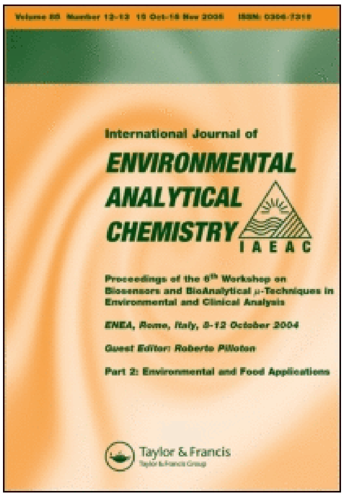

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Mercury in Snow Layers from the Antarctica

Renzo Capelli[a]; Vincenzo Minganti[a]; Carla Chiarini[a]; Rodolfo De Pellegrini[a]
[a] Dipartimento di Chimica e Tecnologie Farmaceutiche ed Alimentari, Università di Genova, Genova, Italy

To cite this Article Capelli, Renzo , Minganti, Vincenzo , Chiarini, Carla and De Pellegrini, Rodolfo(1998) 'Mercury in Snow Layers from the Antarctica', International Journal of Environmental Analytical Chemistry, 71: 3, 289 — 296
To link to this Article: DOI: 10.1080/03067319808032633
URL: http://dx.doi.org/10.1080/03067319808032633

Intern. J. Environ. Anal. Chem., Vol. 71(3-4), pp. 289-296
Reprints available directly from the publisher
Photocopying permitted by license only

MERCURY IN SNOW LAYERS FROM THE ANTARCTICA

RENZO CAPELLI*, VINCENZO MINGANTI, CARLA CHIARINI and RODOLFO DE PELLEGRINI

Università di Genova, Dipartimento di Chimica e Tecnologie Farmaceutiche ed Alimentari, Via Brigata Salerno (ponte), 16147 Genova, Italy

(Received 10 June,1997; In final form 8 Feburary, 1998)

Snow samples have been collected by pushing clean Teflon PTFE samplers in the walls of hand-dig pits from two locations in Antarctica: Hercules Névé and McCarthy Ridge, (Victoria Land). Reactive mercury concentration was determined in 28 samples using the cold vapours techniques with atomic fluorescence detection. Mean concentrations observed were: 0.23 ng L^{-1} and 0.47 ng L^{-1} for Hercules Névé and McCarthy Ridge, respectively

Keywords: Mercury; snow; Antarctica

INTRODUCTION

The study of the concentrations of mercury in snow samples represents an useful tool to assess the atmospheric transport of this element. As far as Antarctica is concerned, it can be noted that the totality of the atmospheric deposition is found in the snow. Furthermore, the scarce human activity ensures the possibility of studying relatively undisturbed successive snow layer acquiring useful indication on temporal variations. On the other hand, the very low concentrations found in such matrixes (ng L^{-1}) make extremely critical the sampling and analysis, and require a meticulous control of contamination.

Extensive literature is available about lead and cadmium concentrations in snow and ice cores from Antarctica and Greenland, and the effect of human activities on such concentrations has been demonstrated[1]. As far as mercury is concerned, scarce information is available, because the studies effected before

---

* Corresponding author. Fax: +39–010–3532684. E-mail: capelli@iatfa.unige.it

that ultra-clean analytical techniques became available, should be considered unreliable because of the possible contamination during sampling and analysis.

EXPERIMENTAL

During the 1993–94 Italian Antarctic Expedition, organised in the framework of the Italian Programme of Researches in Antarctica (PNRA), a total of 28 snow samples have been collected for mercury determination in two locations. The sampling sites have been selected because they represent areas of relatively undisturbed snow accumulation, and because they differ for elevation on the sea level and distance from the coast. The sites considered are illustrated in Figure 1 and their main characteristic are:

- Hercules Névé, elevation 2960 m on the sea level, Latitude 73° 06.378'S Longitude 165° 27.785'E. The distance from the sea is approx. 80 Km. The snow average accumulation rate[2] is 16.6 g H_2O $cm^{-2}yr^{-1}$ and average density[2] is 0.430 g cm^{-3}.
- McCarthy Ridge, elevation 875 m on the sea level, Latitude 74° 36.001'S Longitude 163° 03.131'E. The distance from the sea is approx. 40 Km. The snow average accumulation rate[2] is 23.1 g H_2O cm^{-2} yr^{-1} and average density[2] is 0.420 g cm^{-3}.

Because of the low concentrations expected, sampling was a critical step of the whole procedure. Sampling was carried out by hand digging a pit in the snow by operators wearing 'clean room' clothing. The vertical surfaces of the walls were cleaned by removing the superficial layer of snow with a scoop just before the sampling. Acid-cleaned Teflon PTFE samplers (external diameter 5 cm, inside diameter 4 cm, length 35 cm, with screw cap) were inserted horizontally in the walls of the pit at the required depths. At each depth, two Teflon PTFE samplers were used in order to have replicate samples. At Hercules Névé, a total of 16 samples have been collected at 8 depth ranging 22–211 cm. At McCarthy Ridge, the samples were 12, at 6 depth ranging 20–185 cm. Samples have been kept in the Teflon PTFE samplers, closed in two polyethylene bags, refrigerated at –25°C during transport and storage, until the analysis.

The snow was melted, still closed in the Teflon PTFE samplers, at room temperature just before its analysis. An aliquot (50–60 mL) of the water obtained was transferred into a Pyrex gas-liquid separator containing 20 mL of 10%(m/V) tin(II) chloride diihydrate, 15% (V/V) sulphuric acid solution. All the operations were done under a constant flow of Argon in order to avoid any contact with the atmosphere of the laboratory. The Argon used was purified by means of a gold

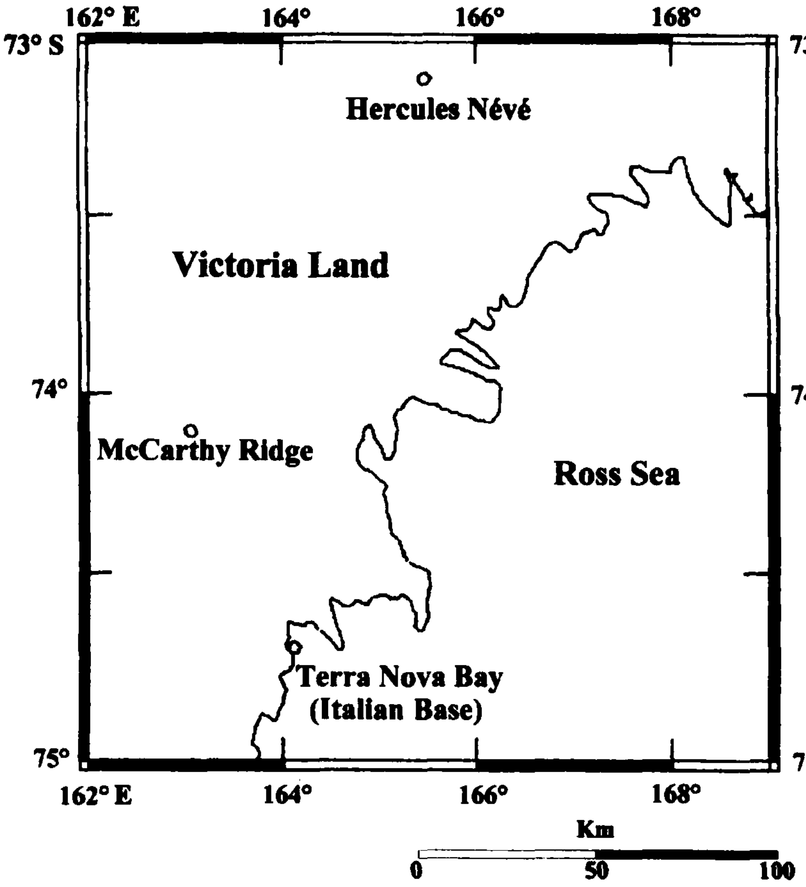

FIGURE 1 The area interested in this work, with the locations of the two sampling sites and of the Italian Base in Antarctica

trap. In this way the sample does not come in contact with the laboratory environment, and no special filtration equipment is required for the ambient air. A stream of Argon (2.0 L min^{-1}) was passed through the solution and the mercury was stripped and collected in a trap made of a gold wire. After 90 seconds the Argon flow was reduced to 0.6 L min^{-1}, and the gold trap was rapidly heated to 500–600°C. Mercury released from the gold trap was detected with an atomic fluorescence detector (PSA Merlin, Mercury Fluorescence Detector). The reducing solution was repeatedly analysed until a low and constant value (system blank) was obtained, before adding the sample.

Signal was recorded, amplified and integrated using a Hewlett Packard 3396 II integrator. Calibration was done by the standard addition techniques. The results obtained with this method are operationally defined as 'reactive mercury', being the fraction reduced by an acid solution of tin(II) chloride, and represents the ionic mercury and the mercury weakly bonded.

Each single Teflon PTFE sampler was repeatedly washed with laboratory detergent, with nitric acid (Merck, Suprapur) and rinsed with tap water and with ultra pure water (specific resistance >18 MOhm cm, Elgastat UHQ). After each washing, the Teflon PTFE samplers were filled with ultra pure water and the water was analysed with the method described in order to verify possible contamination. After cleaning, the Teflon PTFE samplers were heated at 120°C in an oven until completely dry, and, after cooling, they were closed with the screw cap and sealed in polyethylene bags. Results obtained during this control, show mercury concentrations in the water used ranging between 0.01 and 0.12 ng L^{-1}, with a mean value of 0.08 ng L^{-1} and a standard deviation of 0.03 ng L^{-1}. Such blanks represent the contribution due both to the sampler and to the analytical equipment used. For this reason the mean value of the blanks was subtracted from the results obtained for mercury concentration in the samples. Detection limit of the method, calculated as 3 times the standard deviation of the blank, is 0.09 ng L^{-1}, and all but one sample (Hercules Névé, depth 123 cm) showed a mercury concentration clearly above this detection limit. One of the samples (Hercules Névé, depth 20 cm) was analysed 4 times in order to evaluate the reproducibility of the whole procedure. The coefficient of variation obtained is 6.2%.

RESULTS AND DISCUSSION

The two samples obtained for each depth were analysed individually. However, there is no statistically significant difference (at p=0.05) for the two samples of the same depth, and mean value has been used for all consideration. Mean values obtained from 2–6 determinations are reported in Tables I and II for Hercules Névé and McCarthy Ridges respectively. At Hercules Névé, mercury concentrations range from 0.09 to 0.55 ng L^{-1}, with a mean of 0.23 ng L^{-1}. Higher values have been found at McCarthy Ridge, where the concentrations span from 0.16 to 0.71 ng L^{-1}, with a mean of 0.47 ng L^{-1}.

TABLE I Mercury concentrations in snow samples collected at Hercules Névé. Sampling depth (cm), reactive mercury concentration and standard deviation (ng L^{-1}) and number of replicate analysis are reported for each samples. Mercury concentrations are based on the volume of water obtained by melting the snow

Depth (cm)	*Mercury concentration (ng L^{-1})*	*Replicates*
22	0.32 ± 0.10	6
48	0.13 ± 0.06	4
71	0.22 ± 0.15	3
97	0.15 ± 0.04	4
123	0.09 ± 0.01	3
145	0.10 ± 0.01	4
180	0.30 ± 0.06	4
211	0.55 ± 0.16	4

TABLE II Mercury concentrations in snow samples collected at McCarthy Ridge. Sampling depth (cm), reactive mercury concentration and standard deviation (ng L^{-1}) and number of replicate analysis are reported for each samples. Mercury concentrations are based on the volume of water obtained by melting the snow

Depth (cm)	*Mercury concentration (ng L^{-1})*	*Replicates*
20	0.57 ± 0.11	4
53	0.16 ± 0.02	2
86	0.71 ± 0.13	3
119	0.42 ± 0.15	5
152	0.62 ± 0.04	3
185	0.35 ± 0.10	4

The snow layers considered have been dated by Piccardi et al.[2] using a multiparametric approach based on a combination of the concentration profiles of H_2O_2, $nssSO_4^{2-}$, and MSA which shows a seasonal character with summer maxima and winter minima[2,3]. The mercury concentration profiles for the sampling stations examined are reported in Figure 2. Samples from McCarthy Ridge show a higher mercury concentration than those collected at Hercules Névé. Such differences can be attributed to the different elevation on the sea level and different distance from the coast, being, according to Vandal et al.[4], the ocean the dominant source of natural mercury to the Antarctica. Despite scarce data is available in literature for comparison, good agreement is found with mercury concentrations reported by Sheppard et al.[5] for snow sampled on the Antarctic Plateau, near the Victoria Land Dry Valleys (Latitude 77° 32′S, Longitude 159° 50′E, altitude 2200 m, distance form the coast approx. 100 Km), and by Vandal et al.[4] for surface snow sampled in four locations along a transept stretching from the coast (French Scientific Station Dumont d'Urville, Latitude 66° 42′S, Longitude 139° 57′E) to the geographic South Pole. A graphic comparison of data published is reported in Figure 3 as a box and whiskers plot.

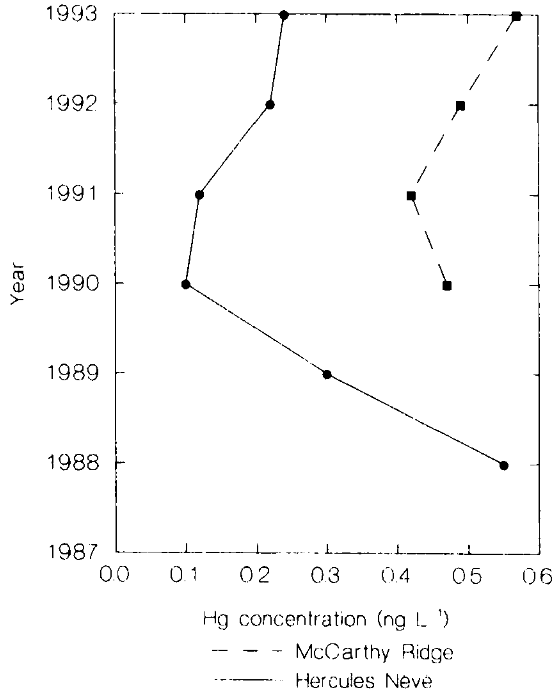

FIGURE 2 Mercury concentrations (ng L^{-1}) profiles in snow layers collected at Hercules Névé and at McCarthy Ridge. Mercury concentrations are based on the volume of water obtained by melting the snow. A mean of all data attributed to the same year has been reported

Piccardi et al.[2] have also calculated the water accumulation for the two sampling station we have considered. Using these data, the mercury deposition was calculated for each year using the mean of the concentration for each year considered.. Results obtained, reported in Figure 4, show a higher deposition rate for Mc Carthy Ridge sampling station (mean 10.2 pg cm^{-2} yr^{-1}). At Hercules Névé the deposition rate is much lower (mean 3.9 pg cm^{-2}yr^{-1})being this location less influenced by the sea. Similar results have been obtained for mercury deposition in Antarctica by Vandal et al.[4] with values ranging from 2.1 to 32 pg cm^{-2}yr^{-1}, obtaining the highest value for the sampling location closer to the coast.

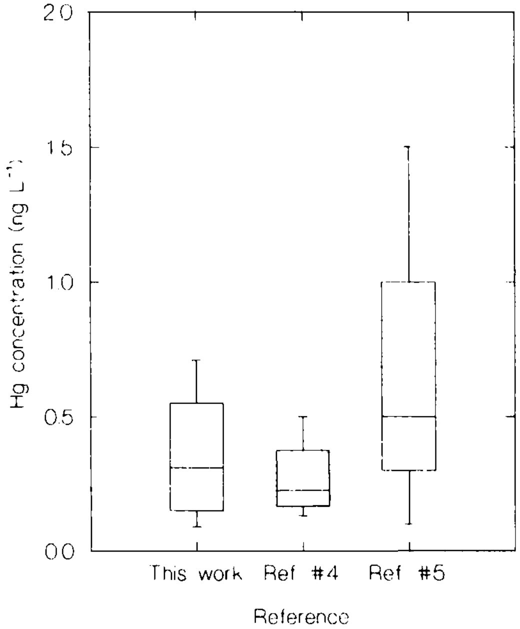

FIGURE 3 Comparison of mercury concentrations obtained in this work with data available from the literature (see references). All concentrations are given in ng L^{-1}

Other metal have been studied in the same samples, and Scarponi et al.[6] have published a study on the lead concentration in snow samples collected at Hercules Névé. The authors have found a lead concentration decreasing from 8.4 pg g^{-1} for the strata dated 1986 to 2.5 pg g^{-1} for 1991, and the decrease is explained by the reduction of use of lead compounds in gasoline. No correlation between lead and mercury concentrations can be observed indicating that the two metal have different origin.

Acknowledgements

This work was carried out in the framework of the "Programma Nazionale di Ricerche in Antartide-Progetto Contaminazione Ambientale", Italy.

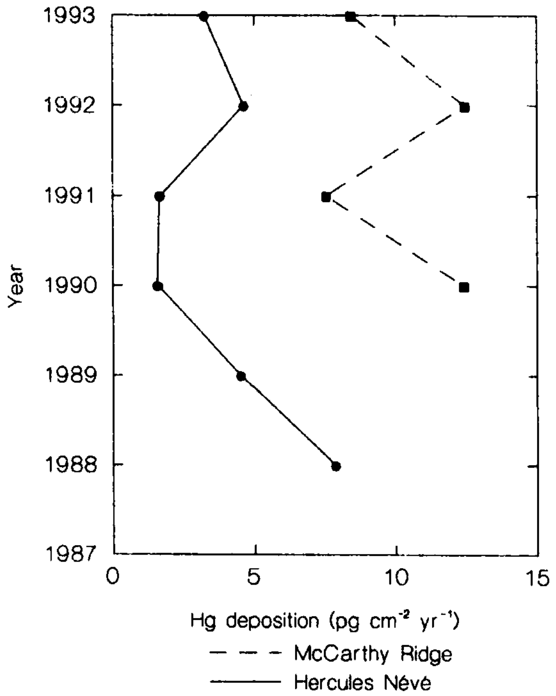

FIGURE 4 Mercury deposition (pg cm^{-2} yr^{-1}) profiles in snow layers collected at Hercules Névé and at McCarthy Ridge

References

[1] C.F. Boutron, J.P. Candelone and S. Hong. *Geochim. Cosmochim. Acta,* **58**, 3217–3225 (1994).

[2] G. Piccardi, E. Barbolani, S. Becagli, R. Traversi and R. Udisti. PNRA/Università di Venezia, Atti del 4° Convegno Nazionale "Contaminazione Ambientale", Venezia 6–7 December 1995; 53–62

[3] R. Udisti. *Intern. J. Enviorn. Anal. Chem.*, **63**, 225–244 (1996).

[4] G.M. Vandal, W.F. Fitzgerald, C.F. Boutron, and J.P. Candelone. *Ice Core Studies of Global Biogeochemical Cycles,* (R.J. Delmas ed., NATO ASI Series Vol I 30, Springer-Verlag, Berlin, 1995) pp. 401–415.

[5] D.S. Sheppard, J.E. Patterson and M.K. McAdam. *Atmos. Environ.*, **25A**, 1657–1660 (1991).

[6] G. Scarponi, C. Barbante, C. Turetta, A. Gambaro and P. Cescon. *Microchemical Journal,* **55**, 23–32 (1997).