

Short communication

The effect of exposure to employees from mining and milling operations in a uranium mine on lead isotopes—a pilot study

Brian L. Gulson^{a,b,*}, Karen J. Mizon^a, Bruce L. Dickson^b, Michael J. Korsch^b^a*Graduate School of the Environment, Macquarie University, Sydney, N.S.W. 2109, Australia*^b*CSIRO Division of Exploration and Mining, P.O. Box 136, North Ryde, N.S.W. 1670, Australia*

Received 9 September 2004; accepted 10 November 2004

Abstract

Potential exposure during mining and milling of uranium ore has resulted in the industry being highly regulated. Exposure can arise from inhalation of the daughter product radioactive gas radon (^{222}Rn), inhalation of radioactive dust particles from mining and milling, direct irradiation from outside the body, and ingestion of radionuclides (e.g. uranium or radium) in food or water. Making use of the highly unusual lead isotopic signature for uranium ores (high $^{206}\text{Pb}/^{204}\text{Pb}$ from the high uranium content, low $^{208}\text{Pb}/^{204}\text{Pb}$ from the low Th/U ratio), we undertook a pilot study of nine male mine employees and three controls from the Ranger uranium mine in the Northern Territory Australia to determine if it was feasible to use lead isotopes in blood to identify exposure to uranium-derived materials. The lead isotopic data for the mine employees and controls plot in two distinct fields which are consistent with predicted isotopic patterns. Assuming retention of 10% of the ingested lead, then the increases seen in ^{206}Pb represent intakes of between 0.9 and 15 mg, integrated over the years of exposure. The small amount of lead does not affect blood lead concentrations, but appears to be sufficient to be detectable with sensitive isotopic methods. Further studies, including those on urine, should be undertaken to confirm the veracity of the lead isotope method in monitoring exposure of uranium industry employees.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Uranium mining; Uranium processing; Thorium; Lead isotopes; Blood; Exposure

1. Introduction

With the well-known deleterious effects of uranium on human health, monitoring of workers exposed during the mining and processing of uranium ore is of

critical importance (Uranium Information Centre; uic.com.au/nip06.htm).

Uranium ores contain much higher concentrations of radioactive elements than other ores and comprise two main isotopes ^{238}U (99.28%) and ^{235}U . The final stable end product of radioactive decay of ^{238}U is ^{206}Pb . The relatively higher amounts of uranium in the ore result in the generation of higher amounts of ^{206}Pb and, if this is expressed as a ratio

* Corresponding author. Tel.: +61 2 9850 7983; fax: +61 2 9850 7972.

E-mail address: bgulson@gse.mq.edu.au (B.L. Gulson).

compared with ^{204}Pb , which has no known radioactive parent, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of tens of thousand can be measured (Hills and Richards, 1976; Gulson and Mizon, 1980). This is generally described as highly radiogenic lead. In contrast to the relatively higher amounts of uranium, the ores generally contain very low concentrations of another radioactive element, thorium, (^{232}Th) whose final stable daughter product is ^{208}Pb . Hence although the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio may be several thousand, the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios remain low and of the order of 36 to 37 as found in so-called ‘common’ lead (Hills and Richards, 1976; Gulson and Mizon, 1980). With such diagnostic lead isotopic signatures, a pilot study was undertaken to determine if lead isotopes could assist in monitoring the exposure of workers in the uranium industry.

Radiological (i.e. radiation) exposure is of particular importance in uranium mining. Such exposure may occur in the following ways: inhalation of the daughter product radioactive gas radon (^{222}Rn), of special importance in underground mining; inhalation of radioactive dust particles from mining and milling; direct irradiation from outside the body, primarily by gamma rays or in some cases beta radiation; and ingestion of radionuclides (eg uranium or radium) in food or water. For workers at an open cut mine such as the Ranger uranium mine, radiological exposure due to radon is generally less important than exposure from dust or gamma radiation (<http://www.deh.gov.au/ssd/uranium-mining/outcomes/human-health/mine-workers.html>).

Workers at Ranger wear radiation dosimeters which measure the dose received due to external irradiation. Some workers also wear personal air samplers to measure the concentration of radioactive dust in air to which the worker is exposed. In addition to personal monitoring, area monitoring of radioactive dust concentrations in air and radon progeny concentrations in air is also undertaken. This information, together with other records of the time spent by workers in certain areas around the minesite allow the calculation of doses to mine workers (<http://www.deh.gov.au/ssd/uranium-mining/outcomes/human-health/mine-workers.html>).

The dose limits recommended by the International Commission on Radiological Protection (ICRP) and enforced at uranium mines in the

Alligator Rivers Region of the Northern Territory of Australia are: 1 milliSievert (1 mSv) per year for members of the public; and 100 mSv over 5 consecutive years with a maximum of 50 mSv in any one year for workers. Radiation doses received by employees at the Ranger mine are all well below recommended limits. Designated employees (those most exposed to radiation) received an average dose of 1.5 mSv in 2002 compared with the recommended average annual limit of 20 mSv averaged over 5 years. For comparison, the average yearly radiation dose received by all Australians due to natural background radiation is approximately 2 mSv and some diagnostic X-ray procedures can deliver several mSv to the patient instantaneously (www.deh.gov.au/ssd/uranium-mining/outcomes/human-health/mine-workers.html).

2. Setting

The following description is from the website of the Uranium Information Centre (accessed <http://www.uic.com.au/emine.htm> August 2004)

The Ranger mine and associated town of Jabiru is about 230 km east of Darwin, surrounded by the Kakadu National Park, a major tourist attraction. This is a monsoonal part of Australia, with pronounced wet season from December to April. The first orebody (Ranger #1) is now mined out and the second one (#3) adjacent to Ranger #1 is now being mined.

The mine started operating in 1980 with full production being achieved in October 1981 at a rate of about 3300 tonnes per year of uranium oxide concentrate. Since 1996 production has been over 4000 tonnes per year. Mining at Ranger #1 was by open pit, and from 1992 to 1995 mining occurred for 6 months of the year during the dry season and the treatment plant was run for the other 6 months. In January 1996 there was a return to year-round milling, using stockpiled ore. Mining at Ranger #3 commenced in June 1997. Uranium recovery is about 91.5%, and up to 93%.

Following crushing, the ore is ground and processed through a sulfuric acid leach to recover the uranium. The ‘pregnant’ liquor is then separated from the barren tailings and in the solvent extraction plant the uranium is removed using kerosene with an

amine as a solvent. The solvent is then stripped, using an ammonium sulphate solution and injected gaseous ammonia. Yellow ammonium diuranate is then precipitated from the loaded strip solution by raising the pH (increasing the alkalinity), and removed by centrifuging. In a furnace the diuranate is converted to uranium oxide product (U_3O_8). Until 1996 tailings from the treatment plant were emplaced in an engineered dam on the lease, but they are now being deposited into the worked out #1 pit. No process or other contaminated water is released from the site.

In allowing the Ranger mine to proceed, the Federal Government stipulated the establishment of the Environmental Research Institute of the Supervising Scientist to conduct research on the environmental effects of uranium mining in the Alligator Rivers Region.

3. Subjects, sampling and analysis

Through the auspices of the Safety Health and Radiation Protection office at Ranger Uranium Mines, several volunteers were enlisted to participate in this pilot study. Some information about employment history and workplace location is listed in Table 1.

Using strict protocols to minimize contamination, a venous blood sample of 2–3 ml was obtained from each volunteer and placed into a precleaned Savillex teflon container. Lead was separated from the blood sample following the procedures outlined in, for example, Gulson et al. (1996). Lead concentrations and isotopic ratios were measured by thermal ionization mass spectrometry, details of which are given in Gulson et al. (1996).

Table 1
Information for subjects

Subject id	Age (years)	Exposure (years)	Sex	Relevant work history
<i>Mine employees</i>				
DN	44	10	M	Commenced with Ranger in June 1981. Employed as a plant operator in the mine for 8 years, then transferred to position of mill-utility person.
DP	48	10	M	Commenced with Ranger in May 1981. Employed in mining of ore as an operator and supervisor. This has required the employee to be working in and around the pit.
DO	42	3	M	Commenced with Ranger in April 1988. Employed in the milling operation of the mine as a maintenance fitter/welder. This has required the employee to work in and around the milling process (grinding of ore, enrichment, leaching, drying and packaging of uranium).
DT	36	7	M	Commenced with Ranger in February 1984. Employed as a plant operator in the mining section. This required the employee to be working in and around the pit.
DU	36	3	M	Commenced with Ranger in 1988. Employed as an electrician and is required to work all over the site. This includes the mine pit and mill areas.
DR	59	10	M	Commenced with Ranger in April 1981. Employed as a marker and then supervisor of the drill and blast crew. This required the employee to be working outside in the pit, setting changes, shoveling, etc.
DM	41	3	M	Commenced with Ranger in April 1988. Employed as a mill utility person/operator since commencement.
DS	48	6	M	Commenced with Ranger in May 1985. Employed as a plant operator in the mining process. This has required driving of machinery in and around the pit area.
DQ	35	7	M	Commenced with Ranger in April 1984. Initially worked in mill as mill operator for 3 years. Transferred to mine as a plant operator in the mining process for 4 years. Was then transferred back to the position of mill operator in the mill.
<i>Controls</i>				
BA	37	na	M	5 years in Jabiru
BT	45	na	F	6 years in Jabiru
BL	38	na		5 years in Jabiru

na: not applicable.

4. Results and discussion

Lead concentrations in blood varied from 2.9 to 12.8 µg/dl, these values compare with the ‘health’ guidelines of the Australian National Health and Medical Research Council of 10 µg/dl. The lead isotopic composition for blood samples fall into two distinct fields of quite different slopes on a plot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 1). One field is represented by the data for the mining employees and has a very low slope, in contrast to the other, incorporating the data for the three non-exposed (control) subjects, which has a steeper slope. The data for the mining employees is consistent with patterns for uranium mineralisation and that expected if any body burden of lead was derived from uranium. The data for the three controls lie along a ‘common’ lead trend, which is consistent with blood lead data we have obtained for more than 630 samples from Australian subjects (e.g. Gulson et al., 1994, 1996). The data for subject DN lies between the two trends. As he has the highest concentration of lead in blood of 12.8 µg/dl, the isotopic composition may reflect a slower rate of exchange from a former higher ‘common’ lead exposure with that from the uranium ore, or ongoing exposure from a ‘common’ lead source, such as making lead sinkers for fishing (Table 2).

Table 2

Lead isotope ratios and concentration in blood

Subject	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	PbB (µg/dl)
<i>Mine employees</i>						
DN	2.0314	0.8489	18.41	15.63	37.40	12.8
DP	1.8768	0.8064	19.52	15.74	36.63	8.4
DO	2.0118	0.8591	18.15	15.60	36.52	4.5
DT	2.1271	0.8999	17.23	15.50	36.65	4.8
DU	2.0949	0.8824	17.56	15.50	36.80	8.4
DR	2.1049	0.8948	17.27	15.45	36.35	6.6
DM	1.981	0.8407	18.60	15.64	36.85	7.3
DS	2.0566	0.8690	17.90	15.56	36.82	10.2
DQ	2.0584	0.8737	17.81	15.56	36.67	5.0
<i>Controls</i>						
BA	2.1343	0.8927	17.36	15.50	37.06	6.9
BT	2.1689	0.9183	16.82	15.44	36.48	2.9
BL	2.157	0.9081	17.12	15.55	36.93	4.2

Uptake of uranium could be via several pathways including inhalation and/or ingestion of fine dust, and/or dermal absorption. Given the tropical conditions, any of these pathways could be significant in contributing to body burden. For example, this environment is conducive to non-compliance for wearing protective clothing or respirators. Likewise, the hot and humid conditions, and consequent perspiration, facilitate dermal absorption of metals from the dust (Florence et al., 1988; Lilley et al., 1988; Mielke

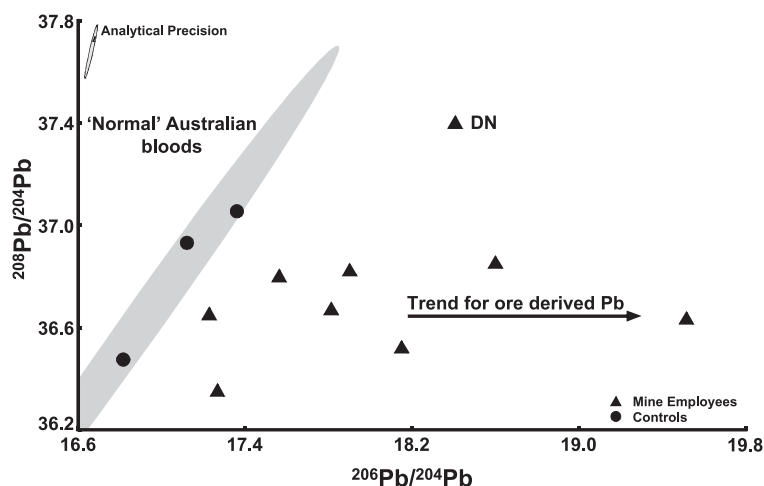


Fig. 1. Isotopic ratio plot comparing the bloods from employees potentially exposed to uranium ore with controls. ^{208}Pb is derived from ^{232}Th and ^{206}Pb from ^{238}U . The shaded ellipse encompasses the blood data for 630 samples from Australian residents. Rock samples containing uranium can have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios >10,000 but with a negligible change in $^{208}\text{Pb}/^{204}\text{Pb}$. The analytical precision of the measurements is denoted by the ellipse in the upper left hand corner.

et al., 1997; Moore et al., 1980; Omokhodion and Howard, 1991; Rastogi and Clausen, 1976; Stauber et al., 1994). Nevertheless, US EPA maintains that uranium is not absorbed through the skin (<http://www.epa.gov/radiation/radionuclides/uranium.htm>).

Because of the preliminary nature of the study, no personal information such as smoking habits was sought. However, as cigarette smoke contains ^{210}Po , a decay daughter of ^{238}U and a precursor of ^{206}Pb , the possibility of smoking leading to elevated ^{206}Pb was investigated. The polonium content of cigarette smoke is in the range 1–27 Bq per cigarette (Hecht, 1999). Taking an average of 11 Bq, assuming a smoking habit of 60 per day and retention of all decay product lead in the body, then such a smoker would take in 4.5×10^{-16} g ^{206}Pb over 1 year. This is inconsequential compared to an average excess body burden of around 6×10^{-7} g in the bodies of the workers (calculation made assuming 5 l of blood and natural ^{206}Pb content estimated from data for the “normal” population shown in Fig. 1). This conclusion agrees with the lack of any trend to higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios amongst the normal population shown in Fig. 1.

Although based on a very small numbers of subjects, no relationship between blood lead and lead isotopic composition and length of exposure or employment location within the mine was found. No information for doses of radiation to individual mining employees was available, although, as mentioned above, recent and past data published by the Federal Department of Health indicate that exposures of the employees at Ranger from personal monitoring were below the radiation guidelines (<http://www.deh.gov.au/ssd/uranium-mining/outcomes/human-health/mine-workers.html>).

The ability to detect lead, probably from uranium, in blood of the employees is intriguing. The increase in ^{206}Pb indicates intake of unprocessed ore is responsible. Uranium ore from this area has extremely high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of over 11,000 (Hills and Richards, 1976; Gulson and Mizon, 1980) and, if the ore had remained geochemically isolated since formation of the deposit at ~1750 Ma BP, would contain roughly 3.7 times as much U as Pb. We do not have figures for Ranger but, at nearby Jabiluka mine, ore with 1% U contains 680 ppm Pb (Binns et al., 1980). Assuming similar amounts of Pb in Ranger ore and retention of 10% of the ingested Pb, then the increases seen in ^{206}Pb

represent ingestions of between 0.9 and 15 mg, integrated over the years of exposure. Intake of product uranium oxide is not detected by Pb isotopes as pure uranium oxide contains no Pb. Uranium stored in the body also contributes insignificant ^{206}Pb . One milligram of U in the body for 10 years would only add 1.3×10^{-12} g ^{206}Pb to the total Pb body burden. This small amount would not affect blood lead concentrations, but appears to be sufficient to be detectable in the isotopic composition. Although both uranium and lead are present at very low concentrations in the blood, as most is excreted, they are preferentially stored in the bone and may be potential sources of toxicity (<http://www.epa.gov/radiation/radionuclides/uranium.htm>).

A similar study to this one was proposed in the giant copper–uranium–gold mine in South Australia but was rejected by the company. As the mining of the ore at Olympic Dam is by underground processes, any lead arising from uranium exposure should be more easily detected at Olympic Dam compared with open pit operations at Ranger.

Any future investigations using this approach should incorporate control of personal measures such as air, personal information and urine analysis. With respect to urine, in March 2004, 20 Ranger employees consumed water containing 400 times the normal limit of uranium (<http://msowww.anu.edu.au/~peterson/drinkuranium.html>). Lead isotope monitoring of blood and especially urine may provide information on clearance of uranium and daughter products from workers suffering such exposure.

Acknowledgements

We thank Glen Riley, formerly of the Office of the Supervising Scientist, for facilitating this study; Rob Authy, Doug Duthie, Sue Resta of Ranger Uranium Mines for agreeing to this study and collection of the blood samples; and the volunteers in the study. We also acknowledge the anonymous reviewer who raised the question regarding polonium in cigarettes.

References

- Binns RA, Ayres DE, Wilmshurst JR, Ramsden AR. Petrology and geochemistry of alteration associated with uranium mineraliza-

- tion at Jabiluka, Northern Territory, Australia Uranium in the Pine Creek geosyncline. In: Ferguson J, Goleby AB, editors. Proc. International Uranium Symposium on the Pine Creek Geosyncline. Vienna: IAEA; 1980. p. 417–38.
- Florence TM, Lilley SG, Stauber JL. Skin absorption of lead. *Lancet* 1988;2:157–8.
- Gulson BL, Mizon KJ. Lead isotope studies at Jabiluka. Uranium in the Pine Creek geosyncline. In: Ferguson J, Goleby AB, editors. Proc. International Uranium Symposium on the Pine Creek Geosyncline. Vienna: IAEA; 1980. p. 439–55.
- Gulson BL, Mizon KJ, Law AJ, Korsch MJ, Davis JJ. Source and pathways of lead in humans from the Broken Hill mining community—an alternative use of exploration methods. *Econ Geol* 1994;89:889–908.
- Gulson BL, Pisaniello D, McMichael AJ, Mahaffey KR, Luke C, Mizon KJ, et al. Stable lead isotope profiles in smelter and general urban communities. Comparison of biological and environmental measures. *Environ Geochem Health* 1996;18:147–63.
- Hecht SS. Tobacco smoke carcinogens and lung cancer. *J Natl Cancer Inst* 1999;91:1194–210.
- Hills JH, Richards JR. Pitchblende and galena ages in the Alligator Rivers region, Northern Territory, Australia. *Miner Depos* 1976; 11:133–54.
- Lilley SG, Florence TM, Stauber JL. The use of sweat to monitor lead absorption through the skin. *Sci Total Environ* 1988;76:267–78.
- Mielke HW, Taylor MD, Gonzales CR, Smith MK, Daniels PV, Buckner AV. Lead based hair products: too hazardous for household use. *J Am Pharm Assoc* 1997;NS37:85–9 [<http://www.aphanet.org/APhA/hair.html>].
- Moore MR, Meredith PA, Watson WS, Sumner DJ, Taylor MK, Goldberg A. The percutaneous absorption of lead-203 in humans from cosmetic preparations containing lead acetate, as assessed by whole-body counting and other techniques. *Food Cosmet Toxicol* 1980;18:399–405.
- Omokhodion FO, Howard JM. Sweat lead levels in persons with high blood lead levels: lead in sweat of lead workers in the tropics. *Sci Total Environ* 1991;103:123–8.
- Rastogi SC, Clausen J. Absorption of lead through the skin. *Toxicology* 1976;6:371–6.
- Stauber JL, Florence TM, Gulson BL, Dale LS. Percutaneous absorption of inorganic lead compounds. *Sci Total Environ* 1994;145:55–70.