

LONG TERM RECORDS OF HEAVY METALS AND RADIOACTIVITY IN CANADIAN ARCTIC AIR

Chunsheng Li ¹⁾ Jack Cornett* ^{1,2)} Richard Hughes ¹⁾ Kurt Ungar ²⁾ Joseph Lam ³⁾

1). WEGS, Trent University, Peterborough, Ontario, Canada K9J 7B8

2). RPB, Health Canada, 775 Brookfield Road, Ottawa, Ontario, Canada K1A 1C1

3). INMS, National Research Council, Ottawa, Ontario, Canada K1A 0R6

*. Corresponding author, Jack_Cornett@hc-sc.gc.ca

ABSTRACT

Lead, Cd, Zn and In in surface air particulates sampled from Resolute Bay, in the Canadian arctic, were analyzed by ICP-MS after leaching. The Pb concentration in air dropped significantly, from 1973's tens ng/m³ to 2000's blank value. The change correlated with the phase-out of leaded gasoline in North America and later in Europe. The declines of Cd and In are only 2 fold, indicating combustion is still an important pollution source. Zn concentration changed little from 1973 to 1985, and then increased gradually. Gross beta radioactivity in the surface air the Resolute bay declined sharply in 60' and 70's since the slowdown of atmospheric nuclear test, but increase slightly in the past decade.

INTRODUCTION

Arctic air pollution has drawn people's attention since 60s. Many monitoring programs were organized to assess the origin, occurrence and pathways of organic and inorganic pollutants in arctic air by measuring the interested chemicals in airborne particulates, biomonitors, ice cores and sediments. Some of the achievements were summarized in the recent reviews by Barrie et al. (1992), Muir et al (1992), Pacyna (1995), Lockhart (1995) and Barrie (1996). The CNRMN (Canadian National Radioactivity Monitoring Net) program within Health Canada has sampled airborne particulates weekly from several arctic stations during the past 40 year, which were achieved very well after measuring the radioactivity in the samples. This provides us a good opportunity to study the historical trends of some pollutants in Canadian arctic surface air in the past 40 years by using the large, unique sample files. In this work, we report summary of gross beta radioactivity of the past 40 years and the concentrations of some heavy metals such as Pb, Cd, Zn and In in surface air of the Resolute Bay station (74.7N, 95.0W, 63.8m), Nunavut, Canada.

METHODS

Sampling

The CNRMN program employed a standard sampling method by using glass microfibre filter (Whatman 41) to collect airborne particulates. The nominal volume past through the filter was 900m³ per day and the exact volume was corrected by taking the relating sampling parameters into account.

The sampler was calibrated regularly. Air particulates were sampled weekly throughout the year, and radioactivity was measured after the sample was transported from the sampling station to CNRMN central laboratory in Radiation Protection Bureau(RPB), Health Canada. After that, the filter was folded and kept in a waxed paper bag and archived in RPB lab.

Radioactivity measurement

Gross beta radioactivity was measured by using a alpha-beta proportional counter. Before 1983, a Nuclear Chicago counter was employed, and after that, it was replaced by a Canberra 2404 α/β counting system. The current counter is a Derthold (LB 770 Win-PC) from EG&G, which was purchased three years ago. The counter was calibrated regularly by using standard sources.

Heavy metals determination

For heavy metal analysis, 5.5% of the filter (equivalent to 350 m³ air) was cut using a clean plastic cone and subjected to a 2-step leaching using HNO₃ and H₂O₂ in a 5mL Teflon vial. Two mL of HNO₃ was mixed with the sample and the vial was put into a ultrasonic bath, 2 hours later, the vial was taken out and heated for 4 hours at 140 °C to predigest the particulate. After the vial cooled down, 1 mL H₂O₂ was added and the vial was heated again for another 4 hours at 120°C . One mL of the digested solution was transferred to a pre-cleaned (leached using 50% v/v HNO₃ for 24 hours and rinsed three times with Mili-Q H₂O) 15 mL polystyrene conical tube (FALCON, Blue-Max) and was diluted with Mili-Q H₂O to 10 mL before analysis using ELAN 6000 ICP-MS (Perkin Elmer Sciex). Peak hopping mode was employed in the determination. Rh and Bi were used as internal standards. The analysis of SRM 1648 suggested the leaching method works pretty good for Cd, Zn and In, and is acceptable for Pb. The filter blanks for new filter, 1978 filter and 1988 filter were measured simultaneously and the detection limits for every metal was calculated as three times of the standard deviation of filter blank value. Elemental concentrations obtained from the experiments were corrected against internal standards and filter blanks, and converted into concentrations in air. Only winter samples (one sample per month from each of December, January, February and March) were analyzed in the initial study.

RESULTS AND DISCUSSIONS

Radioactivity

Figure 1 shows the monthly averaged gross beta activity in Resolute surface air. The sharp decline lasted to 1965 since the ceasing of extensive atmospheric nuclear tests in 1963. High fallout has sustained for the next 20 years due to some atmospheric tests conducted by France in south Pacific and China in northwest desert. From the beginning of the 80s, the gross beta activity in the Canadian arctic surface air has been very stable and maintained at a low level, which implies a dominant natural source. The seasonal variation is very clear and regular, with the activity in winter months higher by one magnitude than that measured in the summer months. However, it seems there is a slightly increase in activity since the end of the 80s, especially in summer time. Such a increase needs to be confirmed, and if true, a comprehensive environmental variation may be implicated.

Heavy metals

Figure 2 (2A-2D) shows the time trends of Pb, Cd, Zn and In in Resolute surface air. The concentration of Pb declined from tens ng/m³ in the beginning of 70s to near blank value in the beginning of the 90s. This correlated with the phase out of leaded gasoline in North America in the 70s and later in Europe. Since the glass fibre filter has a high blank value for Pb, we can not tell the variation of Pb in arctic air in the past 10 years. Preliminary data for Pb in surface air of another arctic station, Coral Harbour, confirmed the same trend. From our other analyses, Pb concentration decreased by a factor of 40 in some southern Ontario cities during the past 30 years. Is Pb in European air also decreased significantly ? The sharp decline of Pb in arctic air is just beyond our expectation, since in the past, people thought Europe is the dominant arctic air pollution source, and North America contribute a very limited portion.

Cadmium and In, two elements mainly come from combustion, incineration and metal production, declined by a very similar factor, 2 to 3, during the same period. The decline is so limited that it shows combustion and incineration continue to be significant to air pollution although people tried to employ cleaning techniques in fossil oriented power production.

The variation of Zn concentration in arctic air is very interesting. It changed little from the beginning of the 70s to the middle of the 80s, but after that, it increased by several times during the past 15 years, as other elements in arctic air declining. Data from Coral Harbour surface air tells the same story. Savarino et al. (1994) and Somonetti et al (2000) found the increasing trend of zinc deposition in Greenland and North Quebec snowpacks and wondered its source. Is Zn in arctic air really increasing?and where it comes from?

REFERENCES

- Barrie LA, Gregor D, Hargrave B, et al. (1992) , The Science of the Total Environment, 112:1-74
Savarino J, Boutron CF and Jaffrezo JL (1994), Atmospheric Environment, 28: 1731-1737
Barrie LA (1996), In: NATO ASI Series Vol.143 : Chemical Exchange between the Atmosphere and Polar Snow. (Ed: Eric W. Wolff and Roger C. Bales), Springer-Verlag , Berlin Heidelberg , pp. 94-129
Lockhart WL (1995), The Science of the Total Environment, 160/161: 631-641
Muir DCG, Wagemann R, Hargrave B, et al. (1992), The Science of the Total Environment, 122: 75-134
Pacyna JM (1995), The Science of the Total environment, 160/161: 39-53
Simonetti A, Garipey C and Garignan J (2000), Geochimica et Cosmochimica Acta, 64(1): 5-20

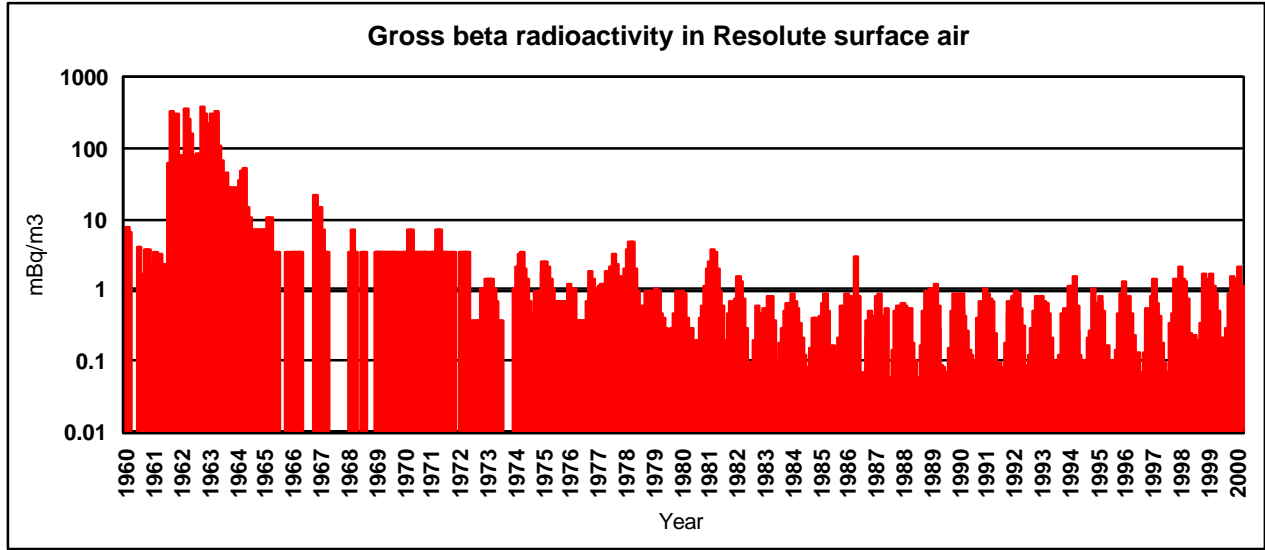


Figure 1: Gross beta radioactivity in Resolute surface air

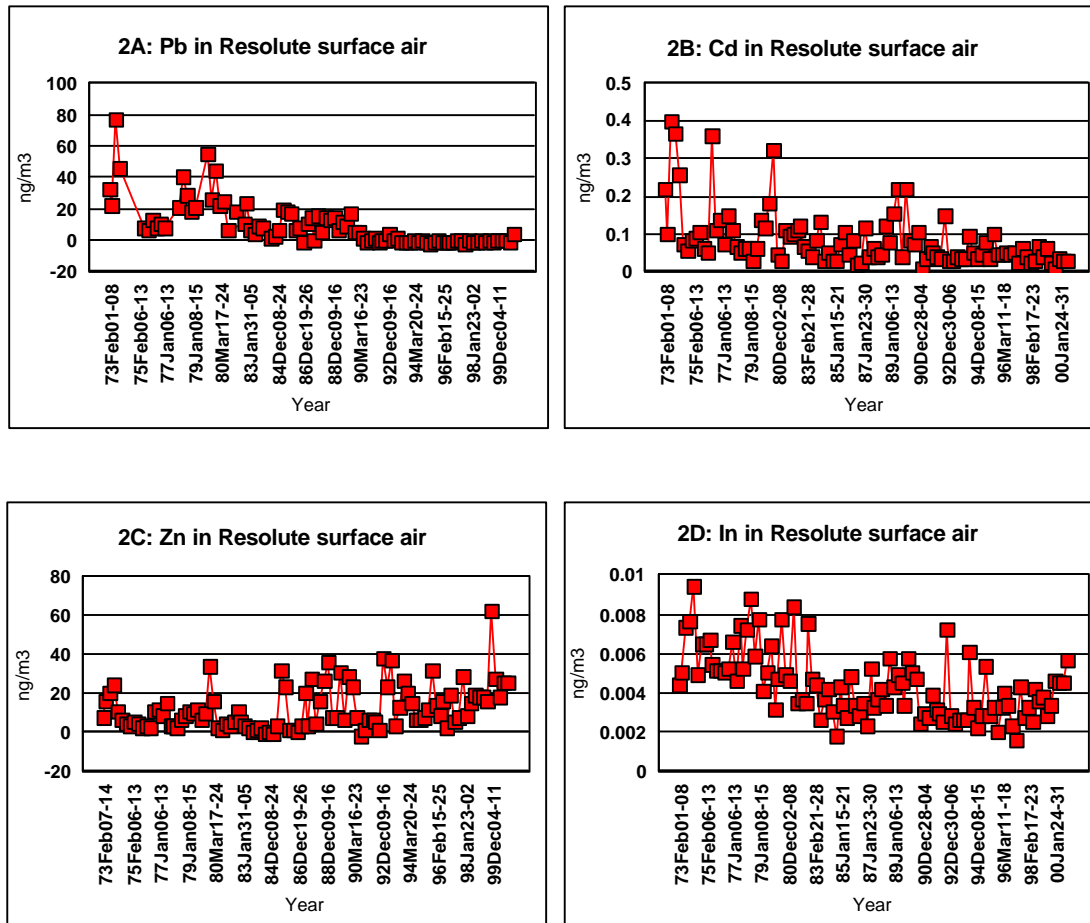


Figure 2: Heavy metal concentrations in Resolute surface air