and high pH-dependent surface charge density (due to aluminol (Al-OH) and silanol (Si-OH) groups), which may determine the high adsorption capacity of these colloids.

Thus, the objective of this study was to estimate the maximum adsorption capacity of Pb in the clay fraction of two soil profiles associated with ornithogenic activities from King George Island, using the Langmuir isotherm. Correlations between adsorption parameters estimated by the isotherm and mineralogical soil attributes were also calculated.

## Material and methods

### *Study area and soil sampling and characterization of two soil profiles*

The study was carried out on the Fildes Peninsula, the largest ice-free area of King George Island, South Shetland Islands, Maritime Antarctica (Fig. 1). At each site pits were dug to bedrock or to the permafrost table (Table I) and soil in all genetic horizons sampled. Collected soils were air-dried and sieved at 2-mm to obtain fine earth for further analysis.

**Table I.** Overview and clay and total organic carbon (TOC) contents of soil profiles from Fildes Peninsula, Maritime Antarctica.

| Altitude (m) | Co-ordinates | Site description | Horizon | Depth (cm) | Morphology | | Clay | TOC |
|---|---|---|---|---|---|---|---|---|
| | | | | | Structure[1] | Consistency[2] | (g kg$^{-1}$) | |
| Profile 1 - Turbic Mollic Cryosol (Ornithic, Oxyaquic, Arenic) | | | | | | | | |
| 38 | UTM 21S WGS 84<br>Lat 0400086<br>Long 3100498 | Upper third ramp, with a colony of papua penguins, and colonization by algae stems. | A1 | 0–10 | SB, M, Sm | H, Sr, Spl, S | 65 | 13.6 |
| | | | A2 | 10–30 | SB, M, Sm | H, St, SPl, S | 90 | 6.2 |
| | | | C1 | 30–40 | SG | SH, St, SPl, SS | 90 | 3.5 |
| Profile 2 - Turbic Histic Cryosol (Ornithic, Reductaquic) | | | | | | | | |
| 42 | UTM 21S WGS 84<br>Lat 400037<br>Long 3100511 | Flat surface with indirect influence of active penguin colony, colonization by mounds of moss; permafrost at 70 cm deep. | A | 0–10 | Ma | H, St, NPl, S | 78 | 8.6 |
| | | | Bp | 10–30 | Ma | H, St, NPl, S | 200 | 4.8 |
| | | | Bp2 | 30–60 | Ma | H, St, NPl, S | 160 | 9.8 |

[1] Structure: type (L = lumps, SG = simple grains, AB = angular blocks, SB = subangular blocks, Ma = massive); development degree (S = strong, M = moderate); size (Sm = small, VS = very small, Me = medium).

[2] Dry consistency (So = soft, SH = slightly hard, H = hard); wet consistency (VF = very friable, Fr = friable, St = steady); plasticity (Pl = plastic, NPl = non plastic, SPl = slightly plastic); stickiness (S = sticky, NS = not sticky, SS = slightly sticky).

**Table II.** Contents of oxides obtained by sequential extractions with sodium pyrophosphate (PYR), ammonium oxalate (AO) and NaOH in the clay fraction of soils from the Fildes Peninsula, Maritime Antarctica.

| Horizon | Depth | PYR | | | | AO | | | | NaOH | | | | TCMR[2] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (cm) | $Al_2O_3$ | $Fe_2O_3$ (g kg$^{-1}$) | $SiO_2$ | SUM[1] | $Al_2O_3$ | $Fe_2O_3$ (g kg$^{-1}$) | $SiO_2$ | SUM[1] | $Al_2O_3$ | $Fe_2O_3$ (g kg$^{-1}$) | $SiO_2$ | SUM[1] | (g kg$^{-1}$) |
| Profile 1 – Turbic Mollic Cryosol (Ornithic, Oxyaquic, Arenic) | | | | | | | | | | | | | | |
| A1 | 0–10 | 26.9 | 41.0 | 2.1 | 70.0 | 11.3 | 29.2 | 3.4 | 43.9 | 1.2 | 0.4 | 12.7 | 14.3 | 673 |
| A2 | 10–30 | 32.6 | 58.5 | 3.0 | 94.1 | 15.0 | 40.0 | 3.8 | 58.8 | 1.2 | 0.24 | 12.5 | 13.9 | 705 |
| C1 | 30–40 | 23.9 | 58.9 | 5.7 | 88.5 | 17.1 | 51.9 | 2.4 | 71.4 | 3.6 | 0.08 | 4.6 | 8.3 | 630 |
| Profile 2 – Turbic Histic Cryosol (Ornithic, Reductaquic) | | | | | | | | | | | | | | |
| A | 0–10 | 8.0 | 10.9 | 2.2 | 21.1 | 12.1 | 32.2 | 5.2 | 49.5 | 4.5 | 0.1 | 6.4 | 11.0 | 380 |
| Bp | 10–30 | 7.2 | 8.9 | 2.1 | 18.1 | 14.2 | 31.5 | 5.1 | 50.8 | 5.2 | 0.04 | 3.3 | 8.6 | 376 |
| Bp2 | 30–60 | 14.7 | 16.1 | 2.3 | 33.1 | 18.3 | 29.6 | 5.4 | 53.4 | 5.9 | 0.04 | 4.3 | 10.2 | 438 |

[1] SUM = sum of the contents of Al, Fe and Si oxides of the corresponding extraction.
[2] TCMR = total clay mass removal by sequential treatments with PYR, AO and NaOH, following the method presented by Simas *et al.* (2006).

These soil were developed from andesitic basalts or moraines formed by similar volcanic rock fragments related to the advances and retreats of the Collins Glacier. Soils were moderately drained and erosion was not apparent, with gentle relief and slopes of less than 5%. Soils were classified using the World Reference Base of Soil Resources (ISSS 1998) (Table I). Clay content (pipette method - Gee & Bauder 1986) and total organic carbon content (wet combustion method - Yeomans & Bremner 1988) were determined in soil samples (Table I).

### *Clay fraction characterization*

Forty grams of < 2 mm air-dried soil samples were shaken in 100 ml of pH 10.0 de-ionized water (1 g of $Na_2CO_3$ in 10 l of de-ionized water) using an orbital shaker at 120 oscillations min$^{-1}$. We avoided using basic substances, such as 0.2 M NaOH, because of the predominance of amorphous mineral material in the Antarctic soils (Simas *et al.* 2006). The sand fraction was retained in a 0.053-mm mesh sieve, and silt and clay fractions collected in 1000 ml cylinders and separated by sedimentation (Gee & Bauder 1986). Due to the small amount of clay (Table I), this procedure was repeated an average of ten times to obtain enough clay for all analytical procedures. Untreated clay samples were subjected to the following sequential extraction (Simas *et al.* 2006): 0.1 M sodium pyrophosphate (PYR) (Dahlgren 1994), 0.2 M ammonium oxalate (AO) (Schwertmann 1973), 0.5 M NaOH (Jackson *et al.* 1986, modified by Melo *et al.* 2002).

The Al, Fe and Si concentrations were determined by inductively coupled plasma - atomic emission spectrometry (ICP-AES) in a Perkin Elmer, Optima 3300 DV model, with axial vision, radio frequency power of 1300 W and 40 MHz, plasma gas flow of 15 l min$^{-1}$ and auxiliary gas flow of 0.7 l min$^{-1}$. The wavelengths used were (nm): Al - 308.2, Fe - 238.2 and Si - 251.6. The results were converted to percentages of Al, Fe and Si oxides (Table II).

The choice of this sequential extraction method was to characterize quantitatively and chemically the amorphous minerals present in high concentration in the clay fraction of Antarctic soils (Simas *et al.* 2006), since the X-ray

**Table III.** Mineralogical composition of the clay fraction determined by X-ray diffraction (XRD) and differential X-ray diffraction (DXRD) of soils from the Fildes Peninsula, Maritime Antarctica.

| Horizon | Depth (cm) | XRD | | DXRD |
|---|---|---|---|---|
| | | Clay fraction without treatment[1] | Clay fraction after treatment for 2:1 minerals[2] | Amorphous minerals |
| Profile 1 - Turbic Mollic Cryosol (Ornithic, Oxyaquic, Arenic) | | | | |
| A1 | 0–10 | mn, pl, mi, le, ja | - | allophane and imogolite |
| A2 | 10–30 | le, pl, mn, mi, il, ja, fd | - | allophane and imogolite |
| C1 | 30–40 | mn, le, px, mi, fd | ch | imogolite |
| Profile 2 - Turbic Histic Cryosol (Ornithic, Reductaquic) | | | | |
| A | 0–10 | mn, le, ka, mt, hb | ch | allophane and imogolite |
| Bp | 10–30 | le, mn, mt, pl, mi, hb | ch | allophane and imogolite |
| Bp2 | 30–60 | pl, le, mn, mt, ka | ch | allophane and imogolite |

[1] ch = chlorite, ka = kaolinite, fd = feldspar, hb = hydrobiotite, il = ilite, ja = jarosite, mt = metavariscite, mn = minyulite, le = leucophosphite, pl = plagioclase, px = pyroxene, mi = mica. The ordering of the minerals in the clay sample without treatments followed the decreasing intensity of their reflections by XRD.
[2] Treatment for identifying 2:1 clay minerals: Mg saturation and ethyleneglycol solvation, K saturation and heating (Whittig & Allardice 1986).

diffraction (XRD) is not, by itself, able to provide numerical data which can be analyzed quantitatively. Such extraction allowed us to divide the different phases of amorphous minerals: linked to the organic matter (extracted by PYR); Fe, Al and Si oxides (extracted by AO) and aluminosilicates (extracted by NaOH). Classical methods of sequential analysis, such as Tessier (Tessier *et al.* 1979), are not used for mineralogical characterization but for partial extraction of the crystalline minerals, in studies of speciation of the total content of heavy metals from soil and clay samples. In these classical methods, each sequential step only determines different forms of heavy metals (soluble, exchangeable, carbonates, organic matter, Fe and Mn oxides, and residual).

Approximately 0.5 g of untreated clay and part of the residue of sequential extractions (PYR, AO and NaOH) was used for mineralogical characterization of samples by XRD (powder method). X-ray diffraction patterns were obtained in a diffractometer with a vertical goniometer, using an angular velocity of 0.5° $2\theta$ min$^{-1}$, range 2–50° $2\theta$, equipped with a Cu tube and a Ni filter. The X-ray tube was operated at 20 kV and 40 mA. Differential XRD (DXRD) was obtained by subtracting the patterns of the clay treated with PYR and AO and also by subtracting the patterns of AO and NaOH (Dahlgren 1994).

To achieve differentiation of 2:1 phyllosilicate minerals, such as smectite, vermiculite and chlorite, samples of untreated clay (Whittig & Allardice 1986) were subjected to the following treatments: Mg saturation, Mg saturation and ethylene glycol solvation, K saturation and air drying, K saturation and drying at 550°C. After these treatments, samples were mounted on glass slides (oriented samples) and analysed by XRD in a range from 3–15° $2\theta$. Mineralogical clay composition is presented in Table III.

### *Pb adsorption in the clay fraction*

The clay samples used in the Pb adsorption experiment were standardized by the following procedures: pH adjusted to 6.0, freeze-dried by lyophilisation, and sieved through a 0.053-mm sieve. Samples of 0.3 g of clay was used, in duplicate, in polyethylene (PET) tubes. The samples were suspended in 15 ml of 0.001 M $Na(NO)_3$ (used as a support electrolyte) and ten Pb concentrations in the form of $Pb(NO)_3$: 0, 200, 1000, 2000, 5000, 10 000, 20 000, 30 000, 40 000, and 60 000 mg kg$^{-1}$ (Dias *et al.* 2001, with modifications). Preliminary tests indicated that the high doses used in this experiment were necessary.

In summary, the factorial arrangement was as follows: four samples were analysed (two horizons of profile 1 and two horizons of profile 2) using, for this case, two PET tubes (i.e. two replicates) and ten concentrations, following a strict analytical control to prevent contamination between samples and to ensure the reliability of results. In total, analysis was made of 80 clay samples.

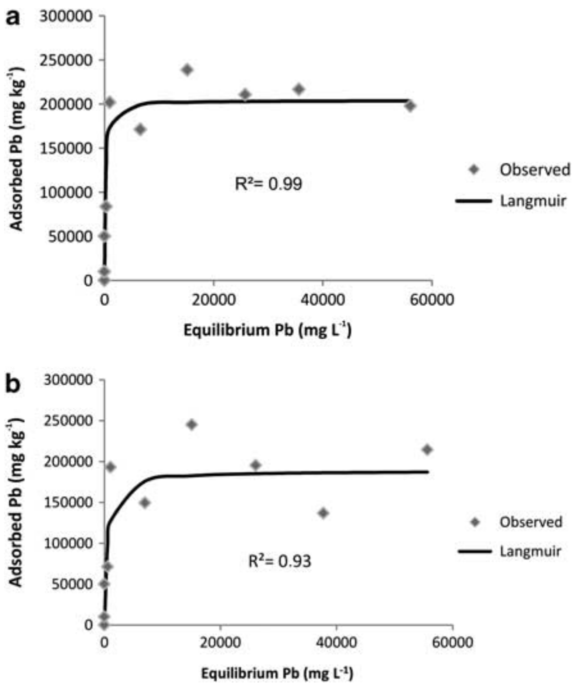

**Fig. 2.** Pb adsorption on clay fractions in the **a.** A2, and **b.** C1 horizons of profile 1 from Fildes Peninsula, Maritime Antarctica.

The tubes were shaken in an orbital shaker at 120 oscillations min$^{-1}$ for 24 hours at 22°C. The contents of the tubes were centrifuged at 24 456 xg for 10 min. Pb concentrations were determined by atomic absorption spectrophotometry, in a Varian AA240FS model, with

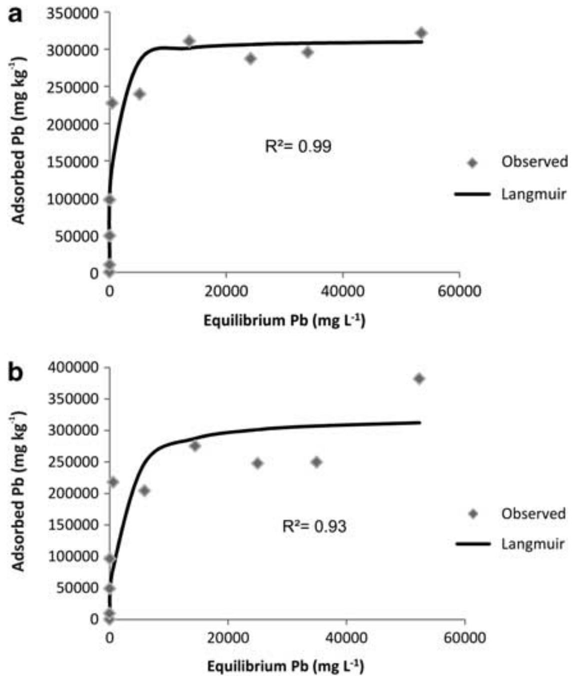

**Fig. 3.** Pb adsorption on clay fractions in the **a.** Bp, and **b.** Bp2 horizons of profile 2 from Fildes Peninsula, Maritime Antarctica.

**Table IV.** Percentage of adsorbed Pb in relation to added concentrations in the clay fraction of soils from the Fildes Peninsula, Maritime Antarctica.

| Pb | Profile 1 | | Profile 2 | |
|---|---|---|---|---|
| (mg kg$^{-1}$) | A2 | C1 | Bp | Bp2 |
| | | (%) | | |
| 200 | 99 | 98 | 100 | 100 |
| 1000 | 99 | 99 | 100 | 100 |
| 2000 | 99 | 98 | 85 | 72 |
| 5000 | 91 | 88 | 81 | 79 |
| 10 000 | 48 | 41 | 34 | 30 |
| 20 000 | 32 | 28 | 24 | 25 |
| 30 000 | 19 | 17 | 14 | 13 |
| 40 000 | 15 | 13 | 11 | 7 |
| 60 000 | 11 | 13 | 7 | 7 |

wavelength range of 185–900 nm, focal length of 250 mm and wavelength slew rate of 2000 nm min$^{-1}$. The adsorbed concentration was calculated based on the amount of Pb (in mg) added to each sample, on the amount of Pb in solution (equilibrium concentration) and on the mass of the sample used in the experiment. To obtain the adsorption parameters we used the Langmuir isotherm: $x = (K\ C\ b) / (1 + K\ C)$, in which x is the amount of Pb adsorbed per unit of mass of clay, C is the concentration of Pb in equilibrium solution, b is the maximum adsorption, and K is affinity constant. The contents of $Al_2O_3$, $SiO_2$ and $Fe_2O_3$ obtained from sequential extractions, and the total mass of the clay fraction removed by extraction with PYR, AO and NaOH were correlated with the Langmuir isotherm parameters (K and b) using the program Statistica for Windows® (StatSoft 2007).

## Results

Considering that PYR, AO and NaOH preferentially extract amorphous minerals, the levels of these minerals in the clay fraction should be between 376 and 705 g kg$^{-1}$ (Table II). These contents were estimated by mass reduction of the clay samples after sequential treatments with PYR, AO and NaOH.

The maximum dose used in the adsorption experiment (60 000 mg kg$^{-1}$) was not sufficient to attain the plateau in the isotherm for two samples, collected in the most superficial soil layers of two profiles (A1 and A). Since the horizons A1 and A of profiles 1 and 2, respectively, did not attain the plateau in the Pb adsorption, the results presented in this work do not show the results of these two horizons. For the other four soil samples, the coefficients of determination of Langmuir isotherms were higher than 0.9 (Figs 2 & 3).

**Table V.** Langmuir constants (affinity constant (K) and maximum adsorption (b)) for Pb adsorption in the clay fraction of soils from the Fildes Peninsula, Maritime Antarctica.

| Profile | Horizon | Depth (cm) | K | b (mg kg$^{-1}$) |
|---|---|---|---|---|
| 1 | A2 | 10–30 | 0.00195 | 312 500 |
| | C1 | 30–40 | 0.00056 | 322 581 |
| 2 | Bp | 10–30 | 0.00581 | 204 082 |
| | Bp2 | 30–60 | 0.00193 | 188 680 |

**Table VI.** Correlation coefficients of regression analysis between mineralogical attributes and the adsorption parameters K (affinity constant) and b (maximum adsorption) estimated by the Langmuir isotherms of soils from the Fildes Peninsula, Maritime Antarctica. Values and meanings of mineralogical parameters are presented in Tables II & III.

| Parameter | K | b |
|---|---|---|
| $Al_2O_3$ PYR | $-0.72^{ns}$ | $0.85^{ns}$ |
| $Fe_2O_3$ PYR | $-0.74^{ns}$ | 0.98* |
| $SiO_2$ PYR | $-0.70^{ns}$ | $0.78^{ns}$ |
| SUM PYR | $-0.75^{ns}$ | 0.96* |
| $Al_2O_3$ AO | $-0.69^{ns}$ | $-0.12^{ns}$ |
| $Fe_2O_3$ AO | $-0.65^{ns}$ | $0.90^{ns}$ |
| $SiO_2$ AO | $0.64^{ns}$ | $-0.93^{ns}$ |
| SUM AO | $-0.77^{ns}$ | $0.84^{ns}$ |
| $Al_2O_3$ NaOH | $0.37^{ns}$ | $-0.85^{ns}$ |

*Significant at 5%.
PYR = sodium pyrophosphate, AO = ammonium oxalate, ns = not significant.

The highest percentages of Pb adsorption were found when low metal concentrations were added to the soil sample (Table IV). In profile 1, almost 100% of added Pb was adsorbed, up to the concentration of 2000 mg kg$^{-1}$. On the other hand, only 7% of total added Pb remained adsorbed in Bp and Bp2 horizons (profile 2) at the highest concentration (60 000 mg kg$^{-1}$).

The values of maximum Pb adsorption (b parameter in the Langmuir equation) were extremely high, with a maximum value of 322 581 mg kg$^{-1}$ to the C1 horizon of profile 1 (Table V). For the affinity constant (K) the values were higher for soil samples from the upper horizons of both profiles (0.00581 for Bp and 0.00195 for A2) (Table V).

A significant and positive correlation was observed between maximum Pb adsorption capacity and $Fe_2O_3$ and total oxides ($Al_2O_3 + Fe_2O_3 + SiO_2$) extracted by PYR. Other clay mineralogical parameters did not correlate significantly with maximum adsorption and the affinity constant (Table VI). A high and positive correlation was also observed between $Fe_2O_3$ extracted by AO and b Langmuir parameter ($r = 0.90$), however, these data were not statistically significant due to the low number of observations in this work ($n = 4$).

Samples with higher concentrations of Fe-AO had the lowest levels of Si-AO (Table II), resulting in negative correlations between these soil attributes (Table VI) and between Si-AO levels and maximum Pb adsorption values ($r = -0.93$; Table VI).

## Discussion

The two profiles can be considered a good indication of soil behaviour in the case of a Pb contamination in the selected area. Michel (2011) studied the morphology of 50 soil profiles scattered over the Fildes Peninsula and only 10% showed any difference in the parent material observed here (andesitic basalts related to the advances and retreats of the Collins Glacier), with the influence of sulfide-bearing in the andesites. The formation of almost 50% of these soils was affected by ornithogenic activities, a condition also observed in the two profiles in the present study. In Maritime Antarctica ornithogenic activity (mainly penguins) accelerates soil genesis, formation of clay and poorly crystalline minerals and induces the process of phosphatization and precipitation of crystalline phosphates (Simas *et al.* 2006).

Some authors have observed a similarly good fit of the Langmuir isotherm to adsorbed Pb in different soils (Veeresh *et al.* 2003, Zuhairi 2003, Serrano *et al.* 2005). The progressive decrease in the percentages of Pb adsorption (Table IV) as a response to increasing rates of added metal is related to continuous saturation of the binding sites of colloids. Other authors have reported the same behaviour for adsorption of heavy metals in Indian soils (Dutta & Singh 2011) and in amorphous iron oxyhydroxide (Benjamin & Leckie 1981). Dutta & Singh (2011) observed that when more Pb is available in solution, the amount of Pb adsorption increased too. At the same time, the percentage of Pb adsorbed decreased because the quantity of binding sites decreases.

The results for maximum Pb adsorption (Table V) highlight the high cation adsorptive capability of the clay fraction of analysed soils from Antarctica. Adhikari & Singh (2003) used Pb concentrations ranging from 0–90 mg $l^{-1}$ in 24-hour equilibrium experiments and two temperatures (24 and 45°C) in soils from five different and representative agro-ecological zones in India and found Pb maximum adsorption (b Langmuir values) ranging only from 62.5–123.4 mg $kg^{-1}$. The larger b value was observed in a Vertic Ustochrept Soil (USDA Soil Taxonomy Classification), which the authors associated with soil physical properties, such as pH, cation exchange capacity and organic matter content.

The Pb adsorption capacity of the clay fraction of these ornithogenic soils (Table V) is very favourable from an environmental standpoint because it represents a high capacity for filtering heavy metals, which may compensate for the low levels of this colloidal fraction in the soils ($\leq$ 200 g $kg^{-1}$; Table I). It may also reduce the potential of human activities in Antarctica for contaminating groundwater in the studied soils. Simas *et al.* (2006) worked with soil profiles scattered in King George Island, and found lower concentration of amorphous minerals extracted with the same methods (PYR, AO and NaOH) in basaltic non-ornithogenic soils (mean of 198 g $kg^{-1}$) in relation to ornithogenic ones (mean of 566 mg $kg^{-1}$, close to the present study value of 533 mg $kg^{-1}$; Table II). These data indicate that the non-ornithogenic soils in Antarctica must have a lower potential for heavy metal adsorption and other studies must be done to confirm this tendency. The main problem in Antarctica in relation to Pb leaching must be the soils formed almost exclusively by physical weathering. Most soils studied by Navas *et al.* (2008) have their development mainly associated with physical weathering and cryogenic processes causing the rock to disintegrate. In addition to various mineralogical constituents, other characteristics important for the retention of pollutants in soil are, for example, the presence (or absence) of vegetation and the level of organic matter.

Sequential extraction allowed the quantification of amorphous minerals in different phases, such as those linked to organic matter (extracted by PYR); Fe, Al and Si oxides (extracted by AO) and aluminosilicates (extracted by NaOH) (Table II). Differential X-ray diffraction was also effective at detecting allophane and imogolite in the clay fraction (Table III). The high contents of these minerals phases in Antarctic soils highlights the differences in pedogenetic conditions, for example, in comparison to humid tropics. Melo *et al.* (2002) studied clay samples of Bw horizons of Oxisols from different regions of Brazil, using a sequential extraction procedure similar to the present study, and found that the content of amorphous minerals estimated by AO and 0.5 mol $l^{-1}$ NaOH amounted to only 36 g $kg^{-1}$. The allophane and imogolite detected by DXRD in the clay fraction (Table III) have high specific surface area and a high density of hydroxyl groups (Al-OH and Si-OH) whose surface charge is pH dependent (Perrot 1977).

Some work carried out on Fildes Peninsula and near that area, suggests that the clay content is relatively low (Jie *et al.* 2000) and the origin of the clay minerals is generally more from physical weathering than from chemical weathering, although the climate is warmer and more humid than other regions of Antarctica (Jeong & Yoon 2001). The major classes of soil minerals in Fildes Peninsula, generally, are smectite, chlorite and interstratified illite-smectite and chlorite-smectite (Jeong *et al.* 2004). However, these studies did not use specific chemical or physical methods to study amorphous minerals in the clay fraction.

The correlations between maximum adsorption capacity and total oxide contents extracted by PYR (Table VI) highlight the importance of amorphous metal-complex organic matter extracted by Na pyrophosphate (Dahlgren 1994) in heavy metals adsorption. The high positive correlation found between the levels of Fe oxide extracted by AO and maximum Pb adsorption was due to the high specific surface area of the oxides extracted by AO (levels ranging between 29.6 and 51.9 g $kg^{-1}$; Table II). The zero point of charge (ZPC) of such oxides is high, ranging from 7–9 (Schwertmann & Taylor 1989), and the predominance of protoned ferrol groups ($-FeOH^{-0,5}$ and $-FeOH_2^{+0,5}$) favours the isotopic exchange of H and $H_2$ by $Pb(OH)^+$ and $Pb^{2+}$ (chemisorption or specific adsorption) (Backers *et al.* 1995). The pH of the clay samples was adjusted to 6.0 before the Pb adsorption experiment (pH less than ZPC of the oxide). The negative correlation between the maximum adsorption and

$SiO_2$-AO (Table VI) was attributed to low contents of this oxide (Table II), which means lower formation of silanol groups (Si-OH) and the formation of negative charge for non-specific adsorption of Pb.

According to the Langmuir isotherm, the adsorption of ions to soil colloids occurs as a monolayer on the surface and maximum adsorption occurs when the surface is completely covered (Fontes & Alleoni 2006). However, adsorption may have exceeded the double diffuse layer due to the large number of adsorption sites (high density of surface negative charge and high specific surface area of amorphous minerals), so that the stoichiometry between the negative charge of colloids and the positive charges of $Pb^{2+}$ or $Pb(OH)^+$ was not achieved.

Regarding the affinity constant (K value of the Langmuir isotherm), some researchers have observed a strong affinity between Pb and Cd (Serrano *et al*. 2005) and Cs (Campbell & Davies 1995) and soil samples from superficial horizons, as observed in the present work for Pb in both soil profiles (Table V). In the clays of profile 1, due to the higher adsorption capacity in relation to profile 2, adsorption may have occurred in more layers of Pb around the particles, which increased the maximum adsorption (b value), but reduced the energy or adsorption affinity (K value) (Table V). One piece of evidence for this behaviour was the opposite signs of the coefficients of correlation between K and b values and the mineralogical parameters. For example, once the occurrence of complexes of Fe-organic matter ($Fe_2O_3$-PYR) was greater, maximum adsorption increased ($r = 0.98$) and binding affinity decreased ($r = -0.74$) (Table VI). Appel & Ma (2002) also observed that the amount of Pb sorbed was much larger than the amount of negative surface charge for samples of an Oxisol, suggesting both inner- and outer-sphere reactions. According to the authors, Pb had a higher affinity for soil sorption sites, as confirmed by its ability to take part in inner-sphere surface reactions, and the adsorption of Pb was divided into two steps. In the first step, Pb was retained by specific forces, such as chemisorption. In the second step, the remaining Pb was retained by simple electrostatic attraction in the diffuse double layer. In the present study, the following groups present in the amorphous minerals must have improved specific adsorption: aluminol (-AlOH) in the allophane and imogolite, ferrol (-FeOH) in the Fe oxides (AO extraction), aluminol in the aluminosilicates (NaOH extraction) and carboxylic and phenolic in the organic matter (PYR extraction).

Veeresh *et al*. (2003) and Serrano *et al*. (2005) observed an inflection point in their adsorption data of Pb, Cd and Ni, with two clearly defined stages. In the first phase, a rapid adsorption at low metal concentrations was found in sites with strong affinity for the element (chemisorption) and high K Langmuir value. This was followed by a phase at high metal concentrations, in which the adsorption occurred on low-energy sites (reversible adsorption). In samples from all soil horizons of the present study, a significant decrease (about 50%) was observed in the percentage of Pb adsorption as a response to increasing concentration of the metal from 5000 to 10 000 $mg\,kg^{-1}$ (Table IV). Specific Pb adsorption in the soil colloids reflects lower environmental risk, since this stronger binding makes Pb desorption and the contamination of groundwater less likely. In Antarctica, ornithogenic activity (penguins and skuas) accelerates soil genesis and the formation of clay and poorly crystalline minerals (Simas *et al*. 2006) and should result in environments that are less vulnerable to leaching of contaminants such as Pb.

## Conclusions

The Langmuir isotherm was a suitable tool for analysis and the values of maximum Pb adsorption of the clay fractions of the ornithogenic soils were very high compared to the other regions of the planet, making Antarctica a unique environment. This behaviour reflected the richness of the clay fraction in amorphous minerals.

It is clear that Pb adsorption occurs in more than one stage: the first when a higher content is adsorbed on the clay fraction and the second when the percentage decreases, until stabilization. The adsorption in the first stage is more environmentally positive, since this stronger binding makes Pb desorption less likely.

From an environmental point of view, soils rich in amorphous minerals, usually associated with ornithogenic activity in Antarctica, should have greater efficiency in filtering Pb, thus reducing Pb leaching and groundwater contamination. Further studies must be done in order to check this behaviour in non-ornithogenic Antarctic soils, which normally are less developed and have lower amorphous minerals in the clay fraction. Only after study of a great number of soil profiles in a specific Maritime Antarctic region, such as Fildes Peninsula, will it be possible to predict the degree of vulnerability of those soils in response to human occupation.

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## References

Adhikari, T. & Singh, M.V. 2003. Sorption characteristics of lead and cadmium in some soils of India. *Geoderma*, **114**, 81–92.

Appel, C. & Ma, L.Q. 2002. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of Environmental Quality*, **31**, 581–589.

Appel, C., Ma, L.Q., Rhue, R.D. & Reve, W. 2008. Sequential sorption of lead and cadmium in three tropical soils. *Environmental Pollution*, **155**, 132–140.

Backers, C.A., McLaren, R.G., Rate, A.W. & Swift, R.S. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Science Society of America Journal*, **59**, 778–785.

Benjamin, M.M. & Leckie, J.O. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science*, **79**, 209–221.

Campbell, L.S. & Davies, B.E. 1995. Soil sorption of caesium modelled by the Langmuir and Freundlich isotherm equations. *Applied Geochemistry*, **10**, 715–723.

Cunningham, L., Raymond, B., Snape, I. & Riddle, J. 2005. Benthic diatom communities as indicators of anthropogenic metal contamination at Casey Station, Antarctica. *Journal of Paleolimnology*, **33**, 499–513.

Dahlgren, R.A. 1994. Quantification of allophane and imogolite. *In* Amonette, E. & Zelazny, L.W., *eds. Quantitative methods in soil mineralogy*. Madison, WI: Soil Science Society of America, 430–448.

Dias, N.M.P., Alleoni, L.R.F., Casagrande, J.C. & Camargo, O.A. 2001. Isotermas de adsorção de cádmio em solos ácricos. *Revista Brasileira de Engenharia Agrícola e Ambiental*, **5**, 229–234.

Dutta, S. & Singh, D. 2011. Sorption and desorption behavior of lead in four different soils of India. *Agricultural Sciences*, **2**, 41–48.

Ferguson, S.H., Franzmann, P.D., Revill, A.T., Snape, I. & Rayner, J.L. 2003. The effects of nitrogen and water on mineralisation of hydrocarbons in diesel-contaminated terrestrial Antarctic soils. *Cold Regions Science and Technology*, **37**, 197–212.

Fontes, M.P.F. & Alleoni, L.R.F. 2006. Electrochemical attributes and availability of nutrients, toxic elements, and heavy metals in tropical soils. *Scientia Agricola*, **63**, 589–608.

Gee, G.W. & Bauder, J.W. 1986. Particle-size analysis. *In* Klute, A., *ed. Methods of soil analysis. Part 1. Physical and mineralogical methods*. Madison, WI: Soil Science Society of America, 383–412.

ISSS Working Group RB. 1998. *World reference base for soil resources*. World Soil Resources Reports, No. 84. Rome: FAO, 165 pp.

Jackson, M.L., Lim, C.H. & Zelazny, L.W. 1986. Oxides, hydroxides, and aluminosilicates. *In* Klute, A., *ed. Methods of soil analysis. Part 1. Physical and mineralogical methods*. Madison, WI: Soil Science Society of America, 101–150.

Jeong, G.Y. & Yoon, H.I. 2001. The origin of clay minerals in soils of King George Island, South Shetland Islands, West Antarctica, and its implications for the clay mineral compositions of marine sediments. *Journal of Sedimentary Research*, **71**, 833–842.

Jeong, G.Y., Yoon, H.I. & Lee, S.Y. 2004. Chemistry and microstructures of clay particles in smectite-rich shelf sediments, South Shetland Islands, Antarctica. *Marine Geology*, **209**, 19–30.

Jie, C., Zitong, G. & Blume, H.P. 2000. Soils of Fildes Peninsula, King George Island, the Maritime Antarctic: Part I. Formation process and pedogenetic particularities. *Chinese Journal of Polar Science*, **11**, 25–38.

Melo, V.F., Schaefer, C.E.G.R., Novais, R.F., Singh, B. & Fontes, M.P.F. 2002. Potassium and magnesium in clay minerals of some Brazilian soils as indicated by a sequential extraction procedure. *Communication in Soil Science and Plant Analysis*, **33**, 2203–2225.

Michel, R.F.M. 2011. *Classificação, cobertura vegetal e monitoramento térmico da camada ativa de solos da Península Fildes, Ilha Rei George e Ilha Ardley, Antártica Marítima*. PhD thesis, Universidade Federal de Viçosa (Minas Gerais, Brazil), 251 pp. [Unpublished].

Navas, A., López-Martínez, J., Casas, J., Machín, J., Durán, J.J., Serrano, E., Cuchi, J.A. & Mink, S. 2008. Soil characteristics on varying lithological substrates in the South Shetland Islands, Maritime Antarctica. *Geoderma*, **144**, 123–139.

Perrot, K.W. 1977. Surface charge characteristics of amorphous aluminosilicates. *Clays and Clay Minerals*, **25**, 417–421.

Santos, I.R., Silva-Filho, E.V., Schaefer, C.E.G.R., Albuquerque-Filho, M.R. & Campos, L.S. 2005. Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin*, **50**, 185–194.

Schwertmann, U. 1973. Use of oxalate for Fe extraction from soils. *Canadian Journal of Soil Science*, **53**, 244–246.

Schwertmann, U. & Taylor, R.M. 1989. Iron oxides. *In* Dixon, J.B. & Weed, S.B., *eds. Minerals in soil environments*, 2nd ed. Madison, WI: Soil Science Society of America, 379–438.

Serrano, S., Garrido, F., Campbell, C.G. & García-González, M.T. 2005. Competitive sorption of cadmium and lead in acid soils of Central Spain. *Geoderma*, **124**, 91–104.

Sheppard, D.S., Claridge, G.G.C. & Campbell, I.B. 2000. Metal contamination of soils at Scott Base, Antarctica. *Applied Geochemistry*, **15**, 513–530.

Simas, F.N.B., Schaefer, C.E.G.R., Melo, V.F., Guerra, M.B.B., Saunders, M. & Gilkes, R. 2006. Clay-sized minerals in permafrost-affected soils (Cryosols) from King George Island, Antarctica. *Clays and Clay Minerals*, **54**, 721–736.

Sinegani, A.A.S. & Araki, H.M. 2010. The effects of soil properties and temperature on the adsorption isotherms of lead on some temperate and semiarid surface soils of Iran. *Environmental Chemistry Letters*, **8**, 129–137.

Snape, I., Riddle, M.J., Filler, D.M. & Willians, P.J. 2003. Contaminants in freezing ground and associated ecosystems: key issues at the beginning of the new millennium. *Polar Record*, **39**, 291–300.

Stark, S.C., Gardner, D., Snape, I. & McIvor, E. 2003. Assessment of contamination by heavy metals and petroleum hydrocarbons at Atlas Cove Station, Heard Island. *Polar Record*, **39**, 397–414.

StatSoft Inc. 2007. *Statistica for Windows*. Version 8.0. Microsoft Corp. www.statsoft.com.

Tessier, A., Campbell, P.G.C. & Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51**, 844–851.

Townsend, A.T., Snape, I., Palmer, A.S. & Seen, A.J. 2009. Lead isotopic signatures in Antarctic marine sediment cores: a comparison between 1 M HCl partial extraction and HF total digestion pre-treatments for discerning anthropogenic inputs. *Science of the Total Environment*, **408**, 382–389.

Veeresh, H., Thipathy, S., Shaudhuri, D., Hart, B.R. & Powell, M.A. 2003. Sorption and distribution of adsorbed metals in three soils of India. *Applied Geochemistry*, **18**, 1723–1731.

Whittig, L.D. & Allardice, W.R. 1986. X-ray diffraction techniques. *In* Klute, A., *ed. Methods of soil analysis. Part 1. Physical and mineralogical methods*. Madison, WI: Soil Science Society of America, 331–362.

Yeomans, J.C. & Bremner, J.M. 1988. A rapid and precise method for routine determination of organic carbon in soil. *Communications in Soil Science and Plant Analysis*, **19**, 1467–1476.

Zuhairi, W.Y.W. 2003. Sorption capacity on lead, copper and zinc by clay soils from South Wales, United Kingdom. *Environmental Geology*, **45**, 236–242.