Arsenic Exposure and Health Effects V
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## Chapter 5

# Arsenic in Yellowknife, North West Territories, Canada

William R. Cullen, Elena Polishchuk, Kenneth J. Reimer, Yongmei Sun, Lixia Wang and Vivian W.-M. Lai

### Abstract

*In the Giant mine, Yellowknife, NWT, Canada, about 260,000 tons of arsenic trioxide (ca. 80% pure) are stored underground in old mine workings and in specially constructed chambers. The options for safe management of this material are discussed. Some promising results, in terms of long-term leachability of material containing up to 50% mine dust, are being obtained from mine dust/bitumen materials. Many fungi such as* Aleurodiscus farlowii *grow underground: some of these have been identified by using 28S ribosomal RNA gene (28S rRNA gene) analysis and their biochemistry with respect to arsenic metabolism is described. A white solid that is deposited in some regions of the mine is a mixture of calcium sulfate (Gypsum) and magnesium arsenate (Roesslerite).*

*Keywords:* arsenic trioxide, solidification/stabilization, bitumen, fungal identification, rRNA gene analysis, fungal metabolites

The first mineral claim in Yellowknife area was staked in 1935 and production began in 1948. The gold is associated with arsenopyrite and pyrite so a roaster (smelter) was commissioned in 1948. The stack gas, mainly arsenic trioxide and sulfur dioxide, was initially released into the atmosphere. However, this undesirable practice was mitigated in 1951 with the installation of an electrostatic precipitator to remove some of the arsenic trioxide. The arsenic recovery system was upgraded over the next decade so that the quantity released in 1949, 7300 kg/day (estimated), had dropped to 75 kg/day (estimated) in 1960. In 1991, two separate measurements of the daily emission gave 59 and 26 kg/day and the numbers were fairly constant until the mine ceased operation in 1999. In the late 1990s the daily recovery of the mine dust was 8–10 tons (Dillon, 1995). The practice of storing the recovered mine dust underground began in 1951 in the belief that the storage areas, initially abandoned mined-out sections, were either located in permafrost or in areas that would revert to permafrost once human activity had ceased in the vicinity. Unfortunately although permafrost conditions were never reestablished, the underground storage was continued and eventually special chambers were constructed to hold the mine dust. At the present time there are 15 storage areas, five of these are abandoned mine workings, and their size ranges from a chamber of 2294 $m^3$ containing about 3000 tons of dust to a mined-out stope of 25,740 $m^3$ containing about 30,000 tons of dust. The total amount of mine dust now in storage amounts to 260,000 tons and comprises about 200,000 tons of arsenic trioxide.

It is worth noting that by the end of 1998, the mine had processed 17,425,000 tons of ore to yield 6,954,250 ounces of gold (worth about $2 billion US).

Many options for the management of the mine dust have been considered including two essentially noninvasive ones that have considerable backing from an economic view, although they ultimately dodge the problem. These are: (1) leave the mine dust in place and pump the mine in perpetuity and (2) leave in place and induce permafrost conditions by means of thermoprobes inserted into the ground around the storage chambers.

Other options involve removal of the material for treatment on the surface and in the process circumvent in some way the obvious difficulties in recovering the dust because of the toxicity and because access is restricted to some of the storage chambers.

Because the dust contains gold, on average 18.1 g/ton, there has always been the "mantra" that the dust should be processed in such a way as to recover the gold to augment the costs. One such process that received considerable backing and remained on the table for many years was named WAROX (White arsenic oxide: note the direct avoidance of the word arsenic). In this process, the dust was to be sublimed to recover pure arsenic trioxide, free of antimony and iron, so that it could be used for wood preservative (CCA) manufacture. Gold would be recovered from the residue. Another process that was considered was to transport the material to another near-by gold mine, the Con Mine, for processing in their pressure oxidation plant. The gold would be recovered and the arsenic converted to Scorodite (ferric arsenate) and related minerals.

From the chemical point of view there is not much that can be easily and economically done to produce a safely disposable product from the dust. Reduction to arsenic metal would be possible (electrochemically with carbon) but the metal would have to be carefully stored and the process could be expensive. There is no obvious way of converting the dust directly to a stable "mineral" form of arsenic such as Scorodite.

Some chemical options become available if the dust is "mined" as a slurry. The most obvious of these would be to first oxidize the arsenic in solution to arsenate and then co-precipitate the product with ferric hydroxide, the so-called "ferric arsenate" of the water purification industry. The product from the water treatment plant is best thought of as a ferric oxyhydroxy phase (known as ferrihydrite), to which is adsorbed anions such as arsenate and arsenite. The co-precipitation is more efficient if the arsenic is in the (V) oxidation state, i.e. arsenate. There is controversy about the long-term stability of the product (Riveros et al., 2001). Dehydration can lead to instability. Recrystallization to geothite, FeOOH, with release of arsenate could occur, and there is the possibility of microbial reaction that again releases the arsenic (Ahmann et al., 1997). In spite of this, the US EPA (2001) considers that the product, which normally passes the TCLP test, can be disposed of in a nonhazardous landfill, even though it is well recognized that the TCLP is not of much value in evaluating the mobility of arsenic species (Hooper et al., 1998). The arsenic would certainly be removed from any solution by using this precipitation technology, but it is our opinion that special storage would be necessary, and in addition the process is not economically attractive (Kyle and Lunt, 1991). Conversion to the insoluble sulfide would require a source of sulfide ion, preferably not the toxic hydrogen sulfide, and the product is thermodynamically unstable with respect to the oxide in an oxic environment. Conversion to calcium arsenate has similar problems with respect to conversion to calcium carbonate and release of arsenic.

A review of the recent literature covering treatment technologies for arsenic contaminated media shows that seven methods have been used for solid matrices. Solidification/stabilization (S/S) and vitrification were the most commonly used.

These were followed by soil washing/acid extraction, prometallurgical treatment; *in situ* soil flushing; electrokinetics; and phytoremediation. All these technologies are available commercially.

In the Yellowknife situation vitrification would probably be too expensive and would probably generate off-gasses containing arsenic (Bauer, 1983), other than S/S, the rest are of limited applicability. The encapsulation of arsenic compounds in cement has been described in a number of publications (e.g. Dutre and Vandecasteele, 1998; Cullen et al., 2002) but usually at low loadings. It is believed that there is a chemical interaction between the arsenic species and the cement that enhances the binding of the arsenic species particularly arsenate. At U.B.C. we have found that pure arsenic trioxide can be incorporated into Portland cement at 1% loading, and the product sets easily. When this product is powdered and subjected to the standard acetic acid leaching procedure (TCLP) that is used to mimic the landfill environment, the leachate contains arsenic in the low ppb range. When the cement product is fabricated into small cylinders, the same leachate test gives very encouraging results: we found leachate concentrations of less than 50 ppm for loadings of up to 20% arsenic trioxide in the cement (Cullen et al., 2002).

Some other early studies indicated that bitumen (asphalt) could be considered as a candidate for stabilizing the mine dust if low concentrations of mine dust were used in the S/S mixture. In order to minimize the consumption of cement or bitumen, and hence reduce the waste volume, as well as the financial cost, we carried out a more detailed and systematic investigation on the encapsulating capacities of cement and bitumen.

## 1. Leaching tests from S/S material containing mine dust mixed with cement, or bitumen, or bitumen plus zeolite

*Cement samples*: Samples with different concentrations of mine dust (15, 17.5, 20, 22.5, and 25%) in commercial Portland cement were mixed in sealed plastic bottles and shaken for 1 h before the addition of water. Manually stirring the mixture produced a uniform blend that was transferred into a Ziploc plastic bag and allowed to cure for 28 days for later leaching tests, TCLP. The arsenic contents of the leaching solutions were well above of the cut-off value of 5 ppm: 15%, 275 ppm; 17.5%, 217 ppm; 20%, 232 ppm; 25%, 1120 ppm. These results, which are the average of two or three duplicate experiments, are sufficiently unsatisfactory that we abandoned further work with mine dust/cement S/S.

*Bitumen samples*: The bitumen, provided by McTar petroleum Co Ltd., Coquitlam, BC, Canada, was carefully heated to a semi-fluid and the appropriate amount of mine dust was added to the stirred bitumen. The stirring was continued until the mixture became homogeneous. The resulting mixture was allowed to cool to room temperature and stored to harden at 4°C. The mine dust/bitumen mixture was cracked into small pieces (freezing in liquid nitrogen is a help). An acetate buffer (pH 5.2) was used as a leaching solution. The arsenic contents of the leachates (Table 1) are satisfactory up to a loading of around 50%.

*Bitumen plus zeolite samples*: Mine dust, zeolite, and bitumen were mixed 1:1:1 ratio, in a similar manner, in the hope that some advantage might be gained by adding zeolites to the mixture. The leachate under the TCLP conditions gave an arsenic content of 3.95 ppm which is no great improvement over the "bitumen alone" samples. The zeolite was obtained from $C_2C$ Mining Corporation, Calgary.

*Table 1.* Arsenic content in the leachate of mine dust/bitumen.

| Mine dust/bitumen (%) | 15 | 17.5 | 20 | 22.5 | 25 |
|---|---|---|---|---|---|
| Arsenic content of leachate (ppm)[a] | 0.040 | 0.114 | 0.186 | 1.422 | 0.048 |
| Mine dust/bitumen (%) | 20 | 30 | 40 | 50 | 60 |
| Arsenic content of leachate (ppm)[a] | 2.45 | 4.25 | 3.30 | 5.50 | 26.90 |

[a] Average of two or three duplicate experiments.

## 2. Possible volatilization of arsenic trioxide and polycyclic aromatic hydrocarbons (PAHs)

Although it is not difficult to mix the mine dust with bitumen by heating the mixture, it is desirable that the process should be carried out at as low a temperature as possible to reduce energy consumption and the loss of toxic volatile arsenic trioxide into the atmosphere. The bitumen/mine dust mixing process (for both type A and C bitumen) was investigated by mounting a cold finger condenser inside the heated round bottom flask that contained the bitumen/mine dust mixture. The production of volatile arsenic trioxide could be easily monitored by visual inspection of the cold finger condenser. In some cases, the cold finger was rinsed and the washings were analyzed for arsenic. Some results are summarized in Table 2.

The cold fingers were also examined to see if they trapped any volatile PAHs. The results obtained by ASL Analytical Service Laboratories, Vancouver, BC, Canada, indicated that the concentrations of PAHs of concern were below detection limits.

*Table 2.* Volatilization of arsenic trioxide.

| Sample | Heating time (h) | Temperature (°C) | Volatile loss |
|---|---|---|---|
| Bitumen alone | 24 | 200 | None |
| | 24 | 140 | None |
| | 24 | 130 | None |
| Mine dust alone | 24 | 200 | Much |
| | 24 | 140 | Less |
| | 24 | 130 | Slight |
| 40% mine dust in bitumen | 24 | 200 | Much |
| | 8 | 140 | Some |
| 30% mine dust in bitumen | 24 | 200 | Much |
| | 8 | 140 | Some |
| | 2 | 130 | Trace[a] |

[a] Quantitative analysis indicates that the volatile loss of arsenic trioxide is less than 0.01% of the original arsenic content of the mine dust/bitumen mixture.

## 3. Investigation of long-term leaching of bitumen/mine dust material

Once it had been established that the bitumen/mine dust S/S material passed the TCLP test, it was necessary to establish that the bitumen samples are durable and safe in an appropriate storage environment over time. There are no standard procedures for testing for long-term stability, so it was necessary to devise a model that would reflect a possible storage scenario. The following experiment is based on the possibility that a bitumen/mine dust monolith would be stored in an open or closed mine shaft that would receive water from the surface. The experiment covers the worst-case scenario in which the shaft is flooded and the monolith becomes immersed in water. In practice fragments of the S/S material, rather than a monolith, were used to provide a greater surface area and thus, test the arsenic retention more rigorously. The slow flow of water was modeled by draining aliquots from the bottom of the vessel periodically for analysis, and replacing them with equal volumes of fresh water. The experiment was carried out at 4°C to mimic the mine temperature.

Granules of mine dust/bitumen mixture (40%, 32.5 g) were loaded into a stainless steel metal net cylinder, to a height of 5 cm. The cylinder was 35 cm long with a diameter of 3.5 cm. The loaded cylinder was suspended inside a glass column that was fitted with a stopcock at the bottom. Deionized water, 650 ml, was added to completely immerse the mine dust/bitumen sample. A nitrogen flow was bubbled through the water periodically, particularly prior to sampling, to facilitate mixing and leaching. When required, 12 ml of the aqueous sample was drained through the stopcock at the bottom and an equal amount of fresh water was added to the top of leaching solution. The experiment has been running for nearly 3 years and the results are shown in Figure 1.

## 4. Leaching studies on mine dust/bitumen monoliths

Some additional experiments have been conducted with mine dust/bitumen cylinders and some results are shown in Figures 2 and 3. For these experiments, done in duplicate, a weighed amount of bitumen was carefully heated to a semi-fluid (*T* less than 140°C) and the appropriate amount of mine dust was added. The mixture was stirred until it became homogeneous, poured into 150 ml beakers lined with aluminum foil, and cooled to room

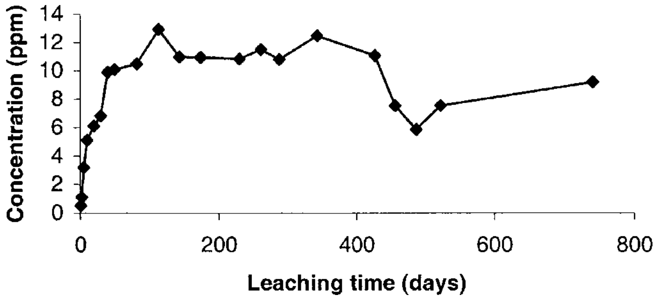

*Figure 1.* Long-term leaching test of mine dust/bitumen (40%).

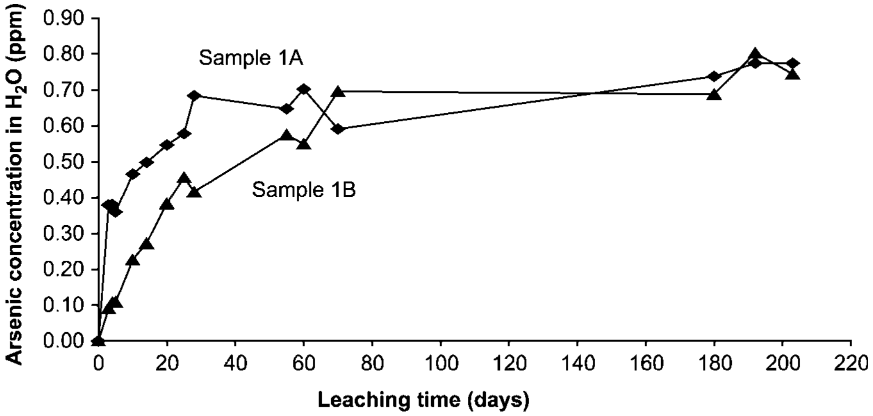

*Figure 2.* Leaching of 47% mine dust/bitumen cylinders into deionized water.

temperature. The samples (*ca.* 75 ml) were then stored in a cold room at 5°C for several days. The aluminum foil was removed from the cylindrical forms which were then immersed in 600 ml beakers containing deionized water as the leaching solution (*ca.* 3 times the weight of the hardened mixture) and then returned to the cold room. Nitrogen gas was bubbled through the leaching solution for about 30 min before sampling the leachate on each sampling day. A sample of 10 ml was taken which was replaced with 10 ml of deionized water to keep the volume constant in the beaker. Figures 2 and 3 show the arsenic content of the leachate, determined by using ICP/MS or HG/AAS at different intervals of time and different mine dust concentrations.

A similar mixture was prepared that contained an equal weight of mine dust, zeolite, and bitumen. The leachate data from the cylindrical forms are shown in Figure 4.

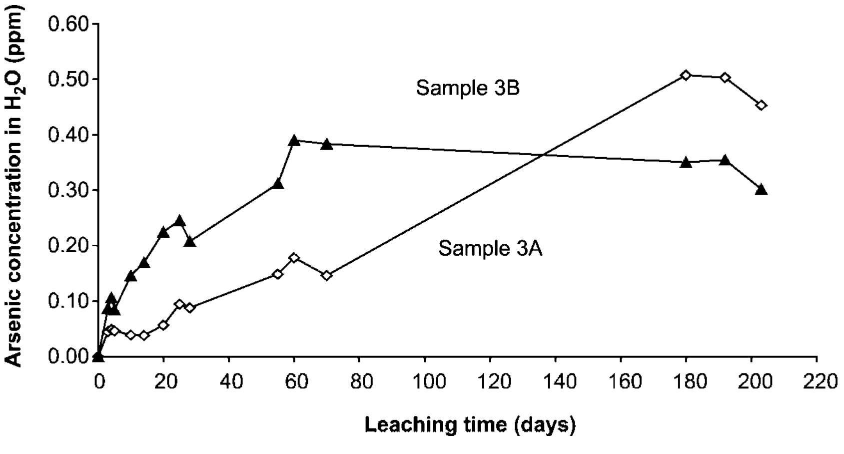

*Figure 3.* Leaching of 29% mine dust/bitumen cylinders into deionized water.

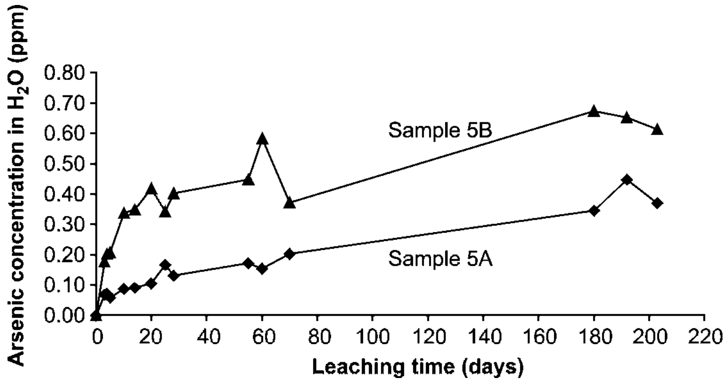

*Figure 4.* Leaching of 34% mine dust/bitumen/zeolite cylinders into deionized water.

A sample of bitumen was used as a blank. The concentration of the arsenic that leached out of the bitumen is below the detection limit, as was the PAH content.

## 5. Leaching from bitumen coated mine dust/bitumen cylinders

In order to model the situation where the S/S material of mine dust/bitumen would be stored in an enclosure that had been previously coated with bitumen, arsenic leaching from bitumen coated solid cylinders prepared from mine dust/bitumen (30–50% mine dust) was examined. Cylindrical forms were first prepared from the mixtures as described above. These were left in the cold room for several days, the foil wrapping was removed, and each cylinder was dipped into hot bitumen. The cooled samples were then placed in the cold room for several more days.

Leaching experiments were carried out as described above, and some results are shown in Figure 5.

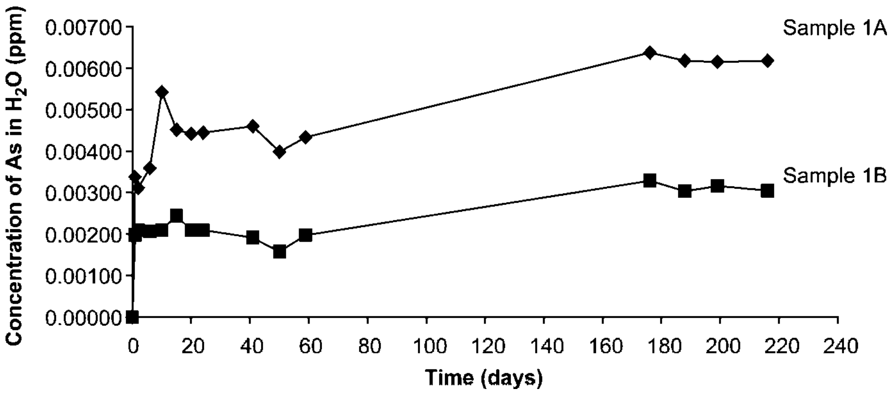

*Figure 5.* Leaching of bitumen coated 47% mine dust/bitumen cylinders into deionized water.

## 6. Discussion

The bitumen (asphalt) used in these experiments is the last cut in the petroleum refinery. These materials are complex mixtures and not well characterized. Most of the compounds are high molecular weight hydrocarbons that contain alcohol, acid, phenolic and thiol groups all of which can interact with the arsenic trioxide. Thus, it is not surprising that the oxide is well retained in the S/S mixture. The trend in the long-term experiment (Fig. 1) is flat. It should be noted that the leaching solution has not been changed and that fresh water is used only to replace the sample taken for the analysis. The initial concentrations in the leachate (Fig. 1) are higher than the concentrations observed in the more recent experiments (Figs. 2 and 3) in spite of the fact that the leachate to solid ratio is much higher (approximately 20:1 vs. 3:1). This may be a consequence of the use of fragmented material with higher surface area (Fig. 1) rather than solid cylinders (Figs. 2 and 3). In addition, there are probably some problems with mixing the materials on a small scale (stirring rods rather than mechanical mixers).

The leaching data from solid cylinders (Figs. 2 and 3) indicate that for a particular sample there is an initial gradual increase in the arsenic content of the leachate with time, as is seen in Figure 1. There appears to be a rough correlation with the amount of arsenic in the leachate and the amount in the sample. However, the data also indicate that there can be large variations in supposedly identical mixtures. This again may be the result of uneven mixing. Nevertheless, the arsenic concentration in all the leachates is satisfyingly low, even with mine dust concentrations approaching 50%.

The addition of zeolite does not seem to decrease the leachability of the arsenic as can be seen by comparing Figures 3 and 4. The higher arsenic concentrations in the leachate may be the result of the reduced bitumen content. Although the zeolite appears to increase the mechanical strength of the mixture there is probably no interaction between the zeolite and the arsenic compounds.

In order to reduce the surface exposure of a mine dust/bitumen mixture to water, it could be desirable to pour the mixture into an enclosure that had been pre-treated with bitumen in order to provide a sealed surface. To model this situation, pre-formed mine dust/bitumen cylinders were dipped into molten bitumen so that they became coated with fresh bitumen. These coated cylinders were then immersed in water at 5°C for leaching studies.

In practice the dipping proved to be difficult because the cylinder melted quite easily. The data shown in Figure 5 indicate the success of the experiment in that very little arsenic is leaching through the protective skin of bitumen (compare with Figure 2).

### *6.1. Underground deposits and growths*

*White solids*: Samples of a white solid that accumulates on the rock and wooden surfaces in one area of the Giant mine (near B shaft) were collected and subjected to X-ray diffraction analysis. Two main minerals were present: Gypsum $CaSO_4{\cdot}2H_2O$ and Roesslerite $MgHAsO_4{\cdot}7H_2O$. The analytical results reflect this conclusion: As, 167,000 ppm; Mg, 47,900 ppm; Ca, 171,000 ppm and there is reasonable agreement between samples although there is some spatial and temporal variation. The atomic ratios suggest that other arsenic compounds are present. The iron concentration amounted to 13,000 ppm in one sample but generally the concentration was below 500 ppm.

The origin of this deposit is not obvious. The deposits appear on rock, wood, and metal and are absent from surfaces that are not in a direct line of an airflow down the tunnel. There is no deposit in the "shadow" of the airflow; thus only one side of a flat wooden surface or metal pipe is coated. Furthermore, the deposit is in a limited area. However, the chemical make up of the deposit seems to point to its formation *in situ* rather than being deposited from an air stream. Roesslerite is a mineral that is not commonly found in Canada (Roberts et al., 1990). Careful examination of the growth of the deposit over time should help unravel this mystery.

*Fungal growths*: A number of rock walls and roofs underground are covered with a rich fungal growth. Some of these growths have been collected for examination because of the possibility that they may be involved in processes that result in mobilization of the arsenic in the underground environment. The miners speak of "slimesicles" that emit gasses. The growths are also of interest because they are thriving in such an apparently hostile environment.

Some of the identifications that have been made, based on partial 28S rRNA gene analysis, are listed in Table 3. The procedures used in-house are outlined in a recent publication (Granchinho et al., 2002).

Very little is known about the biology or chemistry of these organisms and further studies could be rewarding. For example, we find that the pink fungus *A. farlowii*, which we have identified in two separate samples, grows on rock walls where the ambient water has an arsenic concentration of about 2000 ppm. The freeze-dried fungus contains 4650 ppm extractable arsenic (1:1, methanol:water); however, when grown in potato dextrose broth containing 100 ppm arsenate, only traces of arsenite

*Table 3.* Partial 28S rRNA gene analysis: matches from GenBank database.

| Isolation method | Closest GenBank match | % Identity | Number of base pairs |
|---|---|---|---|
| B | Salal root associated fungus | 96 | 398/412 |
| B | *Phialophora gregata* | 96 | 525/545 |
| B | *Euascomycete* RFLP-type | 95 | 528/552 |
| A | *Phialophora gregata* and/or | 86 | 243/281 |
|  | salal root associated fungus | 85 | 224/287 |
| A | *Aleurodiscus farlowii* | 95 | 302/317 |
| A | *Pseudeurotium zonatum* | 96 | 405/520 |
| C | *Nectria vilior* | 98 | 373/377 |
| A | *Sclerotinia veratri* | 88 | 256/268 |
| A | *Geomyces pannorum* var *asperulatus* | 97 | 444/453 |

A: Direct sampling from the specimen as collected. B: A sample was grown on potato dextrose agar (PDA) and then the isolate was grown in potato dextrose broth (PDB). Frequent washing ensured axenic growth. C: A sample was grown in PDA to afford many colonies. The fungus was isolated and subsequently identified.

were observed and no arsenic methylation. Extensive reduction and limited methylation is seen in cultures of other isolates.

*Epilogue*. The material that was presented in San Diego contained some information about the use of principle component analysis to estimate background concentrations of arsenic in an industrially influenced region, a necessity for establishing site-specific criteria for cleanup. This material is now available elsewhere (Reimer et al., 2002). Two other related projects were described in poster format at the meeting: Reimer et al. "Arsenic in a deer mice food chain" and Ollson et al. "Influence of soil type on arsenic bioavailability and its consequences for human health risk assessment".

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## References

Ahmann, D., Krumholz, L.R., Hemond, H.F., Lovley, D.R., Morel, F.M.M., 1997. Microbial mobilization of arsenic from sediments of the Aberjona watershed. Environ. Sci., 31, 2923–2930.

Bauer, R.J., 1983. Arsenic: glass industry requirements. In: Lederer, W.H., Fensterheim, R.J. (Eds), Arsenic: Industrial, Biomedical, Environmental Perspectives. Van Nostrand Reinhold Company, New York, pp. 45–62.

Cullen, W.R., Andrewes, P., Fyfe, C., Grondey, H., Liao, T., Polishchuk, E., Wang, L., Wang, C., 2002. Solidification/stabilization of Adamsite and Lewisite in cement and the stability of arylarsenicals in soils. In: McGuire, R. (Ed.), Environmental Aspects of Converting Chemical Warfare Facilities to Peaceful Purpose. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Dillon, M.M., 1995. Report, Government NWT: Air dispersion modeling of roaster slack emissions Royal Oak Giant Mine Yellowknife, NWT, #94-2491-01-01, revised May 1995.

Dutre, V., Vandecasteele, C., 1998. Immobilization mechanism of arsenic in waste solidified using cement and lime. Environ. Sci. Technol., 32, 2782–2787.

Granchinho, S.C.R., Franz, C.M., Polishchuk, E., Cullen, W.R., Reimer, K.J., 2002. Transformation of arsenic (V) by the fungus *Fusarium oxysporum melonis* isolated from the alga *Fucus gardneri*. Appl. Organomet. Chem., 16, 721–726.

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., Odion, Z., Llejay, Z., Sy, F., Petreas, M., Simmons, B., 1998. Toxicity characteristic leaching procedure fails to extract oxo-anion-forming elements that are extracted by municipal solid waste leachate. Environ. Sci. Technol., 32, 3825–3830.

Kyle, J.H., Lunt, D., 1991. An investigation of disposal options for arsenic trioxide produced from roasting operations. Proceedings of Extractive Metallurgy Conference, Perth, October 1991, pp. 347–353.

Reimer, K.J., Ollson, C.A., Koch, I., 2002. An approach for characterizing arsenic sources and risk at contaminated sites: application to gold mining sites in Yellowknife, NWT, Canada. In: Cai, Y., Braids, O. (Eds), Biogeochemistry of Environmentally Important Trace Elements. Oxford University Press, (accepted Feb. 02).

Riveros, P.A., Dutrizac, J.E., Spencer, P., 2001. Arsenic disposal practice in the metallurgical industry. Can. Metall. Quart., 40, 395–420.

Roberts, W.L., Campbell, T.J.; Rapp, G.R. (Eds), 1990. Encyclopedia of Minerals, 2nd edn. Van Nostrand Reinhold Company, New York.

US EPA, 2001. Fed. Regist. January 22, 2001.