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Article *in* Journal of Radioanalytical Chemistry · March 1982

DOI: 10.1007/BF02516141

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HU ISSN 0134—0719

JRACBN 71 (1-2) 1—310 (1982)

Volume 71 * Numbers 1-2 * 1982

PROCEEDINGS OF THE 1981 INTERNATIONAL CONFERENCE ON MODERN TRENDS IN ACTIVATION ANALYSIS

Toronto (Canada), June 15—19, 1981
Part 3

Journal of

RADIOANALYTICAL CHEMISTRY

An International Journal Dealing with All Aspects of Nuclear Analytical Methods

Elsevier Sequoia S.A., Lausanne

Akadémiai Kiadó, Budapest

Journal of Radioanalytical Chemistry, Vol. 71, No. 1–2 (1982) 59–73

ARSENIC POLLUTION IN THE YELLOWKNIFE AREA FROM GOLD SMELTER ACTIVITIES

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(Received July 7, 1981)

Gold has been mined on a large scale at Yellowknife located in the sub-arctic North West Territories of Canada since 1938. The gold is associated with arsenopyrite ores, with necessitates the oxidation of the arsenic and sulphur by roasting at two Yellowknife smelters. Other metals are also present in the ore, notably antimony. As_2O_3 and SO_2 are emitted into the atmosphere. Large quantities of arsenic were liberated in the past and despite improvements in emission control, significant emissions still occur. In order to assess the amount and extent of arsenic contamination in the local environment and the potential exposures and sources to man, soil samples and samples of the native vegetation were collected in and around the town of Yellowknife and the two smelters. Arsenic and antimony analyses were done by instrumental neutron activation analysis using the SLOWPOKE facility at University of Toronto. Air-dried plant samples were bombarded at a neutron flux of $1 \cdot 10^{12}$ n cm^{2}s and soil samples at $2.5 \cdot 10^{11}$ n cm^{2}s for 6 minute periods. The ^{122}Sb and ^{76}As-ray emissions at 559 keV were analysed after decay periods of 24–48 hours and compared with standard solutions and NBS standards. Zinc, copper, lead and cadmium analyses were done by atomic absorption spectrophotometry.

Arsenic was found to be accumulated in the soils in the vicinity of the two smelters to levels of several thousand ppm. Concentrations greater than 500 ppm occurred in the soil of Yellowknife townsite, and greater than 50 ppm occurred at all sites sampled within 15 km of the town. Antimony levels were about 10% of arsenic and were highly correlated with arsenic. Zinc occurred to 500 ppm around the smelters.

Compared with background levels, the foliage of several native species showed substantial arsenic accumulation, up to several hundred ppm in birch. Only 5–25% of this arsenic could be removed by careful washing. Evidence suggests the arsenic is taken up from the soil creating an ongoing arsenic contamination problem. Soil arsenic levels are also sufficiently high to inhibit root growth in soils over a very extensive area.

Introduction

Arsenic is well known as a potentially toxic element and, especially in its trivalent form, is used as an insecticide, fungicide and is toxic to mammals. Gold production and copper smelting are among many anthropogenic sources of arsenic contamination of the environment. Gold mining and production especially can cause substantial arsenic contamination since gold is very frequently found with arsenopyrite ore bodies. The large quantities of arsenic and sulphur in the pyrite relative to gold, need to be removed. This is normally done by high temperature roasting to oxidise them. Sulphur is converted to SO_2 and arsenic to As_2O_3. Some of these products are released into the atmosphere. The As_2O_3 occurs in the cooler air as particulates and aerosols.

At Yellowknife in the sub-arctic North West Territories of western Canada, gold has been mined on the shores of Great Slave Lake since 1938. Two major mines and smelters have operated, located a few km north and south of the townsite itself. The town has developed on the lakeshore beside an old Indian village on Lathan Island (Fig. 1), where the Yellowknife River enters a large bay of the lake.

Emission control of SO_2 and particulates was very poor in the early days, with up to 22 tons As_2O_3 per day emitted into the atmosphere in the early to mid 1950's. Baghouses reduced this to about 1,000 lbs. per day in the 1960's and to 300-500 lbs. per day through the 1970's. The collected dust is now stored largely underground in stopes where ore extraction has been completed.

Serious concern has been expressed about the health of the miners, the smelter workers, the residents of Yellowknife and the inhabitants of the Lathan Island Indian community at regular intervals since the mid-1950's. This was due to the known toxicity of arsenic to man, and in Yellowknife specifically, to the high exposures of the miners involved in ore extraction, to the high exposures to As_2O_3 in the smelters, to

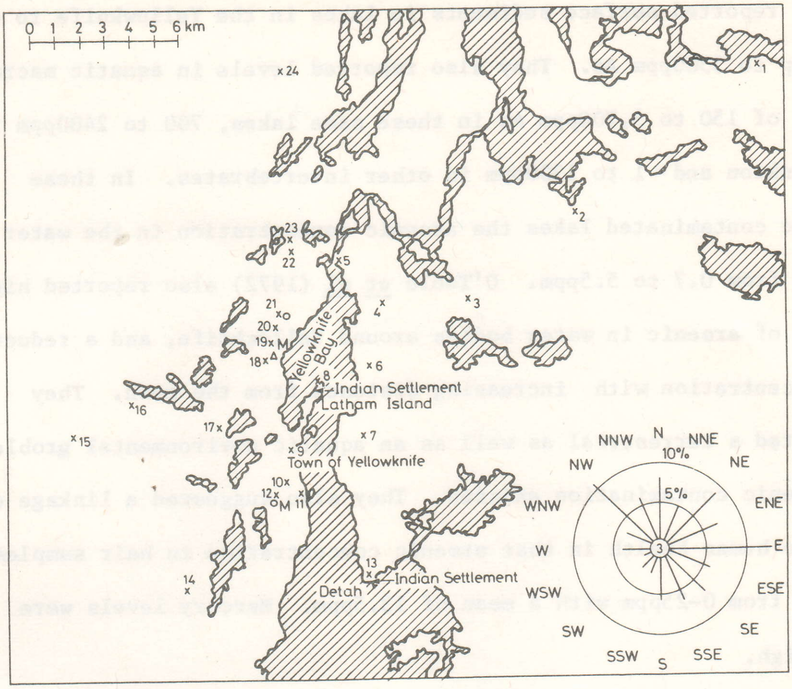

Fig. 1. The sampling sites in the Yellowknife area are marked from 1–24, the smelter mines are marked M. Prevailing wind directions are shown in the wind sore. Water bodies are stippled

contamination of the sediments of Yellowknife Bay which was used as a drinking water source for the town, by mine tailings, and to the high levels of arsenic found in the hair of Yellowknife residents (e.g. Falk et al 1974 O'Toole et al 1972, Smith 1977, Jervis et al 1978, Can. Public Health Association 1977, and Wagemann et al 1978. In the 1950's two Indian children died from arsenic poisoning caused by drinking melted snow. Changes in the source of the drinking water supply were made as a result of the arsenic contamination of Yellowknife Bay (Fig. 1), where Falk et al (1974) reported sediments to contain up to several thousand ppm of arsenic. More recently Wagemann et al

(1978) reported surface sediments in lakes in the Yellowknife to contain up to 3500ppm As. They also reported levels in aquatic macrophytes of 150 to 3,700ppm As in these same lakes, 700 to 2400ppm in zooplankton and < 1 to 1300ppm in other invertebrates. In these arsenic contaminated lakes the arsenic concentration in the water ranged from 0.7 to 5.5ppm. O'Toole et al (1972) also reported high levels of arsenic in water bodies around Yellowknife, and a reduction in concentration with increasing distance from the town. They suggested a terrestrial as well as an aquatic environmental problem of arsenic contamination existed. They also suggested a linkage of this to human health in that arsenic concentration in hair samples ranged from 0-25ppm with a mean of 13.5ppm. Mercury levels were also high.

Jervis and Tiefenbach (1978) carried out a much more detailed examination of the arsenic content of the scalp hair of Yellowknife residents, including native children living near the smelters, and mill workers. They compared these with those in a 'control' subarctic community of comparable size at Whitehorse and at Hay Bay, both of these communities lacking gold smelters. They found strong evidence of substantially elevated arsenic levels in the Yellowknife population, especially in the mill workers. WHO has suggested that > 5ppm As in scalp hair suggests excessive exposure. Jervis and Tiefenbach reported a mean hair arsenic concentration of 6.7ppm and a median of 0.96ppm As. The Hay Bay population gave a mean of 0.33ppm and a median of 0.29ppm. Four Yellowknife mine workers had greater than 100ppm As in scalp hair, with a high of 620ppm As. 33% of the population sampled had > 1ppm. Some

Indian children had elevated levels of arsenic. About 4% of the overall Yellowknife population exceeded 10ppm. None of the Hay Bay population exceeded 1ppm As.

All of this strongly suggests a widespread and severe contamination of the Yellowknife environment. In support of the Jervis study, we have carried out an assessment of the extent and pattern of soil and vegetational contamination by arsenic, antimony and certain other elements in the Yellowknife area. A major purpose was to determine whether exposure to soil and dust by young children could be a factor in their arsenic exposure in Yellowknife, and whether arsenic was being taken up by vegetation growing in the area and could also constitute a further potential food chain source for man. Such has been found to be the case with lead from smelters in Toronto and elsewhere (Roberts et al 1974, 1974a and Landrigan 1975).

Methods

Soils were collected in 1972 and 1974 at 24 sites around Yellowknife and the smelters. Aluminum corers (2.5cm diam) were used to obtain soils from 0-2, 2-4, and 4-6cm depths. Three replicate samples were taken per site. Locations are shown in Fig. 1. Sites were selected for accessibility by road, and similarity of exposure. Exposed granitic outcrops were selected as representing high points un-influenced by drainage but dependent directly upon aerial deposition for arsenic. Sites were at least 100m from the nearest road.

Vegetation was collected in August 1974 at 9 of the sites. Foliage of six species common in the area was collected: alder (Alnus crispa), paper birch (Betula papyrifera), fireweed (Epilobium angustifolium), black spruce (Picea mariana), jack pine (Pinus banksiana) and crowberry (Vaccinium vitis-idaea). Leaves of several individuals were collected at each site.

Vegetation was dried in 2 lots, unwashed and washed (in 1% detergent solution followed by 3 rinses in deionised distilled water). Before analyses the individual samples were homogenised to a fine powder. 0.2g samples were acid digested in a 1:1 nitric:perchloric acid mixture, filtered through a Whatman #1 filter paper and diluted with distilled water. Digests were analysed for Zn and Cu using a Perkin-Elmer 460 atomic absorption spectrophotometer.

Soil samples were air-dried, mixed and screened to 2mm. 1g samples were nitric:perchloric digested for 16 hours and after filtering were made up to 50ml with a 10% nitric acid solution. Analyses for Cu, Cd, Zn and Pb were made by atomic absorption spectrophotometry. Orchard leaf and fly ash standards were used as reference material.

pH measurements were made using a calomelelectrode on soils moistened to a paste with distilled, deionised water.

Arsenic and antimony analyses on both soils and selected vegetation samples were made by instrumental neutron activation analysis, using the SLOWPOKE facility at the University of Toronto. These were made on air-dried plant and soil samples, as well as on selected soil-distilled water extracts placed in polyethylene capsules. Plant samples were bombarded at a neutron flux of 1×10^{12} n/cm^{2}/s, and soil samples at 2.5×10^{11} n/cm^{2}/s, for 6 minute periods. The ^{76}As and ^{122}Sb γ-ray emissions at 559 KeV were analysed after decay periods of 24-48 hours, and compared with the results of similar analyses of standard arsenic and antimony solutions and standard reference material (NBS orchard leaves and fly ash and 1AEC soil). Samples in which As was not detected by the above procedure were re-analysed using a 16h. irradiation at $2.5\text{x}10^{11}$ $\text{n/cm}^2\text{/s}$.

Data on the sensitivity and accuracy of the technique for arsenic are given in Table 1. It is seen that the counting error σ is generally less than 10%, and the detection limit for foliage samples 0.2 to 0.5ppm and for soils, with their sodium interferences, 3.4 to 30ppm. The triplicate analyses of the IAEC soil standard gave our mean as 98.6±8.1 compared with a certified value of 93.9±7.5, which we considered very satisfactory.

The surface soil arsenic data were mapped against distance to the nearest smelter (r=0.89), using the SUMAP computer program (Harvard University, Graduate School of Design). This produced best estimates of arsenic isopleths around the city of Yellowknife, Fig. 2.

Results and discussion

Soil data. Arsenic concentrations in soils collected from around the smelters were extremely high. Values as high as 9300ppm As occurred near Giant Mine north of Yellowknife, and up to 5000ppm As near Con Mine to the south. Concentrations were highest in the top 0-4cm of the soil and were reduced at greater depth. This strongly suggests surface loading from an atmospheric source. Concentrations decreased rapidly with distance from each of the smelters but compared with published data on arsenic levels in normal soils they remained high over large

Table 1
The relative sensitivity of arsenic determination on Yellowknife soils and vegetation and on a standard reference soil from IAEA. The mean and counting errors are given as well as the detection limits

RELATIVE SENSITIVITIES

ARSENIC

Sample		ppm		σ	Detection Limit (ppm)
Vegetation	a	6.56	±	0.26	0.52
	b	23.1	±	0.2	0.3
	c	42.4	±	0.2	0.2
Soils	a	6330	±	30	30
	b	23.5	±	1.5	3.4
	c	375	±	11	24
	d	7240	±	30	20

STANDARD REFERENCE MATERIALS

ARSENIC IN IAEA SOIL-5

		µg/g		σ
Our data	a	103	±	8
	b	104	±	7
	c	89.2	±	4.8

Our mean: 98.6 ± 8.1

Certificate: 93.9 ± 7.5

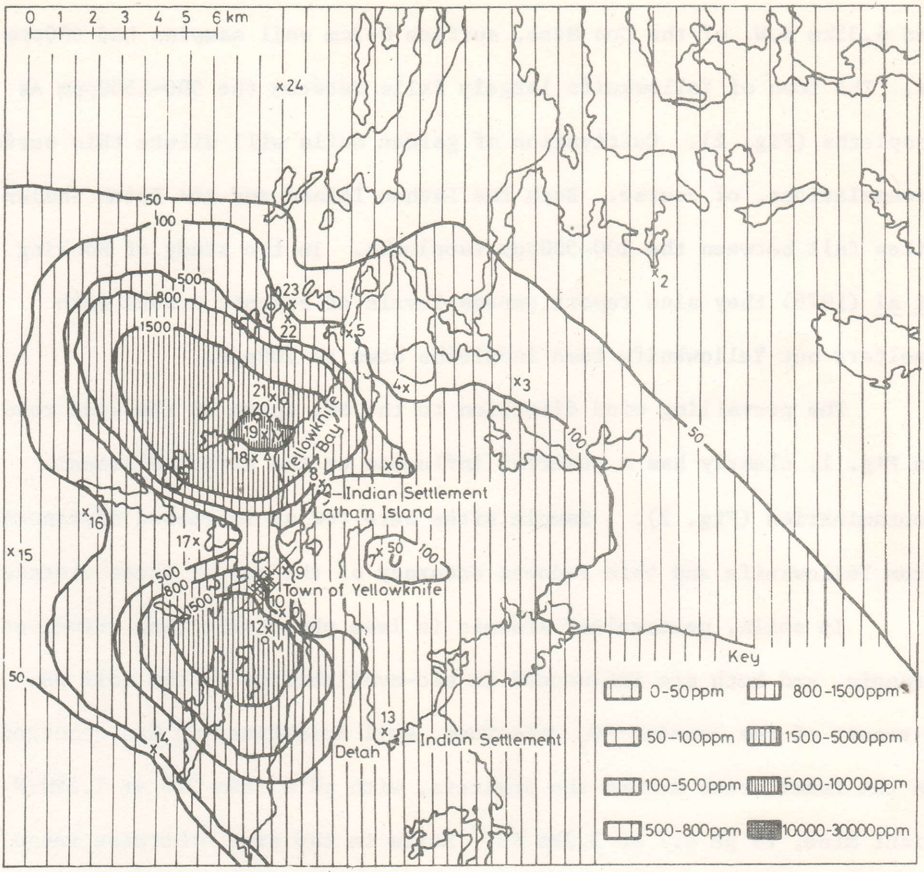

Fig. 2. The isoplethes of arsenic concentrations in surfacing soils of the Yellowknife area are shown ranging from <50 ppm to >5000 ppm. Sampling sites are marked from 1–24. The two smelters are marked M

distances. Thus, Bowen (1966) quotes 6ppm as a normal level for As, while the Ministry of Environment Phytotoxicity Section, Ontario sets 40ppm As as the upper limit above which levels are considered excessive. Fig. 2 showns the arsenic isopleths for the Yellowknife area, from which it is apparent that soil concentrations of greater than 50ppm As occur to distances of 10-15km out from each smelter. The inner areas are massively contaminated. For example, at a site 3.7km E of Giant Mine and 6.35km N.W. of the Con Mine, surface 0-2cm soil samples had 600ppm As. The town of Yellowknife largely falls between the 500-1500ppm As isopleths (Fig. 2). Cultivation of garden soils will dilute this surface accumulations, of course. Both the Lathan Island and the Detah Indian sites fall between the 100-500ppm isopleths. In the study of Hocking et al (1978) they also report excess levels of arsenic around both smelters but Yellowknife town isopleths down to 200ppm.

The prevailing wind direction to the NW, shown on the wind rose on Fig. 1, clearly has a powerful influence on the airborne arsenic contamination (Fig. 2). Sample sites were few at increased distances from Yellowknife and this reduces accuracy of the map at these distances.

In soils, pentavalent arsenic is less phytotoxic than trivalent arsenic, and both are influenced in bio-availability by the soil pH. As a result of the ongoing SO_2 emissions, soil acidification has occurred in the inner areas around the smelters, with pH's from 3.8 at 1.6km N of Giant Mine, to pH 4.7 at 3.2km SW. Soils in the area otherwise range fro pH 4.75 to 6.2. This acidification of surface soils probably enhances root uptake of As.

One measure of As availability from soils is by means of water extracts. From one soil profile containing 7058, 2480 and 800ppm As in total, water extractable arsenic levels of 20.1, 14.1 and 10.3ppm were obtained. Concentrations of up to 91.5ppm As were obtained in water extracts around the Giant Mine, while concentrations of $<$ 0.22ppmAs occurred at a site where total soil levels of 7.4 to 53.8ppmAs were found. From various studies, it is shown that arsenic concentrations of >5-100ppm can be highly phytotoxic to root growth when in soil

Table 2

Correlation values for metal concentrations in Yellowknife soil versus distance from the smelters

	n	r	Significance
Arsenic, log soil conc. versus log distance (km)	45	-0.832	$p < 0.01$
Antimony, log soil conc. versus log distance (km)	27	-0.648	$p < 0.01$
Copper, log soil conc. versus log distance (km)	45	-0.446	$p < 0.01$
Cadmium, log soil conc. versus log distance (km)	45	-0.667	$p < 0.01$
Lead, log soil conc. versus log distance (km)	45	-0.620	$p < 0.01$
Zinc, log soil conc. versus log distance (km)	45	-0.501	$p < 0.01$
Arsenic in soils versus Antimony in same soil	27	0.949	$p < 0.01$
Arsenic in soils versus Zinc in same soil	45	0.571	$p < 0.01$
Arsenic in soils versus Cadmium in same soil	45	0.657	$p < 0.01$
Arsenic in soils versus Copper in same soil	45	0.539	$p < 0.01$
Arsenic in soils versus Lead in same soil	45	0.751	$p < 0.01$

solution. Further, in studies of various crops affected by arsenic excess in soils, 'total' soil arsenic concentrations of greater than 50-75ppm have been shown to be phytotoxic (Anastasia and Kender 1973, Grimmet 1939). The clear implication is that arsenic concentrations are sufficiently high in 'total' soil analyses and in water extracts of those soils to constitute a potentially adverse soil factor over wide areas around Yellowknife.

Antimony was also found to be highly elevated in the soils and highly correlated with the distribution of arsenic (Table 2). A smelter origin is again suggested. Antimony occurred at about 10% of the concentration of arsenic in the soils. Thus, the highest Sb levels were 970ppm at a site 0.5km N of Giant Mine; while background levels of $<$9ppm Sb occurred at the most distant sites.

The mutual occurrence of As and Sb from ore roasting has been noted in other studies, e.g. Paciga 1975, and O'Toole et al (1972) reported Sb up to 280ppm in arsenic contaminated soils in the Yellowknife area.

Of the other metals analysed in the soils, zinc, lead and cadmium all showed limited increases compared with uncontaminated soils and the pattern with distance and depth suggested a smelter source. This is borne out by the correlation coefficients of soil concentrations on distance from the nearest smelter (Table 2). Even lead yielded significant results. Maximum concentrations found were 500ppm for zinc, 130ppm for copper, 110ppm for lead and 4ppm for cadmium.

The correlations of metals with each other in the soil samples are also shown in Table 2. The best correlation was of antimony on arsenic (r=0.949), with lead on arsenic next at r=0.751.

Vegetation data. In two previous studies where foliar analyses for the Yellowknife area have been given, O'Toole et al (1972) reported arsenic levels in plants growing in the township site to have levels of 12.6-89.4 ppm in 'grass' and 15.4-138.0ppm in rose bushes, while Hocking et al (1978) report collecting willow and black spruce for analyse and state that "analyses of foliage indicated little uptake of arsenic which, together with the presence of SO_2 symptoms, point to SO_2 as the main phytotoxic factor". Unfortunately, no data are given. For lichens, they do give data, with concentrations up to several thousand ppm near smelters, falling to 12ppm As at 75km.

Our data are at variance with Hocking's in that in the higher plants we found up to several hundred ppm As. In black spruce (Picea mariana) in unwashed foliage at site 23 (see Fig. 1), a concentration of 123ppm occurred, with 101ppm in washed foliage. At site 24 this was reduced to 8.9ppm and 8.7ppm for unwashed and washed foliage. Highest levels occurred in birch, with 526ppm at site 23.

The effect of washing was found to reduce foliar levels only from 5-25%, which suggests that the arsenic is not surface deposited from particulate deposition but, rather, is taken up from the soils through the roots. Some confirmation for this hypothesis is provided by the correlation data in Table 3 which show that for most species foliar arsenic correlated better with soil arsenic at the site of collection rather than with distance from the smelter. However, it is also clear that distance from smelters is also a factor, since it also determines to a large extent soil arsenic concentrations.

Since soil uptake seems to be the major route to the foliage tested, it is clearly highly undesirable to raise vegetables or fruit for human consumption on the contaminated Yellowknife area soils. This is borne out by the analyses of O'Toole et al (1972) referred to earlier and by a series of growth experiments and analyses we have completed.

In summary, extensive contamination of soils by arsenic and antimony is found in the Yellowknife area, centering on the smelters. The townsite is part of this area of contamination. Soils levels could add to the body burden of children ingesting soil or dust. Elevated levels of arsenic are also found in native vegetation and washing reduces this not more than 5-25%. Root uptake is suggested as the major route

Table 3
Correlation values for metal concentrations in Yellowknife vegetation with distance to nearest smelter or soil metal

	n	r	Significance
Fireweed Epilobium angustifolium			
log plant arsenic vs log distance	11	-0.734	$p < 0.05$
log plant arsenic vs log soil arsenic	11	0.748	$p < 0.01$
Black spruce Picea mariana			
log plant arsenic vs log distance	5	-0.942	$p < 0.05$
log plant arsenic vs log soil arsenic	5	0.911	$p < 0.05$
Paper birch Betula papyrifera			
log plant arsenic vs log distance	7	-0.851	$p < 0.05$
log plant arsenic vs log soil arsenic	7	0.922	$p < 0.01$
Jack pine Pinus banksiana			
log plant arsenic vs log distance	8	-0.217	N.S.
log plant arsenic vs log soil arsenic	8	0.286	N.S.
Vaccinium vitis-idaea			
log plant arsenic vs log distance	11	-0.560	N.S.
log plant arsenic vs log soil arsenic	11	0.786	$p < 0.01$

to plants, rather than direct leaf surface deposition from the atmosphere. Arsenic levels in the soils may be sufficiently high to seriously reduce root growth of native plant species and hinder seedling establishment.

*

Financial assistance has been provided by a National Research Council Operating grant to T. C. HUTCHINSON. Technical assistance and field assistance of B. THORPE, W. GIZYN, L. CUNNINGHAM and B. HUTCHISON-BENSON are gratefully acknowledged.

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