

A clean protocol for determining ultralow heavy metal concentrations: its application to the analysis of Pb, Cd, Cu, Zn and Mn in Antarctic snow

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ABSTRACT

Clean laboratory facilities and procedures established in the laboratory of Polar Research Center of Korea Ocean Research & Development Institute, which are used to determine various heavy metals at or below the pg g^{-1} concentration level encountered in Antarctic snow, are described. They include production of ultrapure water, careful choice of proper laboratory materials and reagents and methods for cleaning sample storage bottles, containers and other labware in a Class 100 clean room. Preliminary results of Pb, Cd, Cu, Zn and Mn concentrations in 10 Antarctic surface snow samples were obtained by graphite furnace atomic absorption spectrometry using the clean protocols described. Eight of the samples were collected at King Sejong in King George Island and two at Ruperto Elichiribehety at the northern tip of the Antarctic Peninsula in the framework of joint research between Korea Ocean Research & Development Institute and Uruguayan Antarctic Institute. Our data represents that sea salt spray is a major source of the atmospheric Cd and Zn in King George Island. For Pb, its concentrations in snow are likely to be largely influenced by local emissions at sites near the Antarctic stations. At Ruperto Elichiribehety, the concentration levels of all five heavy metals measured in snow are found to be highly elevated when compared with those at King Sejong. This is due mainly to a remarkable influence of local crustal inputs on heavy metals distribution.

Key Words: Antarctic snow, heavy metals, clean procedure, blank, preconcentration, pollution

Introduction

The Antarctic snow and ice caps preserve a record of large-scale changes in various atmospheric compositions over time. In this context, numerous studies have been undertaken to unravel valuable clues in understanding the past large-scale environmental changes of the Earth's atmosphere, based on temporal variations in concentrations of elements of interest in these frozen archives (see, e.g., Barnola et al., 1987; De Angelis et al., 1987; Delmas et al., 1992; Petit et al., 1999). They have indeed provided precious information on natural variability of the composition (especially, greenhouse gases and aerosols) of the ancient atmosphere characterized by a strong correlation with Antarctic temperature changes.

An assessment of the global atmospheric pollution by heavy metals is of special concern, in view of the fact that environmental metal pollution has become a global phenomenon (Nriagu, 1990). To elucidate to what extent and also from what time global contamination by anthropogenic heavy metals occurred, various investigations have been performed to determine the occurrence of some metals such as Pb, Cd, Cu and Zn and to reconstruct a reliable time series for these metals in the Antarctic snow and ice (see, e.g., Boutron and Patterson, 1987; Görlach and Boutron, 1992; Wolff and Suttie, 1994; Hong et al., 1998). Although such investigations give access to an outline of the human perturbation of the distribution of certain heavy metals in the remote Antarctic environment, however, the lack of comprehensive data hampers still to integrate a large spatial and temporal variation in heavy

metals concentrations. This is mainly because the extremely low concentrations at or below the pg g^{-1} level ($1 \text{ pg g}^{-1} = 10^{-12} \text{ g g}^{-1}$) of most of the metals to be measured make the skills, effort and understanding of ultra-trace analysis required for obtaining reliable data. The reliable measurement of such a low metal concentration demands unequivocally very meticulous control of artificial contamination introduced during the whole procedures of sample collection, handling and analysis.

Up to now, only a few research groups have produced reproducible data on changes in the occurrence of various heavy metals in Antarctic snow and ice, using strict contamination control during the collection, handling and analysis of samples. Polar Research Center (PRC) of Korea Ocean Research & Development Institute (KORDI) has since two years ago established ultraclean facilities and analytical procedures designed to reduce and control the contamination for the determination of heavy metals at ultralow concentrations in various environmental samples. For that, the use of a clean laboratory together with very careful choice of labware, ultrapure water and reagents is mandatory to reduce the risk of contamination (Patterson and Settle, 1976; Boutron, 1990; Howard and Statham, 1993; Nriagu et al., 1993). This paper describes in some detail our all practical procedures employed in the laboratory and recent results obtained from its application to the determination of heavy metals in Antarctic surface snow. From our preliminary results obtained, relative contributions of natural and anthropogenic sources in snow deposited at coastal Antarctic sites near the stations in King George Island and at the northern tip of the Antarctic Peninsula are also assessed and then discussed.

Clean Laboratory Facilities

Since contamination is a major factor affecting reliable measurement of heavy metals and of other elements at extremely low concentrations, special precaution and clean procedures for minimizing artificial contamination are absolutely necessary in the laboratory. Successful trace metal analyses are based on carefully designed and executed protocols, which in turn are based upon knowledge of potential problems, which can arise during the work.

A Class 100 clean room

The determination of ultralow trace metals must be performed in a “dust-free” clean laboratory pressurized with air filtered through high efficiency particulate (HEPA) filters. A schematic plan of the Class 100 clean room used at PRC of KORDI is shown in Fig. 1. It was made of transportable container which measures 5.90 m long \times 2.35 m wide \times 2.39 m high (external dimension). The internal structure is divided into two rooms: 1.00 m long \times 2.24 m wide ante-room and 4.48 m long \times 2.24 m wide clean room (internal dimension). External air is first prefiltered through 2 prefilters (610 \times 305 \times 20 mm thick), 1 carbon-coated prefilter (610 \times 305 \times 20 mm thick) and 1 medium filter (610 \times 305 \times 150 mm thick) located inside an antechamber of air supply. And then prefiltered external air is flushed into the clean room through 6 HEPA filters (610 \times 610 \times 150 mm thick) attached to the ceiling of the clean room. In the case of the prefilters and medium filter, they are often changed (every 2 to 4 weeks for prefilters and 2 months for medium filter) at need. Air supply to the clean room is 4400 m³/h made up of 20% prefiltered external air and 80% recirculating air. The clean room is

maintained at a positive pressure.

Where practical, the fixtures and fittings in the clean room are fabricated from plastic materials to remove a possible metal corrosion due to acid vapor in the clean room, which makes very serious problems of contamination. The walls and ceiling are made out of 5-mm thick sheets of polyvinyl chloride (PVC) and any unavoidable metal surfaces are coated with epoxy resin. Various workbenches and shelves are entirely made of polypropylene.

Although the entire clean room is pressurized with air filtered by 6 HEPA filters, the cleanliness in the area between HEPA filters is suspected to be no better than the Class 100 level. All the cleaning of laboratory materials, sample handling and analytical procedures are, therefore, done on the workbench placed directly under the HEPA filters. In fact, an average of particulate count above 0.5 μm in the working space flushed directly with laminar flow clean air through HEPA filters is found to be less than 10 particles/ m^3 . At all times, the analysts wear full clean room clothing with a hair cap, boots and disposable polyethylene gloves, because they are a primary source of contamination in the clean laboratory environment.

Production of ultrapure water and selective use of various reagents

The purity of water used in the laboratory is of great concern for reducing the metal contents of the analytical water and thus for increasing the reliability of the measurement of trace metals of interest at extremely low concentrations in natural water samples. Various available methods of water purification are used in different laboratories to produce ultrapure water (Loss and Rosman, 1987; Boutron, 1990; Suttie and Wolff, 1992a; Barbante et al., 1999).

They include the use of high purity mixed bed ion exchange resins, of the sub-boiling distillation stills made of quartz or Teflon, of reverse osmosis (RO) system, or of a combination of at least two steps of these techniques. For example, ultrapure water used at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), Grenoble, France, is produced by passing tap water through a succession of activated charcoal and mixed bed ion exchange resins columns (Boutron, 1990). At British Antarctic Survey (BAS), Cambridge, UK, ultrapure water is derived from two steps: ordinary tap water is first deionised and then doubly distilled in a glass still; the preliminarily purified water is subsequently fed into a modified Milli-Q purification system (Suttie and Wolff, 1992a).

The ultrapure water used in our laboratory is derived from three-stage distillation processes within the clean room. Ordinary tap water is first filtered through 1 micro prefilter and 1 carbon prefilter and then purified with Millipore RO water purification system (Model Elix-3) combined with the electrodeionization module. The output from this unit is fed into 30-l polyethylene reservoir, which is protected against external airborne contaminants, and stored for direct use or further purification. The first purified RO water is then fed into Milli-Q purification system (Millipore Corp., Model Milli-Q Academic) consisting of an Q-Gard purification pack, a Quantum ultrapure cartridge, and a Millipak filter unit (0.22 μm). The heavy metals concentrations of Pb, Cd, Cu, and Zn in the Milli-Q ultrapure water produced in the second stage are given in Table 1. They represent that Cu and Zn contents in Milli-Q ultrapure water are comparatively higher than those in ultrapure water used at LGGE and BAS, while Pb and Cd concentrations are found to be comparable.

Although ultrapure water produced from Milli-Q system in our laboratory is considered to

have proper water quality for ultratrace heavy metals investigation in Antarctic snow and ice, we pass the Milli-Q ultrapure water through a sub-boiling distillation still (Berghof BSB-939-IR, Germany) exclusively made of PTFE or PFA Teflon only as a further purification process to reduce the blank values. The sub-boiled water is produced at a rate of 1200 ml per 24 hours directly into an acid leached 1000-ml PFA Teflon bottle. When produced into a PFA Teflon bottle, it is transported to an acid cleaned 20-l low-density polyethylene (LDPE) container and stored until use. The heavy metals concentrations in Teflon sub-boiled water are shown to decrease a factor of 3 for Pb and Cd and to a lesser extent a half for Cu and Zn (Table 1). This water is used for the final washing stages during the cleaning of labware and for the preparation of reagents and reference standards. The ultrapure water so produced by the Milli-Q system and a Teflon sub-boiling distillation still in our laboratory are preferentially used in different analytical steps in purpose to be mentioned in next sections.

The purity of reagents used in the laboratory also becomes a critical factor ensuring the reliable measurement of all trace analysis (Howard and Statham, 1993). In our laboratory, HNO₃ is the most extensively used mineral acid both for the cleaning of laboratory materials and during the pretreatment of samples to be measured (see next section). The reagent grade HNO₃ from Merck is used for the first acid cleaning baths and for the cleaning of polyethylene bags, in which the acid cleaned bottles and containers are packed. Merck “Suprapur” grade HNO₃ is dispensed for the second acid cleaning baths and for the first cleaning stages of the LDPE vials for the autosampler equipped to a graphite furnace atomic absorption spectrometry (GFAAS) and of the tips of micropipettes. As for the purest HNO₃, which is used for the third and fourth acid cleaning baths (see next section), for acidifying

samples and GFAAS reference standards and for the final cleaning stages, we purchase ultrapure “Optima” grade HNO₃ from Fisher. The certified Pb, Cd, Cu, and Zn concentration values given by the manufacturer for this acid are as follows: <1 pg g⁻¹ for Pb, Cd and Mn and <2 pg g⁻¹ for Cu and Zn.

Besides several purity grades of HNO₃, Merck “Suprapur” grade HCl and HF are employed for the first rinse solution for containers and small items made of Teflon. In addition, reagent grade chloroform is widely used to remove grease or other production-derived impurities from new labware surface at the early stage of the cleaning procedure (see next section).

Selection of laboratory materials

All the common items of laboratory equipment such as storage bottles, beakers, flasks, pipettes etc., which contact directly the samples to be analyzed, play an important role in trace analysis, because it may introduce contaminants into the samples or present an active surface onto which the analyte may be absorbed, and hence lost from solution (Moody and Lindstrom, 1977; Howard and Statham, 1993). The accuracy of ultralow heavy metals concentrations determined will therefore be highly dependent upon the prudent choice of laboratory materials and the adopted cleaning procedures of these items. Careful selection of material for trace analysis application will vary from element to element and with the analytical sequence to be used. In our laboratory, the best choice of laboratory materials is mainly based on those employed by C. Patterson and coworkers at the California Institute of Technology (CIT) for their Pb analysis (Patterson and Settle, 1976) and by C. Boutron and coworkers at LGGE for

the measurement of heavy metals in polar snow and ice (Boutron, 1990).

In brief, LDPE sample bottles and containers (volumes ranging from 15 ml up to 20 l and fitted with a polypropylene cap) are always used when temperature and acid concentrations are not too high. We purchase them from Nalgene, Nalge Company, Rochester, New York, USA. When commercially available, FEP or PFA Teflon material is employed for the preparation and storage of reference standards, containers which are to contact concentrated acids and preconcentration of the samples by non-boiling evaporation (see next section). They include various kinds of bottles, Erlenmeyer flasks, jars, graduated cylinders, and beakers from Nalgene or Flon Chemical Inc., Osaka, Japan. Polypropylene (PP) is used only for pans, which are used to receive ultrapure water during wash treatments; for the tips of the Eppendorf micropipettes; and for the tongs, which are used to transfer all the items between the acid cleaning baths.

Method for cleaning laboratory materials

The cleaning of all the containers and the labware follows a successive acid cleaning procedure that is adopted and slightly modified from the method employed at LGGE as described in detail by Boutron (1990). We use three series of covered acid cleaning baths constructed from 10 l and 20 l LDPE carboys from Nalgene. All the cleaning procedure is carried out within the clean room.

Most new bottles, containers and labware are coated to a greater or lesser extent with grease or other production materials. Thus LDPE bottles and other LDPE containers are first degreased with chloroform, and then rinsed well with Millipore RO water. They are then

immersed for at least 3 days in the first acid bath (25% Merck reagent grade HNO₃ diluted in Milli-Q ultrapure water) at room temperature. After rinsing with Milli-Q water, they are then immersed for a week in the second acid bath (25% Merck “Suprapur” HNO₃ diluted in Milli-Q water) heated on hotplates with a surface temperature of 45°C. We lowered the actual temperature of acid solutions in the baths in comparison with that employed at LGGE (Boutron, 1990). This is because when temperature is too high LDPE cleaning baths are subject to cracking due to slow attack by hot aqueous acid, which leads occasionally to a catastrophic leaking of strong acid to the floor of the clean room. The subsequent two baths contain 0.2% Fisher “Optima” grade ultrapure HNO₃ in Milli-Q water. After rinsing thoroughly with Milli-Q water, LDPE bottles and other LDPE containers are cleaned by immersion for a week in each of the last two acid baths. After taken out from the fourth acid bath, they are finally rinsed with Milli-Q water. They are then filled with 0.1% “Optima” grade HNO₃ in Milli-Q water, capped and packed in acid washed polyethylene bags before use. Here it should be noted that we use always acid cleaned PP tongs to rinse and transfer all the items when they are immersed in 4 successive acid baths.

In the case of FEP and PFA Teflon containers and other small items, cleaning procedure is similar to that for LDPE bottles and other LDPE containers except that before immersion in the second bath (25% Merck “Suprapur” HNO₃ diluted in Milli-Q water), they are immersed for at least a week in concentrated Merck “Suprapur” HNO₃ at room temperature. For PFA beakers used for the preconcentration of the samples by non-boiling evaporation, we leave them immersed in the last acid bath until use.

PP tips of Eppendorf micropipettes are first cleaned by simple immersion for a week

inside a 1000-ml PFA jar, which contains concentrated Merck “Suprapur” HNO₃. We then clean PP tips by sucking concentrated “Optima” ultrapure HNO₃ into the tip and discarding and then washing with Milli-Q water many times just before use.

Analytical Procedure

Instrumentation for the determination of ultratrace heavy metals

The samples are analyzed by means of GFAAS (Perkin Elmer, Model 4110ZL) equipped a Zeeman background corrector. The instrument is placed within a Class 100 laminar flow clean bench. The furnace system of a Perkin Elmer 4110ZL spectrometer is a Transversely-Heated Graphite Atomizer (THGA). The THGA furnace provides a uniform temperature distribution over the entire tube length. The THGA graphite tube also includes an integrated, low mass L’vov platform coated with pyrolytic graphite. The combination of uniform tube temperature, rapid heating and an integrated L’vov platform allows to maximize the signals of the analyte and minimize interference, giving a large increase in analytical sensitivity. The sample injections are performed using the AS-72 autosampler. The parameters conditioned with reference standard for GFAAS measurement are presented in Table 2.

The GFAAS reference standards were prepared by diluting Fisher certified atomic absorption standards (1000 µg ml⁻¹ solutions) in Teflon sub-boiled ultrapure water. The concentration ranges of the final standard solutions are as follows: 125-2000 pg g⁻¹ for Pb and Cu; 25-500 pg g⁻¹ for Cd; 50-800 pg g⁻¹ for Zn and Mn; 25-400 ng g⁻¹ for Al and Na, respectively. They were acidified (0.2% with “Optima” grade ultrapure HNO₃) to the same

acidity as the pre-concentrated samples or the samples to be used for direct GFAAS measurement.

Blank determination

The most commonly encountered problem, which causes a systematic error, is contamination by the introduction of analyte into the sample during the sample preparation and analysis. To validate accurate measurement of heavy metals of interest at the pg g^{-1} level, therefore, the procedural blank from the use of ultrapure water and reagents including acidification of the samples, walls of sample containers and the air in the clean room must be carefully determined. In fact, however, each blank contributed independently from the above sources is very difficult to be determined. On that account, we evaluated the total blank contribution by analyzing the Milli-Q ultrapure water, in which the heavy metals concentrations were already known, after putting inside LDPE 160 ml vials (acid cleaned as mentioned in previous section) and leaving the cover off for 24 h in the clean room. The Milli-Q water was then pre-concentrated by non-boiling evaporation (see next section), acidified to 0.2% HNO_3 with “Optima” ultrapure HNO_3 , and analyzed by GFAAS for Pb, Cd, Cu, Zn and Mn. The differences in concentrations of all measured metals were found to be within the instrumental noise level of GFAAS and thus to be undetectable.

Accuracy and Precision

The accuracy was estimated through the measurement of a certified Standard Reference Material (SRM) 1643d (Trace Elements in Water) of National Institute of Standards and

Technology (NIST). To put the range of concentrations of selected metals in the SRM 1643d to the same orders of magnitude as the GFAAS standards, the SRM 1643d solution was diluted by factors of 50 for Pb, Cd, Cu and Al and 250 for Zn, Mn and Na, respectively, with Teflon sub-boiled ultrapure water. As listed in Table 3, the measured concentration values are found to be in excellent agreement with certified values of the SRM 1643d.

The precision of the measurements can be estimated from mean concentrations and standard deviations reported in Table 4, assuming that the analytical blank is not only negligible but reproducible. The precision appears to be less than 5% for the highest concentrations and to increase up to about 20% at concentrations close to the detection limit.

Measurement of Ultralow Heavy Metals in Antarctic Surface Snow by GFAAS

Using the clean protocols as demonstrated in the previous sections, we analyzed 10 samples of fresh or slightly aged Antarctic surface snow collected at two coastal Antarctic stations, namely, the Korean station King Sejong (62° 13'S, 58° 47'W) located in King George Island, South Shetland Islands and the Uruguayan station Ruperto Elichiribehety (63° 26'S, 57° 03'W) at the northern tip of the Antarctic Peninsula. The sampling sites and collection dates are given in Table 5. The samples at Ruperto Elichiribehety were collected as part of joint cooperation between KORDI and Uruguayan Antarctic Institute (URI). Eight samples at King Sejong were collected just shortly after precipitation events, but two at Ruperto Elichiribehety were taken from slightly aged snow. They were collected at each site by pushing wide mouth 500-ml LDPE bottles horizontally into the snow at a depth of 2-3 cm from the surface and

then kept frozen until use at PRC. The bottles had been stringently cleaned before use as described in previous sections. Extreme care was taken in all stages of sample collection, handling and storage to avoid contamination.

In the laboratory, the samples were melted at room temperature and then aliquoted for subsequent GFAAS measurement of heavy metals. The direct injection method (sometimes multiple injections up to $7 \times 50 \mu\text{l}$) was used when the concentration levels of metals measured were higher than detection limits given in Table 2. For heavy metals such as Pb, Cd and Cu at extremely low concentrations, however, a preconcentration step was required.

Preconcentration

In our laboratory, the preconcentration by non-boiling evaporation is adopted for the snow samples, in which heavy metals concentrations determined are below detection limits listed in Table 2. This method is a complete duplicate of that developed and used at LGGE (Görlach and Boutron, 1990). Simply describing the process, melted snow is evaporated in 50-ml PFA beakers cleaned as mentioned in the previous section, to a drop at about 80°C inside six cylindrical holes perforated on the aluminum block placed on dry bath with hot plate (Thermolyne, USA, Model DB28100). PFA beakers are preconditioned by filling them with Teflon sub-boiled ultrapure water and heating them for at least 30 min. When the evaporation process is achieved, the beakers is removed from the aluminum block and then 1 ml of 0.2% HNO_3 (diluting “Optima” ultrapure HNO_3 with Teflon ultrapure water) is added. The preconcentrated samples are then transferred into 15-ml LDPE bottles and kept frozen until analysis.

According to the calibration of the evaporation procedure with 60 ml of unacidified synthetic ultralow concentration standards (Görlach and Boutron, 1990), it was found that loss of metals investigated took place during the evaporation process. Loss rates calculated from the slopes of the regression lines account for 18% for Pb, 24% for Cd, 11% for Cu and 15% for Zn, respectively. As a result, the concentration values obtained by GFAAS after preconcentration by non-boiling evaporation are corrected for these loss rates, except for Mn, for which calibration was not made using standards by Görlach and Boutron (1990). At this time, however, it is expected that evaporation process may not give rise to significant loss of this metal from solution, because Mn is mainly crustal in origin (being strongly bound to aluminosilicate material) and thus relatively less volatile.

Checking the efficiency of preconcentration method

Although an evaluation was previously made from three central Greenland surface snow samples for Pb, Cd, Cu and Zn, except for Mn, and found to be highly reliable (Görlach and Boutron, 1990), it is necessary to exclusively assess if the preconcentration method of non-boiling evaporation is also satisfactory for determining these heavy metals concentrations at the pg g^{-1} level in Antarctic snow. This is because the chemical forms of individual metal in Antarctic snow could be very different from those in recent central Greenland snow, depending upon the difference in quantity of anthropogenic and natural impurities in snow deposited in geographically different regions. If so, the different behaviors during the evaporation process are assumed to take place and consequently lead to large uncertainties in the concentrations values determined for heavy metals after preconcentration.

To evaluate that, the selected Antarctic surface snow samples were analyzed for Pb, Cd, Cu, Zn and Mn both by direct injections into the graphite furnace and by GFAAS after non-boiling evaporation. The comparative concentration values are presented in Table 4. As in the case for Greenland surface snow by Görlach and Boutron (1990), it is well observed that both sets of mean concentration values are in an excellent agreement for all the measured metals, even including Mn, for which any correction for loss rates are not made (see previous section). In consequence, our quantitative investigation validates an application of non-boiling evaporation to preconcentration method for the analysis of heavy metals at or below the pg g^{-1} level in the Antarctic snow samples containing different kinds of impurities.

Preliminary Results and Discussion

Presentation of Pb, Cd, Cu, Zn and Mn concentrations and comparison with other data

Table 5 summarizes Pb, Cd, Cu, Zn and Mn concentrations, which were measured by direct GFAAS or by GFAAS after non-boiling evaporation, in 10 Antarctic surface snow samples. They tend to be highly variable from site to site and in addition depending on the sampling date. The concentrations of all five heavy metals are found to be particularly elevated in snow collected in August 21, 1999. The September 16 and October 21 snow samples show relatively high concentrations of Cu, Zn and Mn, Table 5.

The mean concentrations of Pb, Cd, Cu, Zn and Mn in 8 snow samples collected at King Sejong appear to be anomalously high when compared with the representative concentrations found in recent Antarctic snow and in Holocene ice, as seen in Table 6. For example, their

enhancement factors with respect to typical concentrations in recent snow amount to about 3 (Pb), 30 (Cd), 6 (Cu), 84 (Zn) and 3 (Mn), respectively. In part of the samples, however, the measured concentrations of all five heavy metals are found to be very low, Table 5, as we expect for these metals at other Antarctic regions.

Contributions from natural and anthropogenic sources

Prior to an assessment of natural contributions for our snow samples, it should be emphasized that an estimate of natural contribution can be only order-of magnitude, because of the wide range of global inventories of emission factors given by previously published data. Natural sources include on a global basis wind-blown dusts, volcanoes, sea salt spray, wild forest fires and biogenic activities (Nriagu, 1989).

Contribution from the crustal material can be evaluated from the Al concentrations measured in the samples, Table 5, and mean ratios of heavy metals/Al concentration in soil or rock, for which we use the ratios in the continental crust given by Wedepohl (1995). The contributions so calculated for each metal are shown in Fig. 2. This calculated contribution is found to be variable from one metal to another. For Mn, the crustal input is very significant (up to 100% with an average of 43%) for most of the samples, except for the August 21 sample (sample no. 3), Table 5. For Pb, this contribution is found to be considerable for the September 16 sample (~ 20%) at King Sejong, in which the concentrations are relatively low, and for two samples (~ 50%) at Ruperto Elichiribehety. For Cd and Cu, the calculated crustal contribution represents to be very small for all the samples (less than 10%). In the case of Zn, this contribution represents approximately 20% only for two samples at Ruperto

Elichiribehety, but minor for the other samples (less than 5%).

After correction for the crustal contribution, our Na values, Table 5, can be used to estimate marine contribution from sea salt spray, combined with the heavy metal/Na ratios in surface bulk seawater and very limited available data on the metal enrichments in sea-derived aerosols relative to bulk seawater. We use the lowest concentration values reported for seawater adjacent to the study area or of the world ocean: 4 pg g⁻¹ for Pb, (Flegal et al., 1993), 0.2 pg g⁻¹ for Cd (Bruland, 1980), 60 pg g⁻¹ for Cu (Boyle et al., 1981), 5 pg g⁻¹ for Zn (Weisel et al., 1984) and 13 pg g⁻¹ for Mn (Martin et al., 1990). Enrichment factors used for calculation are 100 for Pb, 10,000 for Cd, 200 for Cu, 20,000 for Zn and 1000 for Mn, respectively (Weisel et al., 1984; Boutron and Patterson, 1986; Arimoto et al., 1987; Dick, 1991). The magnitude of these enrichment factors in sea salt aerosols is still very uncertain. Marine contributions so calculated are also seen in Fig. 2. This contribution is found to be always significant for all metals, except for Pb, for which it averages a few percent only. For Cd, the calculated contribution of marine inputs are shown to be overestimated for part of the samples, but give the clear evidence that sea salt spray is a dominant source of this metal to the snow in the coastal Antarctic. As seen in Fig. 2, most of the measured Zn concentrations are also estimated to originate from sea salt spray, except for two samples at Ruperto Elichiribehety. On the other hand, marine contribution is insignificant in most cases for Cu and Mn with being rather high (more than 20%) in part of the samples.

As a whole, the above estimates lead to the conclusion that the concentration levels of Cd, Zn and Mn in our samples are dominated by natural crustal and marine inputs. For Pb and Cu, these two natural contributions are significant only for part of the samples. At present, the

contributions from the other natural sources cannot be estimated from our available data. However, it is suggested that they may constitute minor part of all heavy metals in our samples, based on the global emission rates given by Nriagu (1989).

Apart from natural contributions described above, we can assume that another possible contributor of heavy metal deposition to the samples is anthropogenic, because it seems that local atmospheric pollution for heavy metals takes place by emissions from 8 permanent Antarctic stations in King George Island. The major local source of atmospheric pollution is thought to be the burning of fossil fuels. According to the analysis of aerosols and lichen samples collected in King George Island (Artaxo et al., 1992; Hong et al., 1999), it was found that atmospheric heavy metals like Pb, Cu and Zn were highly loaded over this area, indicating local or regional air pollution. This observation could be an explanation for part of some heavy metals contents in our samples that cannot be compensated by the calculated natural contributions, as can be seen in Fig. 2. In particular, a very likely candidate for source of highly enriched Pb, Fig. 2, with respect to natural contributions is local emissions from King Sejong and partly from the other stations in King George Island. This tentative assumption is supported by the fact that Pb concentrations in the August 21 and January 9 snow samples, Table 5, for which the sites are the closest to King Sejong, are very high when compared with those in the other sites at King Sejong. The August 21 sample shows especially elevated concentration values of all five heavy metals. This may be due to a greater extent of local pollution or to direct transport of contaminants to the site from local source(s) and/or to a combination of two factors.

For two samples at Ruperto Elichiribehety, the situation makes an interpretation difficult.

As seen in Fig. 2, the concentrations of all five heavy metals are very high and the estimated natural contributions cannot account for the measured concentrations, except for Mn, for which the whole part of the measured concentrations is estimated to be crustal in origin. A possibility of local pollution is likely to be weak, because the katabatic winds predominate at the northern tip of the peninsula, which interferes with the transport of anthropogenic contaminants emitted from Ruperto Elichiribehety and Esperanza bases to the sampling sites. If that is the case, an alternative explanation is the natural contributions from unknown sources or uncertainty in estimating the crustal and marine contribution. We here suggest that local difference in the ratios of heavy metals/Al used for calculating the crustal contribution may give rise to erroneous crustal contribution. In fact, the Al concentrations in the samples at Ruperto Elichiribehety are much higher than those at the other sites, Table 5, indicating certain local inputs of mineral dusts derived from the exposed rocks in the study area. If some metals in these exposed rocks are enriched with respect to Al concentrations in the continental crust given by Wedepohl (1995), the previous calculations could underestimate the crustal contributions for the samples at Ruperto Elichiribehety. Our suggestion is tentative until confirmed by the analysis of a sequence of snow samples collected at other coastal sites around the Antarctic Peninsula.

In summary, although it is difficult to draw a conclusive interpretation on the distribution of heavy metals in snow deposited around the northern tip of Antarctic Peninsula, our data exhibit strong influence of local sources on snow composition in this area. In King George Island, sea salt spray is a major contributor to some heavy metals flux to the surface snow. This is the case for Cd and Zn. From our observation, it appears that heavy metals (especially

Pb) contents in snow are significantly affected by local emissions at sites near the Antarctic stations, as generally expected. On the other hand, the samples at Ruperto Elichiribehety show a remarkable influence of local crustal inputs on heavy metals distribution in snow. It is necessary to continue the surface snow sampling at various sites to understand spatial variability of heavy metals concentrations in the present Antarctic snow.

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Figure Captions

Fig. 1. A sketch of the Class 100 clean room used at PRC of KORDI. **A** top view; **B** cross section; 1 panel of urethane; 2 sheet of PVC; 3 blower and motor; 4 HEPA filter; 5 opening to acid fume exhaust fan; 6 door; 7 relief damper; 8 partition plate of PVC for acid cleaning baths; 9 opening to recirculating air; 10 prefilter; 11 sheet of PVC; 12 fluorescent lamp; 13 floor of PVC.

Fig. 2. Pb, Cd, Cu, Zn and Mn concentrations and estimated crustal and marine inputs in 10 surface snow samples collected at King Sejong and at Ruperto Elichiribehety. Sample number is the same number as those described in Table 5.

