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Atmospheric transport of radiogenic lead in the vicinity of Ranger uranium mine determined using lead isotope ratios in dust deposited on acacia leaves

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Abstract

To investigate the effect of uranium mines on the airborne dust Pb isotopic composition, a case study was carried out to study the distance that radiogenic dust travels from Ranger Uranium mine, the only open cut uranium mine in Australia. Acacia leaves were utilized as passive dust collectors to obtain a spatial snapshot of Pb deposition. In addition, an annual cycle of Pb concentration and Pb isotopic composition of aerosols was obtained at Jabiru East using low volume air samplers to investigate temporal differences due to the distinctively different wet and dry seasons in the Alligator Rivers Region.

The project is part of a larger study, that was instigated at Curtin University of Technlogy, Perth. During 1999 and 2000 baseline aerosol Pb concentrations and isotopic compositions had been obtained at the Cape Grim Baseline Air Pollution Station (Rosman et al., 2000a). Those samples showed extremely low airborne Pb concentrations and occasionally an influence from highly radiogenic Pb, of which uranium mines can be a likely source. The question arose as to what and where the likely source of radiogenic dust might be and a preliminary study was carried out measuring the Pb isotopic composition of dust collected on leaves from 11 sites within Kakadu National Park.

The precision of the measurements of Pb isotopic ratios collected on the leaves during this preliminary stage of the project was quite low, attributed to organic interference occurring during chemistry procedures and analysis using Thermal Ionisation Mass Spectrometry. The interference issue was solved by additional chemistry techniques whereby leaf sample solutions were processed adding 1.5-2 ml 1:5 H_2O_2/HNO_3, combined with microwave digestion and a double column procedure to dissolve and separate organic material from elemental Pb. At least a tenfold increase in precision was observed on selected samples.

However, a consequence of using the new sample preparation technique was the addition of a high blank. The H_2O_2 used was unable to be cleaned effectively; other reagents used in the column chemistry process (HCl, HBr) were also found to contain high levels of Pb that were deemed uncleanable using standard distilling techniques. A method implementing HNO_3 was tested and combined with a double column procedure to obtain blanks of 20-60pg for sample sizes ranging from 200pg-100ng.

A total of 33 leaf samples were collected around the Ranger Uranium Mine during the dry season in June 2002 to measure the dispersion of radiogenic Pb from the mine site. In adition, aerosol samples have been collected between May 2001 and July 2002 and were measured at Curtin University of Technology, Perth, for Pb concentration and isotopic composition in April 2003.

Pb isotope ratios were more radiogenic during the dry season, and showed natural background dust Pb isotope ratios during the wet season. Airborne Pb isotope ratios of up to 4.000 for $^{206}Pb/^{207}Pb$ and as low

as 1.550 for $^{208}Pb/^{207}Pb$ have been determined in Jabiru East. A contribution of up to 30% radiogenic Pb originating from Ranger U mine to overall Pb levels at Jabiru East during the dry season could be detected.

It was revealed that radiogenic Pb, borne from the decay of ^{235}U and ^{238}U, can be detected up to 40 km away from the Ranger uranium mine site, although the contribution to Pb concentrations is quite small. In addition, Pb isotope ratios are more radiogenic in a northwesterly direction of the mine site, following the main wind direction.

This internal report has been adopted from Honours Dissertation 499-2, Curtin University of Technology, Perth, by R. Honeybun. Temporal Pb isotope data have been measured in April 2003 and were added to the overall results.

1 Background

In 1999 aerosols from the Southern Ocean were collected at Cape Grim, Tasmania in an effort to measure the baseline airborne Pb concentration and isotopic composition in the southern hemisphere and identify sources of pollution worldwide. The results showed that airborne Pb concentration was extremely low and comparable to Antarctic aerosols. It was expected that the Pb isotopic composition would show a composite of anthropogenic Pb emissions from countries in the southern hemisphere, blown across the Southern Ocean to Tasmania with the 'Roaring Fourties'.

However, some of the aerosol samples exhibited a distinct radiogenic influence (represented by a notable shift in the ^{206}Pb//^{207}Pb and ^{208}Pb/^{207}Pb isotope ratios). The question arose as to what factors can cause such a shift: a likely candidate is radiogenic dust originating from uranium rich minerals. For example, dust from uranium mines, either from tailings or created during blasting, crushing and milling of uranium ore, or dust from uranium bearing tailings from gold mining industry, have a radiogenic Pb component as a result of their high ^{235}U and ^{238}U content (Gulson et al., 1994; Winde, 2002). This results in relatively higher ^{206}Pb//^{207}Pb and lower ^{208}Pb/^{207}Pb isotope ratios as compared to crustal Pb isotope ratios.

Subsequently, a preliminary study of the fallout of Pb originating from dust from a uranium mine was initiated. Ranger Uranium mine, the only active open cut uranium mine in Australia, was chosen for the case study. The study involved the collection of leaves at increasing distance from the mine site (Honeybun, 2001). In this preliminary study it was found that Pb concentration decreased with increasing distance from the mine and that ^{206}Pb/^{207}Pb isotope ratios observed close to the mine were highly radiogenic. It was expected that the Pb isotopic composition could be used to confirm the minesite as the source of the Pb, however due to organic interferences present in the leaf processing procedure, the source could not be identified.

During 2001-2002 a procedure was developed that allowed for the measurement of Pb collected on leaves to be measured with high precision (Honeybun, 2002). Various other procedures were reviewed, including microwave dissolution; ultrasound agitation; centrifuging and wet/dry ashing involving reagents such as HF, H_3PO_4, H_2SO_4, $HClO_4$. A method combining two anion exchange columns and a H_2O_2/HNO_3 microwave procedure was chosen for the sample preparation. The procedure was applied to samples previously mass spectrometrically analysed to demonstrate the improvement that was achieved. The precision of the ^{206}Pb//^{207}Pb ratios measured in samples was consistently better than 0.04-0.08% for 1-2 ng samples measured on a Daly detector (95% confidence interval). This represented at least a 10-fold improvement. The improvement in precision was accompanied by significant changes in the Pb isotopic ratios, of which some were due to a reduction in the level of interferences in the mass spectra. Other shifts indicated however, that the new procedure was subject to a significant increase in the blank Pb contribution.

Teflon filters have been used to collect Pb in aerosols on a global scale, resulting in a world map of Pb isotope ratios (Bollhöfer et al., 1999; Bollhöfer and Rosman, 2000, 2001, 2002). Leaves however have the advantage of ease of aerosol collection at remote sites without the need for a power source associated with filter collection systems. A successful correlation of leaf and filter Pb isotope data may allow leaves to be used in place of filters at any location.

2 Introduction

Southern Hemisphere aerosols were collected at Cape Grim Baseline Air Pollution Station during 1999-2000. It was expected that the isotopic composition of the Pb at Cape Grim would give a background composition for the Southern Hemisphere from anthropogenic sources such as petrol and industry emissions (Figure 1).

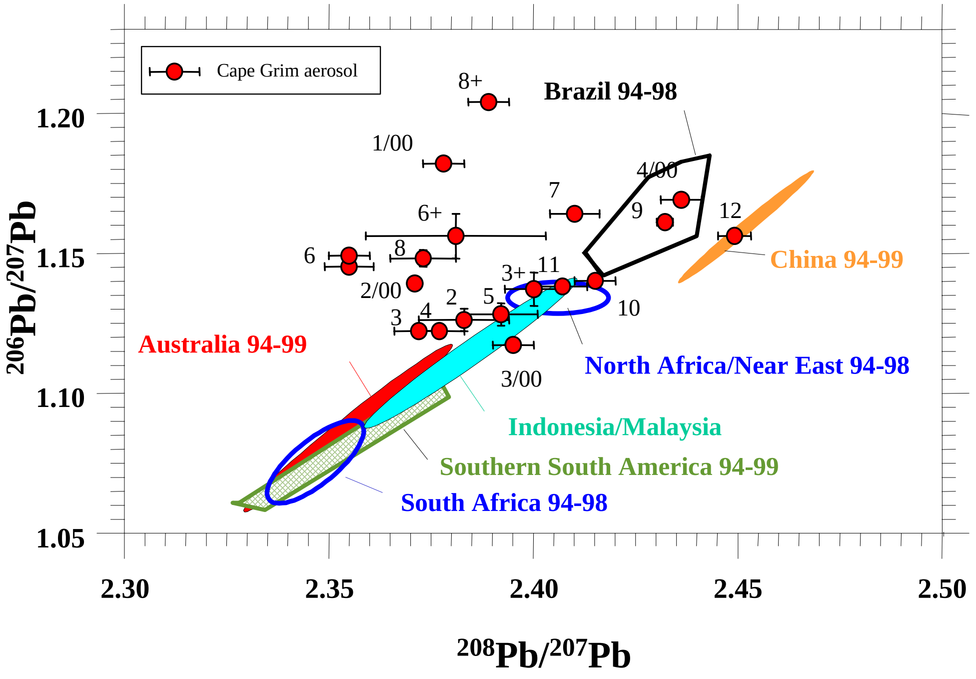


Figure 1 Pb isotopic composition of aerosols in the Southern Hemisphere (Bollhöfer and Rosman, 2000) superimposed with Cape Grim aerosol data (Rosman et al., 2000a)

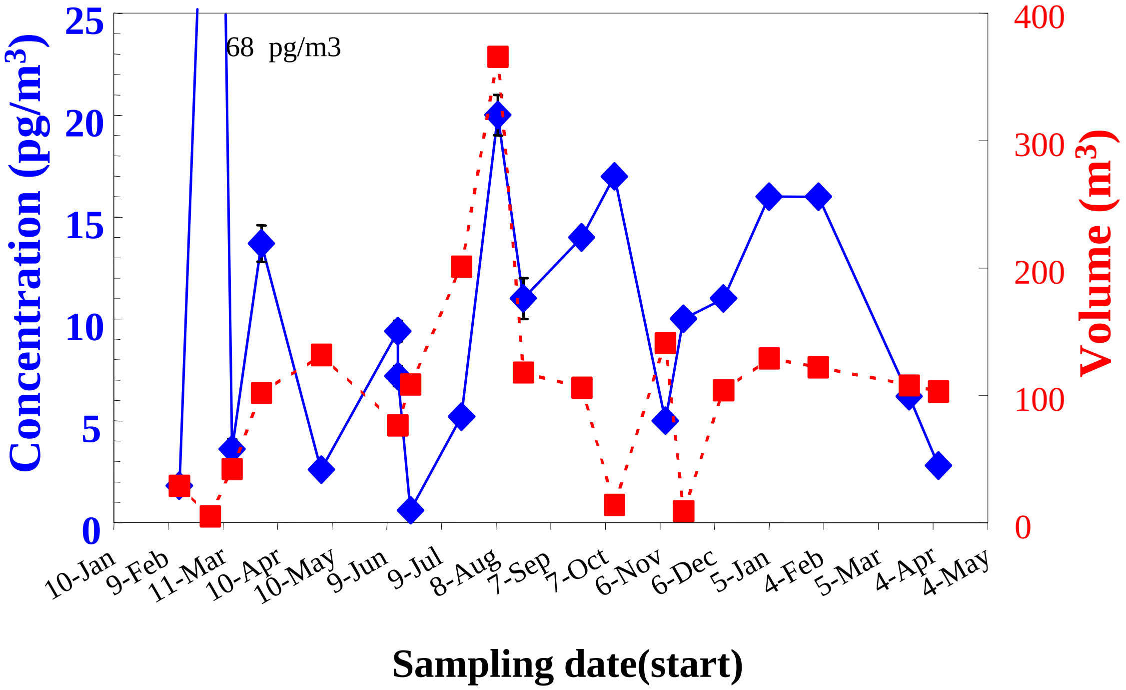


Figure 2 Pb concentration of baseline air at Cape Grim (Rosman et al., 2000a)

The results however show a significant radiogenic shift in 8 of 19 of the data points. The question was raised as to what could be contributing to the shift in the Pb isotope ratios; one of the possible candidates being dust with a large proportion of radiogenic Pb originating from uranium mines.

The source of the radiogenic Pb can possibly be determined by identifying U mines operating in the southern hemisphere during the aerosol sampling period at Cape Grim during 1999-2000. During this period only two mines were producing and extracting uranium ore in Australia (Figure 3), namely Olympic Dam and the Ranger Uranium Mine. Olympic Dam is an underground, low U yield (0.053% ore grade) mine site (UIC, 2000), producing $2x10^5$t of Cu and 10^3t Au in addition to $5x10^3$t U_3O_8 per year.

Ranger is an open cut uranium mine (0.2–0.4 % U_3O_8) and was chosen for our case study to investigate the influence of uranium rich dust on the Pb isotopic composition of aerosols. Leaves were collected near the Ranger uranium mine and preliminary results showed that the radiogenic Pb could be easily identified using the leaves as collectors (Figure 4).

Dust at Cape Grim was collected only when the wind was blowing from the 190°-280° sector (fig. 3) and back trajectories measured during the sampling period at Cape Grim showed that Ranger uranium mine is a very unlikely source of radiogenic Pb measured at Tasmania. However, there may be several other sources in the southern hemisphere, for example in Southern Africa.

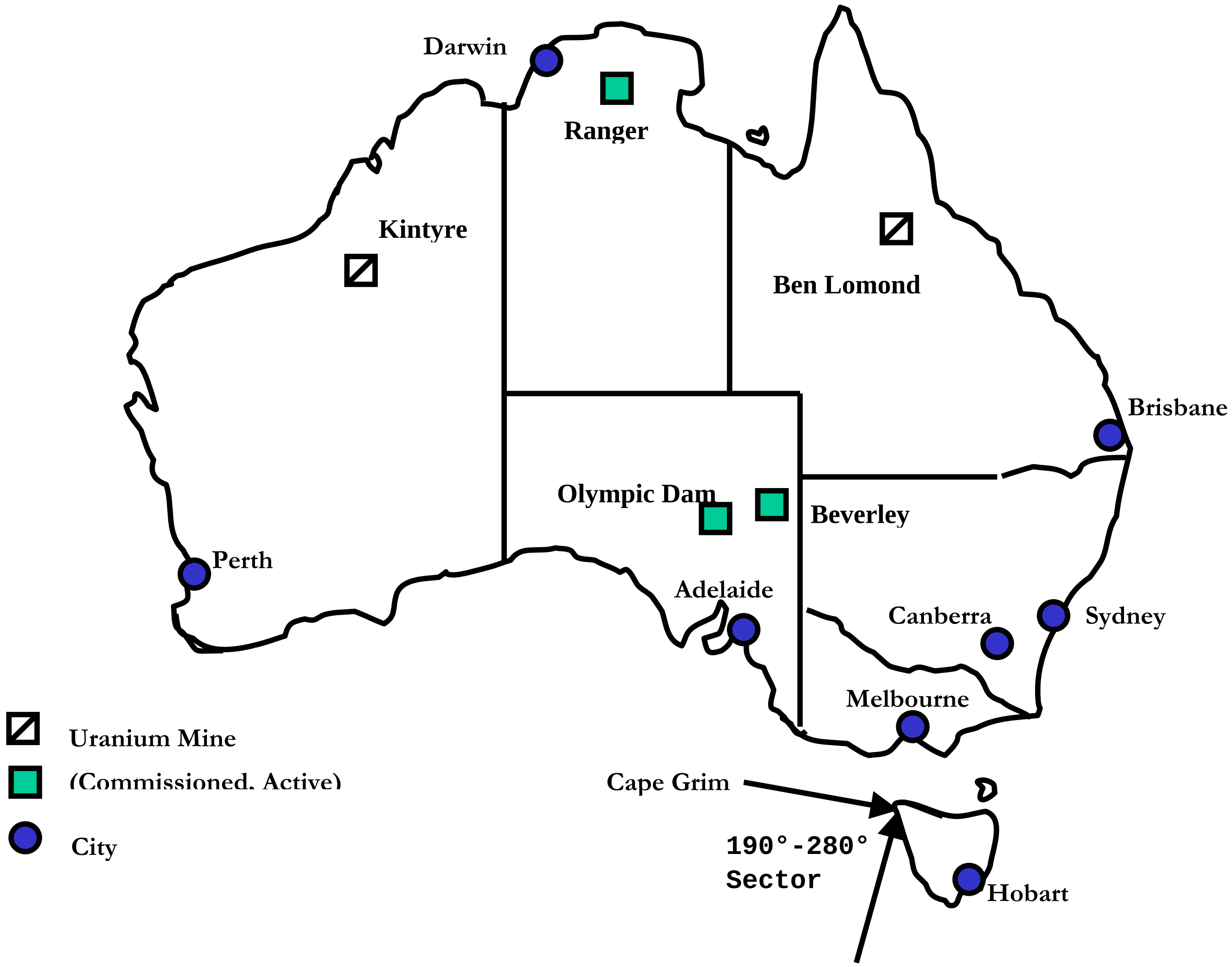


Figure 3 Current and prospective U mine sites in Australia

Although the distance is much greater, Gabon in central west Africa is extensively mined for uranium and might be a source of radiogenic Pb. Supporting this possibility, the Earth Probe TOMS (Total Ozone Mapping Spectrum, http://toms.gsfc.nasa.gov) aerosol index satellite data shows this region to be a source of aerosols and demonstrates that they can travel down the west coast of Africa and then eastward across the Southern Ocean towards Australia within a few days. Biomass burning in Gabon is expected to be significant source of fine dust particles, containing highly radiogenic Pb. In addition, gold mining in South Africa represents a potential source of radiogenic Pb in dust. In general, uranium is associated with gold ore bodies and over 10 times more uranium bearing tailings exist in South Africa, in the greater area of Johannesburg, than in 18 other countries worldwide. More than 600.000 t of uranium in tailings from gold mining are exposed to the biosphere in the Witwatersrand area in South Africa alone (Winde, 2002 a,b). Possibly, fine, highly radiogenic tailings particles are a source of the radiogenic Pb identified at Cape

Grim. Pb isotope data from tailings dumps in South Africa show radiogenic $^{206}Pb/^{207}Pb$ ($^{208}Pb/^{207}Pb$) ratios of 2.88 (1.71) (H. Coetze, pers. Comm.).

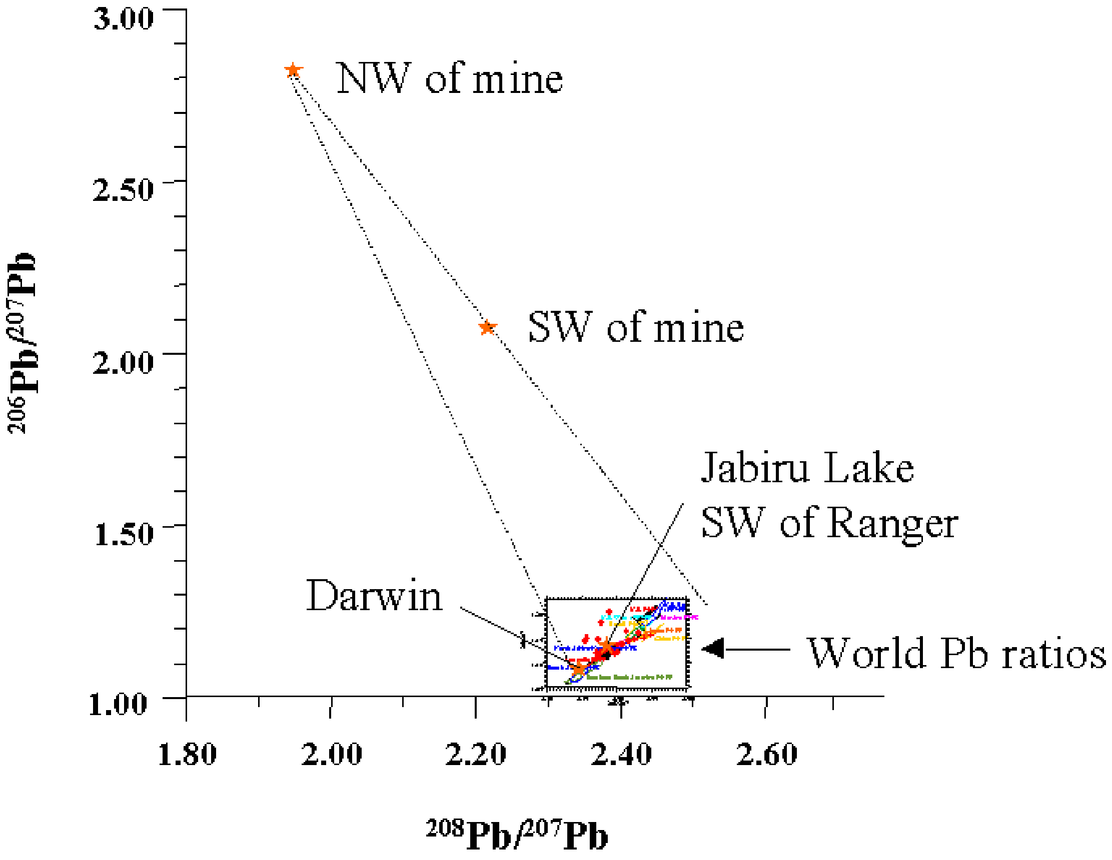


Figure 4 Aerosol Pb near the Ranger Mine, NT (Rosman et al., 2000a).

2.1 Results of samples analysed in 2001

The effects of long range transport of radiogenic Pb should be readily discernible over increasing distance from the mine site. Leaf samples were acquired at various distances (and directions) from the mine site in 2001 (figure 5). It was expected that points closer to the mine site would exhibit higher concentrations of radiogenic Pb per leaf area, and that the isotopic ratios should follow suit. Table 1 and figure 6 show the results of the Pb isotopic composition and concentration measurements.

The uncertainty on each point shown in figure 7 was found to be unacceptably large as large interferences in the ion beams were generally present. On some occasions the measurement failed completely when no ion beam was produced. (Honeybun, 2002). It was suggested that a method be developed to improve the reliability, precision and accuracy of measurements. A new procedure developed during a summer project (2001-2002) was adopted in the present study and is described in Section 4.3.

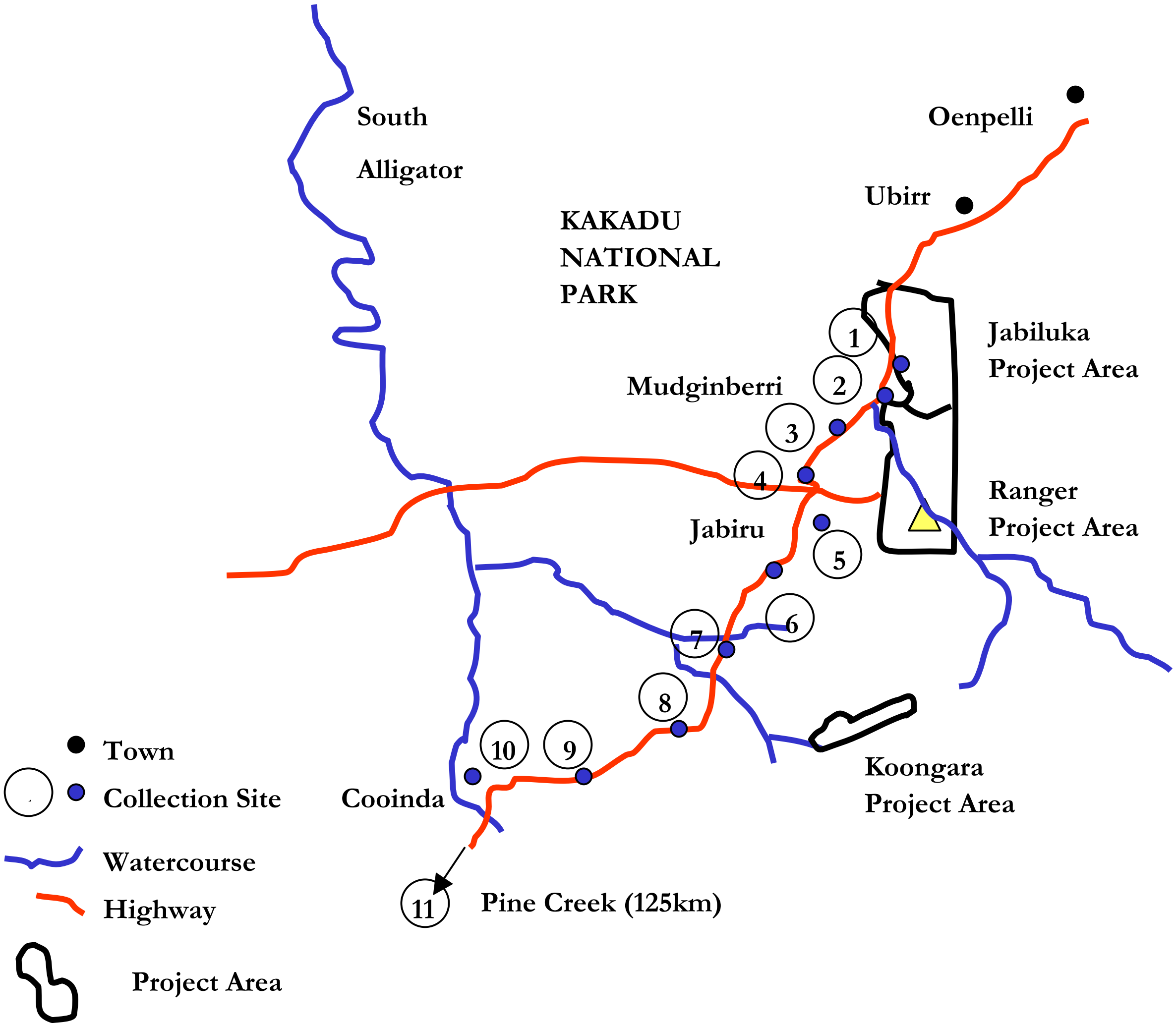


Figure 5 Leaf collection sites around the Ranger mine. Numbers identify leaf samples collected in 1999.

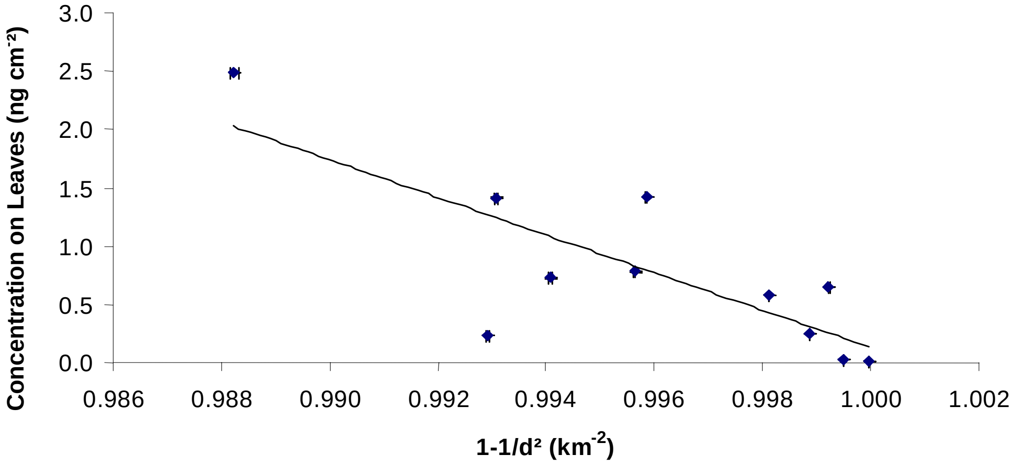


Figure 6 Pb concentration on leaves with increasing distance from mine site (Honeybun, 2001).

Table 1. Ranger leaf Pb amount and isotopic ratios corrected for blank (Honeybun, 2001)

Sample	Concentration ng/cm^2	Error*	Distance(km)±3%	206/207	95% CI	208/207	95% CI
Ranger Leaf 1	0.786	0.008	15.1	1.17	0.01	2.52	0.02
Ranger Leaf 2	0.729	0.005	13.0	1.200	0.008	2.43	0.02
Ranger Leaf 3	1.411	0.006	12.0	1.150	0.005	2.44	0.01
Ranger Leaf 4	0.233	0.003	11.9	1.81	0.01	2.19	0.02
Ranger Leaf 5	2.488	0.006	9.2	1.699	0.003	2.246	0.006
Ranger Leaf 6	1.422	0.004	15.5	1.158	0.004	2.450	0.008
Ranger Leaf 7	0.5859	0.0003	23.0	1.121	0.001	2.411	0.002
Ranger Leaf 8	0.2505	0.0005	29.8	1.147	0.009	2.39	0.02
Ranger Leaf 9	0.6468	0.0005	36.0	1.289	0.129	2.525	0.252
Ranger Leaf 10	0.0251	0.0005	44.3	0.92	0.02	1.94	0.06
Ranger Leaf 11	0.0186	0.0004	175.0	1.29	0.02	2.72	0.04

*Discounts the uncertainty in the ^{204}Pb composition uncertainty (±20%).

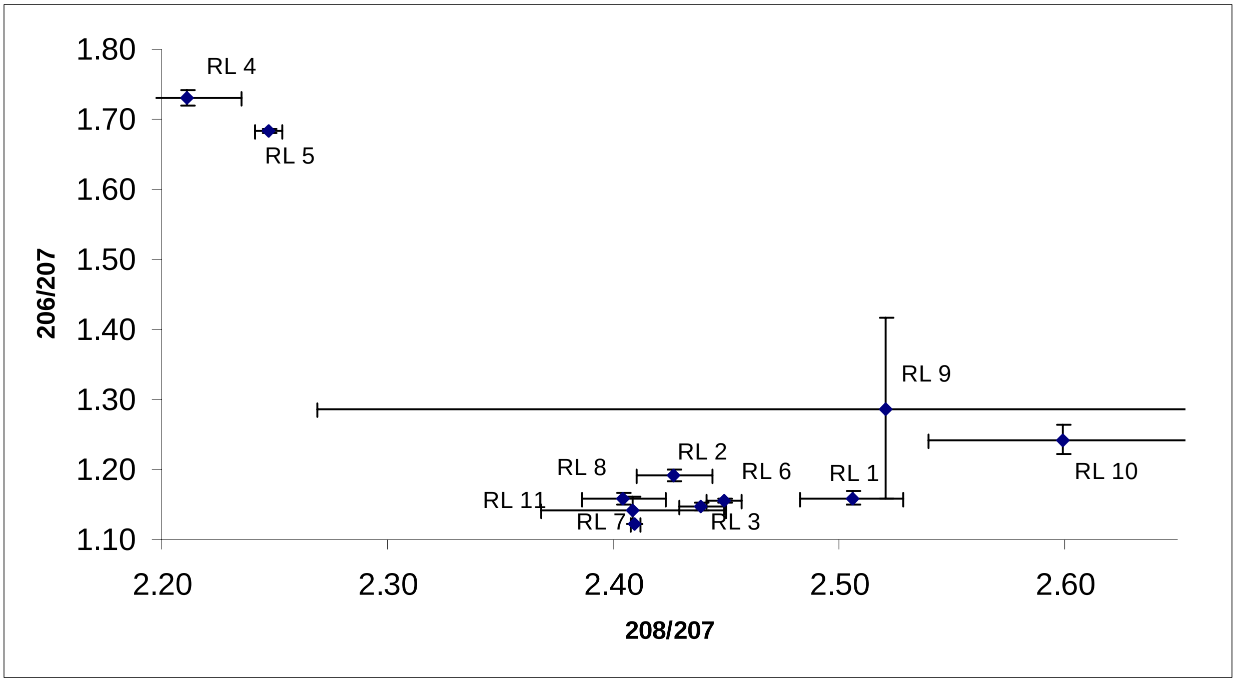


Figure 7 Ranger leaf sample ratios corrected for blank.

3 Relevant Research

In this section the main topics are reviewed, including the development of improved chemistry methods, isotopic fingerprinting and atmospheric tracing studies as well as details of dust dispersion and detection. This section is part of the original Honours Dissertation 499-2 by R.Honeybun (2002).

3.1 Chemical Procedures and Methods

A number of chemical methods exist whereby separation of the organic component from solution is required before processing via ion exchange column chemistry.

Numerous papers have been reviewed, among which it is suggested that reagents used in organic decomposition include nitric acid (HNO_3), hydrochloric (HCl), hydrofluoric (HF), perchloric ($HClO_4$) and hydrogen peroxide (H_2O_2). These papers are discussed in the following sections.

3.1.1 Digestion of Known Organic Compounds

A study of the amount of Pb present in a maple syrup was carried out by Bhandari and Amarasiriwardena, (2000). The organic structure of maple syrup is known, making it possible to combat organic material in the sample using existing chemistry techniques.

The source of contaminants in food products can be traced easily by studying the concentration of Pb in a given sample. The Pb contamination in commercially available maple syrup was measured in a variety of brands. The Pb concentration in all products tested was below the acceptable 500ng/g, and it was determined that, although there was perhaps some contamination from processing, it was not significant (Bhandari and Amarasiriwardena, 2000). This highlights an indirect industrial application of mass spectrometry in monitoring and maintaining food standards for heavy metals. Heavy metal concentration is easily determined provided an adequate spike (Section 4.6.1) and elemental separation procedure is available.

An obstacle encountered in the processing foodstuffs for heavy metals was the organic content present in the maple syrup investigated by Bhandari and Amarasiriwardena (2000). The first stage of trace metal analysis of sugar based materials is the decomposition and dissolution of the organic matrix in order to obtain a homogeneous solution. Microwave assisted closed vessel digestion techniques can be used in the dissolution of various organic matrices (Bhandari and Amarasiriwardena, 2000).

The digestion technique was designed for use in graphite furnace atomic absorption spectrometry (GFAAS), whereby the sample is initially digested with HNO_3 and/or H_2O_2. The final solution is then subjected a microwave digestive procedure, operating at 950±50W, 2450 MHz.

3.1.2 Particulate Surfaces

Sediment analysis requires the separation of all materials from the sedimentary particles, including any organic structures that may be inherent to the system. Studies carried out at Curtin University have previously analysed Pb in sediment samples in order to characterise a lake's history via its Pb concentration and isotopic composition (Best, 2000). This data could then be used to show possible pathways of contamination available to the lake. Applied to general living and health standards, this data can be used to determine the source of contaminants as well as suggest ways to minimise them. The more difficult task however is to find an effective chemistry procedure that allows for the separation of the Pb from the sediment (Section 3.1.4).

Sediment samples have previously been treated using hydrogen peroxide and sodium pyrophosphate (Mitra et al., 1999). Samples were subjected to overnight incubation in 10ml, 30% H_2O_2 and 40ml, 0.1M sodium pyrophosphate. Solutions were brought to ~80°C, adding peroxide until any bubbling ceased. Residual Mineral grains were washed in 10% acetone in order to remove salt, centrifuged and freeze dried. This procedure was implemented prior to surface area analysis.

While this procedure was designed for a analysis of a robust sample, its principles could still be applied to organic residue digestion in leaf leachates. The procedure was designed specifically to separate polycyclic aromatic hydrocarbons (PAH), where the source and sediment deposition patterns and sediment particle geometry were significant factors affecting the PAH distribution (Mitra et al, 1999). This procedure is unlike most elemental procedures as its goal was to analyse the organic component, and not the sediment.

3.1.3 Microwave Dissolution

The accumulation of trace rare-earth and radioactive metals on plant material requires the removal of any residual organic matter in order to acquire reliable results. A microwave assisted digestion technique, coupled with ICP-MS analysis, is an alternative, and more precise, method to radiometric techniques.

The study assumed that plants absorb trace metals from both the air and soil: measuring the concentration of a number of elements such as Ce, Sm, Eu, Tb, U and Th should therefore give some indication as to the pollution levels in the surrounding area (Alvarado et al., 1996). Plant leaves and tissue were collected for this purpose, requiring an appropriate method to either digest or dissolve the organic material. As the lanthanide and actinide concentrations absorbed by the plants were to be measured, the entire sample needed to be either digested or decomposed to return a reliable analysis.

Two methods were applied according to sample size. The samples were initially placed in beakers and dried at 105°C for 24 hours. After being transferred to a crucible, the sample was placed in a muffle furnace for one hour at 100°C, where the temperature was increased by 50°C every 30 minutes up to 500°C, till ashing is complete (Alvarado et al., 1996).

Wet ashing involved the sample placed in a beaker with 30ml UP HNO_3 and 10ml concentrated H_2SO_4. The beaker is placed on a heated mantle and refluxed (boiling) for 2-3 hours (Alvarado et al., 1996). Although H_2SO_4 may be an effective digestant of organic matter, its boiling point is far too high to be used in combination with teflon beakers, as used in sample preparation for TIMS analysis. An ion exchange procedure involving an SO_4^{2-} solution could be implemented, however it is far more convenient to use HBr for this purpose.

The microwave digestion procedure involved the addition of 10-15ml HNO_3 (70%) and 1ml H_2O_2 (30%) to the samples, stepping 100-600W at 2 - 5 minute intervals (Alvarado et al., 1996). The procedure used in Alvarado et al. formed a basis for what was to become the current microwave digestion + H_2O_2/ HNO_3 method used in the digestion of residual organics during leaf leaching.

An alternative microwave procedure was employed by Watkins et al. (1995) in an effort to study the presence/population of rare earth metals captured in coal samples. The removal of a large organic presence (elemental and molecular C) was required, this most easily achieved by applying large quantities of acids to the sample. 3ml of 14N HNO_3 was added to 0.1g of the finely powdered homogenised coal. The sample is irradiated in a pressure vessel, requiring 3 minutes at 25% power, then 4 minutes at 50%. The sample is cooled then 1ml 32% H_2O_2 is added and the microwave procedure repeated. This method produced results showing no residual organic products. Inorganic coal constituents were digested using 4ml of 28 M HF, and subjected once again to the irradiation procedure (Watkins et al., 1995).

3.1.4 Sediment Leaching

The analysis of sediments requires a large number of procedures in order to separate the elements to be analysed and any known interferences. Tessier et al. developed a number of procedures to remove organic matter and other unwanted compounds found in sediments. The amount of each compound was measured after each stage to measure the relative effectiveness of each reagent, and this has been used as a digestion benchmark for the development of numerous organic removal procedures henceforth. Methods involved the removal of exchangeable ions, carbonates, Fe-Mn oxides, organics, and residual compounds such as silicates. The most relevant of these procedures includes the removal of organic matter from the sample, the details of which are listed below.

A solution 3ml 0.02M HNO_3, 5ml 30% H_2O_2 adjusted to pH 2 with HNO_3 is added to the sample, and the mixture is heated to 85±2°C for 2 hours with occasional agitation. A second identical aliquot of H_2O_2/ HNO_3 solution was added to the sample and heated to 85±2°C for a further 3 hours (including intermittent agitation). Further processing is required to separate unwanted matter from the sediment, though these can not be applied to organic in solution from leaf leaching. The procedure used by (Honeybun, 2002) is an adaptation of the method mentioned, where used (Tessier et al., 1979) using similar reagent quantities and ratios; addition of reagents and agitation was continued until all organic matter was digested.

3.1.5 Bulk Organic Digestion

Pb isotope composition and concentration has been measured in the wood of trees adjacent to a main road in Firenze, Italy. As the method is designed for elemental lead, it can be assumed that the procedures followed should produce reliable results if applied to other organic collectors, such as leaves. This procedure was initially developed for radiocarbon analyses of wood (Kalin et al., 1995), and was tested to verify it's suitability for the removal of exchangeable heavy metals. (Tommasini et al., 2000)

Samples are placed in an ultrasonic bath with MQW for 6 hours at 50°C, then desiccated in an oven at 80°C for 2 days. The samples are then leached in distilled toluene for 6 hours at 50°C to remove any resins or tars, then rinsed thoroughly with MQW. Sugars are removed by washing in an ultrasonic bath with MQW for 6 hours at 50°C, then rinsed again with MQW. The samples are finally dried on a hotplate at 80°C.

After oxidation on a hotplate at 120°C with 10ml of 14N HNO_3 for 12 hours, the solution is evaporated to dryness at 80°C. The step is repeated with 5,4,3 and 3ml of 14N HNO_3 until organic matter has been completely destroyed. Sample is dissoluted in 10ml 6N HCl at 120°C for 24 hours and dried. The Pb was then complexed in to 1ml of 0.7N HBr, centrifuging the residue. The outcome of this study concluded that trees are effective biochemical tracers of heavy metals, and tree rings can be used as an archive of pollution history.

While the above procedure has been implemented successfully in the digestion of organic material, there are a number of issues that arise when applying this procedure to leaves as aerosol collectors. The first instance concerns the digestion of the collector: the area of a leaf will determine the total aerosol count, and in turn the amount of Pb measured on the leaf. Without knowledge of the leaf's area, it is not possible to make any observations based on the composition and/or concentration of Pb observed and it's relation to collector size. This issue can be resolved by digesting a standard leaf area, though due to samples limits, this would only be a small amount of organic material.

Another problem faced is the amount of Pb leached off the leaf. In a previous study, the amount of Pb measured on leaves was between 0.02 and 2.5ng/cm² (Honeybun, 2001). At such low levels, the blank (though less than 100pg) can become a significant factor, reducing the precision of any measurement due to the uncertainty on the blank. Due to the rarity of the sample, a digestion method such as the one described above would not be suitable for low Pb level measurements.

3.1.6 Non-reagent Dependent Techniques

Other organic separation, decomposition and digestion techniques include ultrasound agitation, double ion exchange columns or microwave digestion. Some of these methods are used in conjunction with reagents, though the majority of them are reagent free. If clean procedures (HEPA filtered labs, acid cleaned containers/utensils) are employed a low blank may be expected, a critical factor when analysing very small samples.

Other chemical methods also exist that allow for accurate isotopic/elemental separation, such as HPC-X-DIS/Supercritical Fluid Extraction analysis techniques. Samples prepared using these methods undergo gas chromatography (sample is leached in-situ) (Turner, 2002) and is unsuitable for the analysis of Pb due to lack of precision, applicability and probable blank contribution.

3.1.7 Microwave Digestion

As detailed in Sections 3.1.3 and 3.1.5, the microwave digestion technique usually involves the destruction of the collector upon which aerosols or particulates are collected. It is standard procedure to irradiate the sample, intermittently: 2 minutes on, 2 minutes off etc. This allows for any changes in the sample to be observed during these break periods. This procedure was carried out with good effect on a random leaf sample from outside the Physics Building of Curtin University (Honeybun, 2002). The changes apparent in response to increasing t in the microwave were noted and are displayed in Table 2.

Table 2. Effects of microwave dissolution on organic leachate after adding HNO_3- H_2O_2 (Honeybun, 2002)

Time	Observation
1 minute	Solution has gone bright yellow
2minutes	Solution appears orange-red
After 1 minute in microwave	Dark orange gas in teflon beaker. Solution is dark yellow
After 2 minutes in microwave	Yellow gas. Light Yellow Solution.
After 3 minutes in microwave	Little (visible) gas. Solution darker
After 5 minutes in microwave	No gas apparent. Less liquid in solution - >perhaps darker still
After 10 minutes in microwave	No gas. Solution almost colourless
After 15 minutes in microwave	Solution is transparent, though coloured slightly

From this data it was decided that a total time of ten minutes microwave, with intermittent cooling periods (allowing for any dissipation of gaseous products/pressure escape) was required. The condition of solution after periods of 10 and 15 minutes was attributed to readsorption of gaseous products produced during microwave excitation (Honeybun, 2002).

Reagents are added and teflon beakers sealed, for user safety reasons samples are further encased in teflon bombs. Microwave digestion is applied intermittently for 10 minutes to achieve total organic digestion (Honeybun, 2002).

3.1.8 Summary

The methods mentioned in Section 3.1.1-3.1.7 involve either a large number of reagents, increasing blank contribution, or involve the digestion of the sample completely using strong and dangerous acids (HF-$HClO_4$). Other reagents, such as H_2SO_4 may be unsuitable due to their high boiling point, or inability to be distilled and ultimately cleaned. There are three important factors to consider when using leaves as collectors. These are a) there is only a small quantity of Pb to be analysed, b) the area of leaf analysed must be known in order to synthesize a meaningful analysis and c) the chosen technique must contribute as little blank as possible, while decomposing organic matter. Also the resulting solution must be compatible with anion exchange chemistry.

It was concluded that the sampling method should remain the same (leaching in dilute HBr), however the method developed will involve the addition of suitable digesting reagents that will remove the organic component. After rigorous testing of combinations of reagent methods and column chemistry, a technique used to process leaf samples was developed as a standard procedure (Honeybun, 2002).

The objective of combining microwave dissolution with a simple HNO_3/ H_2O_2 process is to minimize any blank contribution that may occur. The blank was assumed to be insignificant to the sample size in the study by Bhandari and Amarasiriwardena (2000), a direct application of organic digestion and importance of Pb quantification. The blank contribution was not accounted for in the final sample size. This is an acceptable practice for the point of the study: if high levels of Pb were detected in foodstuffs, the isotopic ratios could be used to identify the source of contamination.

The procedure developed in (Honeybun 2002) for organic dissolution of leached material from leaves has shown to contribute a blank ~500 pg. Compared to a blank size of <50 pg, this is significant contribution in sample sizes of 1-2 ng. The chemistry procedure must be developed and refined for the study of leaves. Isotopic Pb ratios, not the concentration, are the main indicator of the dispersion of dust emanating from Ranger Mine. It is imperative that a reliable and virtually contaminant free leaf processing procedure is developed in order to achieve the best results.

3.2 Isotopic Tracing

3.2.1 Atmospheric Transport of Pb

Isotopic fingerprinting of aerosols with Pb isotopes has been used to trace the atmospheric transport of lead around the world (Bollhöfer and Rosman, 2000, 2001). The phasing out of leaded petrol (unleaded petrol still has a Pb content of <0.026gl^{-1}) (Nriagu, 1990) in the US has aided in the understanding of the atmospheric transport of Pb. Another example is the transport of Pb from the Rio Tinto Pb mine in Spain to Greenland, where pollution from the mine, operating between 600BC & 300AD, has been discovered in Greenland ice (Rosman et al., 1997). A two-century history of lead pollution has been stored in the French Alps (Veysseyre, 2001), where Pb aerosols characteristic of US based petrol, has been found to have been a contaminant in snow/ice core samples (Rosman et al., 2000). Sources of pollution in the NE Atlantic Ocean (Hamelin et al., 1997), lake sediments in Central Europe (Kober et al., 1999), tree rings in Italy (Tomassini et al., 2000) are just a selection of the collection media and archives have been studied. The influence of organo- and alkyl-lead in petrol on worldwide Pb levels has been traced in Greenland snow (Rosman et al., 1993). In the Southern Hemisphere, Antarctic ice cores have been used to trace the Earth's Pb level history (Rosman and Chisholm, 1996). These studies have shown Pb aerosols are readily transported through the atmosphere, and can significantly affect sites at great distances from the original source of pollution.

Isotopic ratios are not the only means used to identify sources of pollution. Dust particle size (diameter; mass) has been successfully employed to characterise the source(s) of pollution in Budapest (Salma et al., 2000) and France (Vèron et al., 1999) in the same way isotopic ratios are used to fingerprint a source. This is perhaps a more useful approach to short range transport of pollution, and may be correlated to meteorological data including temperature, relative humidity, amount of rainfall (Wròbel et al., 2000), wind speed (Hitchins et al., 2000; Wyers and Veltkamp,1996) The mean particle diameter containing Pb has been studied, producing a Gaussian distribution with particles sizes ranging from 1.1-2.2 μm for anthropogenic aerosols (Kim et al., 1997). Precipitate size (rain droplets) has also been used to study pollution via the concentrations of selected elements (Harrison and Williams, 1982; Ebert and Baechmann, 1998), and has been correlated to traffic density, population and topographical variation (Wròbel et al., 2000). The concept of aerosol scavenging, the absorption of dust particles by water droplets, may be quantified (Hales, 1986) and has shown that elemental atmospheric concentration decreases accordingly (Wròbel et al., 2000). Elemental concentration is useful in determining the levels of pollution, as well as providing information about the source. Correlating particle size to isotopic composition and concentration would be particularly relevant to the understanding of dust dispersion.

3.2.2 Long Range Transport

The long range transport of aerosols from China to Hong Kong was studied by Fang et al. (1999). Metals found in organic compounds (octadecenoic acid, cooking reagent) namely Al and Fe were used as a signature/fingerprint of aerosols from urban areas. Remote sensing methods such as backtrajectories and mesoscale flow modelling were used to confirm that mineral aerosol transport can occur over long distances (2500km) (Fang et al., 1999).

The Pb concentration measured at distance d from a point source can be approximated from the amount of Pb at the source dispersed evenly throughout the volume of a sphere radius d, similar to the $1/r^2$ intensity decrease observed for a light source. Isotopic ratios are only applicable in such a case where there is a background concentration and isotopic composition different to the source. This is consistent with the situation involving the Ranger Mine data set, which exhibits Pb with isotopic ratios with a high radiogenic component. Meteorological data may be used to correlate the effects certain conditions have on observed isotopic ratios and concentrations. The $1/r^2$ model is effective for short range effects, however factors such as aerosol dispersion and aging are not considered.

3.3 Measurement of radiogenic dust dispersion

A study was carried out on the dispersion of radionuclides from the Ranger Uranium mine (Petterson and Koperski, 1990). This was facilitated by the use of 'sticky vinyl' sheets that were oriented to collect dust from horizontal (active) and vertical (passive) air flow(s). The results were compared to results from high volume air filter samplers. Dispersion of dust from the mine was measured as a radionuclide flux ($Bqm^{-2}d^{-1}$) and the velocity of dry deposition (cms^{-1}). The data collected was compared to the output from computer program LUCIFER (Petterson and Koperski, 1990) which models aerial dispersion implementing the diffusion-transport equation given by Pasquill:

$$C(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z\mu}\exp\left(\frac{-y^2}{2\sigma_y^2}\right)\times\left[\exp\left(-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right)+\exp\left(-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right)\right] \text{(Pasquill, 1961)}$$

Petterson and Koperski concluded that the predicted and measured data using sticky vinyl collectors correlated well. In addition, they show in their paper, that even at points several kilometeres away from the mine site, dust $^{230}Th/^{232}Th$ ratios are still at least one order of magnitude higher than soil ratios, emphasizing the influence of a uranium rich source on the dust composition in the region.

4 Experimental Procedure

In this section, procedures developed prior to the project are mentioned, ranging from the initial filter cleaning required prior to sample collection, to the transfer of the sample onto a triple rhenium filament.

4.1 Teflon Filter Preparation

4.1.1 37mm filters

37 mm Teflon filters (Savillex Corporation #1123, #1163) were cleaned and prepared using the technique described by Bollhöfer et al. (1999) (table 3).

4.1.2 47mm Filters

47 mm teflon filters (Savillex Corporation #1121, #1151) were prepared for use with a remote location solar powered aerosol collection device. The procedure utilised a cleaning procedure that did not require a hotplate. The technique is available in table 4.

Table 3 Cleaning procedure for 37mm teflon filters used to collect aerosols

Place filter(s) in teflon beaker with ethanol and HF/HCl (~1.5 M/~7 M).
Agitate in an ultrasound bath for ~2 hours
Empty solution, rinse filters with MQWx3
Empty solution, add 1M HNO_3
Transfer beaker to hotplate (24 hours)
Replace HNO_3 with MQW, transfer to hotplate for 24 hours
Empty solution and dry under HEPA-filtered air flow

Table 4 Filter Cleaning procedure without hotplate

Add filter to teflon beaker
Add ethanol (~70%) and HF/HCl (~30%) to beaker
Agitate in ultrasound bath for 1 hour on, 1hr off (x3)
Rinse filters with MQWx3
Add 1M HNO_3 to beaker
Agitatate in ultrasound 1hour on, 1hr off (x2)
Replace HNO_3, agitate 1hour on, 1 hour off (x2)
Rinse with MQW. Add MQW to filter and agitate 1hr on, 1hr off (x2)
Leave under clean hood to dry.

4.2 Sample Collection

Filters have been collected at ***eriss***, Jabiru East (NW of Ranger) for mor than one year to provide an annual cycle of Pb isotopic composition of dust aerosols at Jabiru East. The sampling kit used is described in Bollhöfer et al. (1999). The diaphragm pump was set up on top of a 5 m tower and connected to the mains at ***eriss*** along the main wind direction during the dry season. The filters were contained in plastic monitors connected to the diaphragm pumps with approximately 1 m of Teflon tubing.

To obtain geographical information, leaves from Acacia trees distributed throughout the Park have been collected in June 2002 (figures 8 and 9).

To be able to compare the two collection media, two sets of filters and leaves were analyzed that collected dust simultaneously for ~1 month. It was hoped for a correlation between airborne Pb and Pb deposited on the leaves. The collection procedure for the leaves of the comparison study involved the following steps.

1. Washing the leaf down with dilute (1M) HNO_3 and MQW

2. Collecting dust for a month

3. Storage in acid cleaned bags.

4.2.1 Collection sites and procedures to measure dispersion

Samples were collected using PE gloves, and stored in acid cleaned PE bags (Fig 8) located around the Range Mine, NT (Fig. 8). The majority of samples collected were species of acacia. Two or more leaves were collected at each sampling site.

Figure 8 Sample collection

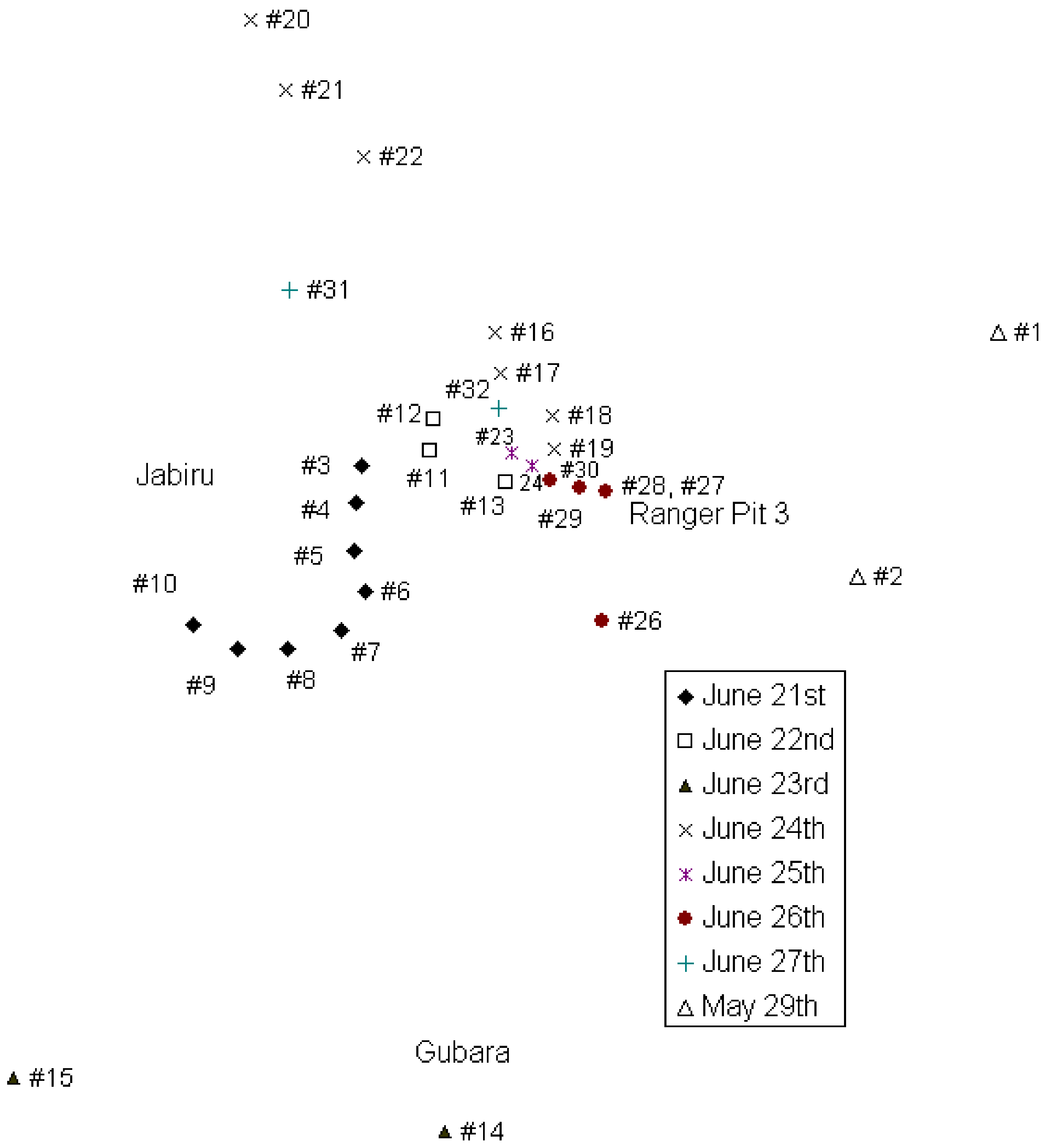


Figure 9 Leaf collection sites used to measure dispersion of radiogenic Pb from Ranger.

Samples#1, #14, #15, #20, #21 are considered background samples. These should show little radiogenic contribution and provide a background measurement for the rest of the data to be compared to. Samples NW of the mine are along the main wind direction during the dry season. Analyses of these samles may provide a fallout rate for radiogenic Pb in dust from the mine. Samples W and WSW of the mine provide supplementary data for the NW transect (not main wind direction). Samples #3-#7 are along a common radial from the mine, and are expected to change with directional change from the mine site.

4.3 Sample Processing

When subjected to an acid of given molarity, the anion exchange resin retains a scavenging coefficient, which is dependent on the type of acid used and its molarity. The resin may be prepared in such a way that it will capture all Pb in a dissoluted sample while ignoring most other elements and compounds. An ion exchange column is constructed to allow for reagents to be passed through the resin. (see figure 10).

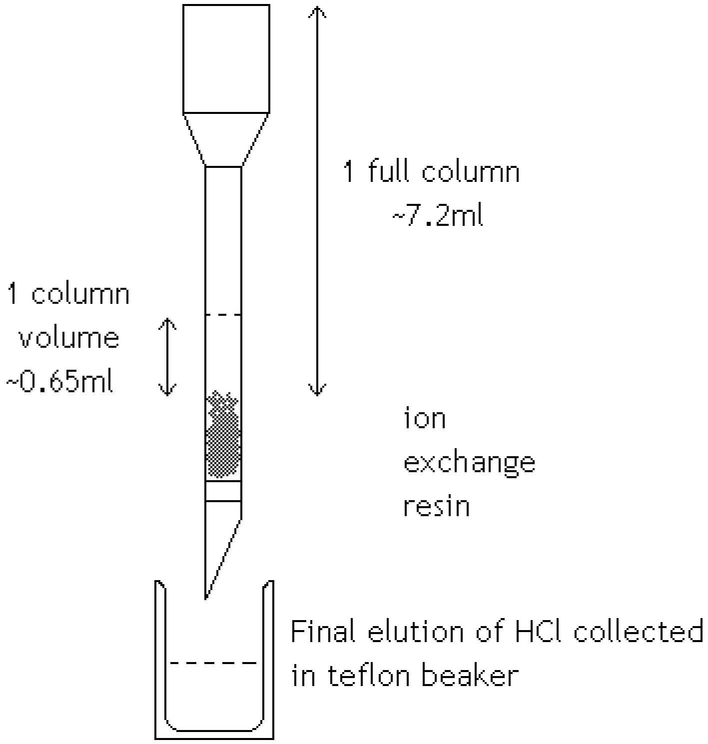


Figure 10 Ion exchange column.

4.4 Sample Dissolution and Pb Separation

This section details chemistry procedures used for soluting samples and processing them via ion exchange column chemistry.

4.4.1 Filter Leaching Method

Filter sections containing aerosols have been measured extensively at Curtin University using a standard process. The standard procedure for processing of filters for mass spectrometric analysis involves:

1. Sample soluted in low molarity (<1M) HBr for half an hour.
2. Sample is taken out of solution, rinsed with MQW allowing backwash flow into the beaker. The sample is then stored in a PE bag.
3. Sample solution undergoes anion exchange column chemistry (Table 5).
4. Sample solution is evaporated in beaker on hotplate
5. 4ul Si Gel/H_3PO_4 is used to transfer sample to triple rhenium filament before loading in carousel and mass spectrometric analyses.

A filter sample is processed using an ion exchange column following the procedure outlined in table 5. Leaves using the double column procedure/reagent method use half volumes stated.

Table 5 Processing a filter using ion exchange column chemistry

1	~2 cm (1 cv) of resin
2	3-5 full columns of MQW
3	2 full columns of dilute (0.5M)HBr
4	Elution of Pb in resin with 4ml (6cv) 9M HCl
5	1 column MQW
6	1 column 0.3M HBr
7	Sample in solution (HBr) is added
8	4 columns 0.5M HBr
9	Prepared teflon beaker is placed to collect
10	Pb in Sample is eluted with 4ml (6cv) 9M HCl

The organic anion exchange resin, has a high scavenging coefficient for Pb in low molar HBr media. This allows for capture of a sample’s Pb for later elution via high molarity (>8M) HCl, for which the Pb has a low capture cross section with the anion exchange resin.

The HCl solution containing the final filter sample solution is evaporated on the hotplate (100-120°C) with 4ul H_3PO_4/Si gel pipetted into the beaker.

4.4.2 Leaf preparation using H_2O_2

It was assumed the same procedure could be implemented for leaf sample dissolution. Due to the leaching of organic material in the leaf structure however, a new method was required. Honeybun (2002) details the development of a procedure for organic decomposition dissolution for dealing with leaf sample loading in a Thermal Ionization Mass Spetrometer. An additional procedure was developed employing a HNO_3/ H_2O_2 mixture and microwave procedure to dissolve organics. The steps are indentified in table 6.

Table 6 Organic dissolution method using HNO_3 and H_2O_2

1	Evaporate aqueous solution of HBr and sample on hotplate
2	Add HNO_3 (1-1.25ml) to obtain the sample in solution
3	Add 0.25ml-0.3ml (1 drop) H_2O_2.
4	Microwave Solution for 5min on; 5m off; 2m on; 2m off; 2m on; 2m off; 1min on; 1min off
5	Evaporate solution on hotplate, resolute in HBr
6	Pass solution through anion exchange column
7	Repeat Steps 1-6
8	Evaporate final solution on hotplate
9	Transfer evaporate with H_3PO_4/Si gel to Re filament.

This procedure was found to increase the precision of Pb isotope ratio measurements by a factor of 10 to 50 (Honeybun, 2002). A consequence of this study revealed a shift in the isotopic ratios, implying an inaccuracy in earlier measurements (Honeybun, 2001).

4.4.3 Dissolution Summary

The previous work done in this area allows for the development and analysis of a number of procedures concerning the analysis of leaves for the tracing of Pb and other elements. The first objective is to reduce the blank to an acceptable level, allowing for confidence in obtaining accurate data. Then, refinement of any procedures and ultimate determination of a filter-leaf correlation may be carried out. Leaves have been compared to filters to determine collection efficiencies (amount of Pb collected per unit area) of ~3% (Honeybun, 2001).

The previous studies have confirmed that leaves may be used in tracking Pb fallout. Combined with the leaf processing procedure and a reduced blank, it is expected that reliable and repeatable results be obtained from leaves.

5 Mass Spectrometry

This project utilises the VG354 thermal ionisation mass spectrometer (figure 11). The features of the TIMS include a 270 mm radial axis with 9 Faraday cups and one Daly collector, consisting of an secondary electron dispersion unit (Daly doorknob) and photomultiplier. The Faraday detection limit is of the order 10^{-13}A, while the Daly threshold is $<10^{-16}$A.

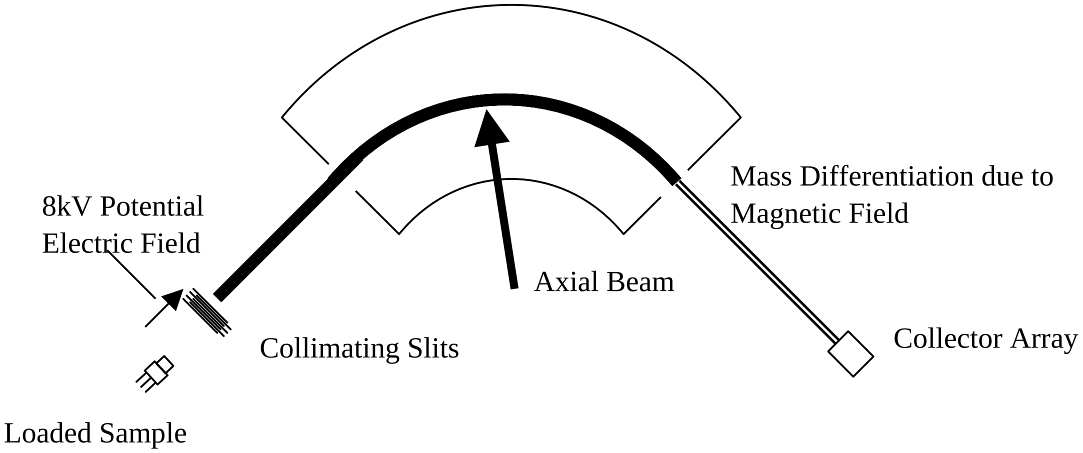


Figure 11 Schematic of VG354 Mass Spectrometer

Pb in loaded samples is initially ionised by heating the filament to ~1300°C. Positive ions (Pb^+) are accelerated by an electric field potential (V), giving ions a velocity (v) dependent on their mass (m) and charge (q)

$$qV = \frac{1}{2}mv^2$$

7 collimating plates are used to focus the ion beam, which then travels the axial arm of the mass spectrometer. The ion beam encounters a magnetic field sector, which differentiates the isotopes according to their mass. A magnetic field of 0.7T is required to achieve a 208u axial.

$$\frac{mv^2}{r} = qvB$$

therefore

$$\frac{m}{q} = \frac{B^2 r^2}{2V}$$

Ions exit the magnetic field sector perpendicular (90°) to their entry angle, travel down the axial arm of the mass spectrometer and are collected in the Faraday cups or Daly collector. There are nine Faraday collectors which may be used to collect ions simultaneously, and one Daly collector used to discriminate beams individually, most effective for very small ($<10^{-13}$ A) ion beams.

5.1 Sample Preparation

Once a sample is loaded in the carousel, the chamber is evacuated with the aid of a turbo molecular pump combined with 24 hour cold trap to cool the source. This achieves source pressures between 10^{-9} and 10^{-8} mbar. Triple rhenium filaments utilise the side filaments in the procedure known as degassing. This is carried out by applying a 1.9A current through the necessary circuit(s), heating the side filaments causing evaporation and/or ionisation of volatile elements/compounds on the central filament.

5.2 Ionisation

In the case of Pb, samples are loaded on a triple rhenium filament with 4ul Si gel/H_3PO_4. The Si gel is known to vastly increase the ionisation efficiency of a number of elements including Pb. Including H_3PO_4 in the final loading will help to further digest any residual organic material (Dickin, 1997; Manton, 1988).

The aim of the loading process is to create an Si glass from which the Pb may be ionised. It is fundamental that other elements, including Si, are ionised simultaneously. The aim of the column chemistry procedure (Section 4.4) however is to reduce or remove the presence of other elements, thereby it is expected that scanning the appropriate mass units should yield only background count(s).

5.3 Fractionation

Fractionation is a natural process that can be readily observed for light isotopes in nature. The lighter isotopes of an element are subject to processes such as ionisation first as (slightly) less energy is required to remove an electron (e- is further from the nucleus). This may be confirmed using quantum mechanical analysis of ionic interaction in elements, due to the higher potential of the electron in a heavier isotope. (Beiser, 1981)

The effect of fractionation is less pronounced in heavier isotopes as an almost linear relationship to the fractionation coefficient may be derived from the mass dependent reaction. This will affect the observed ratios during mass spectrometric analysis as the lighter isotopes will show enriched values. The standard equation used to describe this effect is

$$R_C^{\,i/j} = R_O^{\,i/j}(1 + \Delta m \times f_c)$$

where

i and j are the measured and reference isotopes respectively

Δm is the difference in mass units of the isotope ratios (j-i)

$R_C^{i/j}$ is the corrected fractionated data (ratios)

$R_O^{i/j}$ is the observed data (ratios)

f_c is the fractionation coefficient.

5.4 Data Analysis

5.4.1 Isotope Dilution Mass Spectrometry

To calculate the Pb concentration the presence of an Pb additive of known amount and isotopic composition, usually referred to as a spike, is required. Isotopic dilution mass spectrometry (IDMS) is a standard procedure for elements with more than 2 isotopes. However, the isotopic composition of the sample must first be known, making it possible to calculate concentration using any isotopic ratio.

For any isotopic ratio, the amount of sample (A) is determined by

$$A = \frac{N_A W_A}{N_S W_S} T$$

N_A, N_T Number of atoms in sample, spike

W_A, W_T Atomic Weight of sample, spike

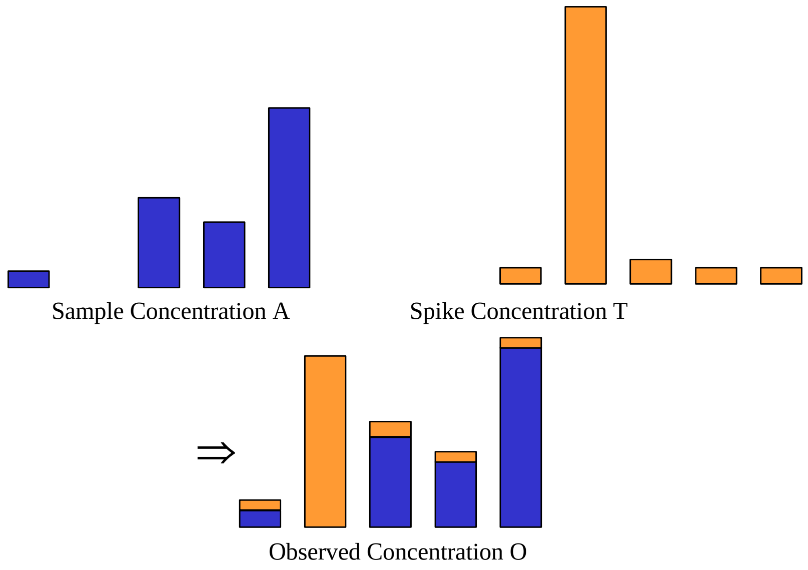


Figure 12 Isotope Dilution Method

5.4.2 Blank Quantification and Assessment

The blank is the amount of contaminating Pb added to the sample using the procedures described in Sections 4.1-4.4. This amount of contaminating Pb may be quantified running a procedural blank, a method that implements the same organic digestion, solution evaporation, column chemistry methods and loading techniques but no sample. A procedural blank operation is carried out for each batch of samples.

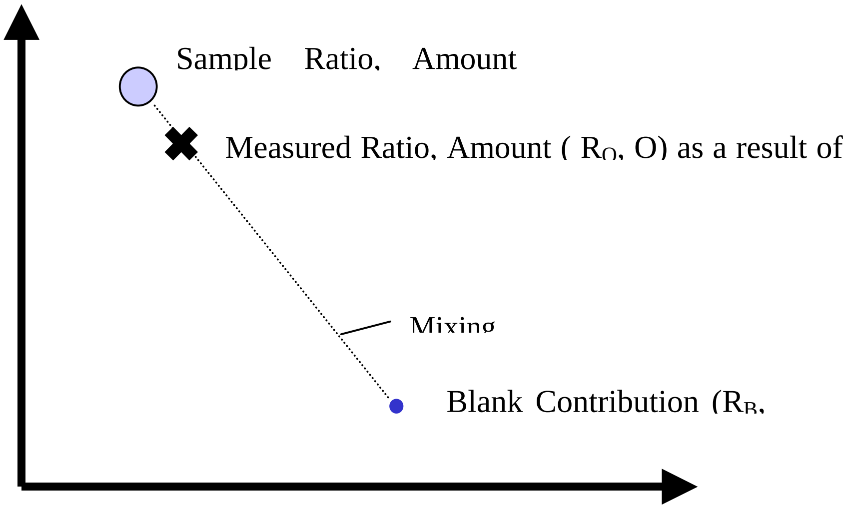


Figure 13 Mixing of blank and sample to obtain observed isotopic ratios and sample quantity

The isotopic ratios and sample quantities can be derived using

$$R_S = \frac{R_O O - R_B B}{S} = \frac{R_O O - R_B B}{O - B}$$

R_S, R_B,R_O are sample, blank and observed isotopic ratios

S, B, O are sample, blank and observed amounts

A full derivation plus analytical error calculation is given in the Appendix.

5.4.3 Pb 205 Spike

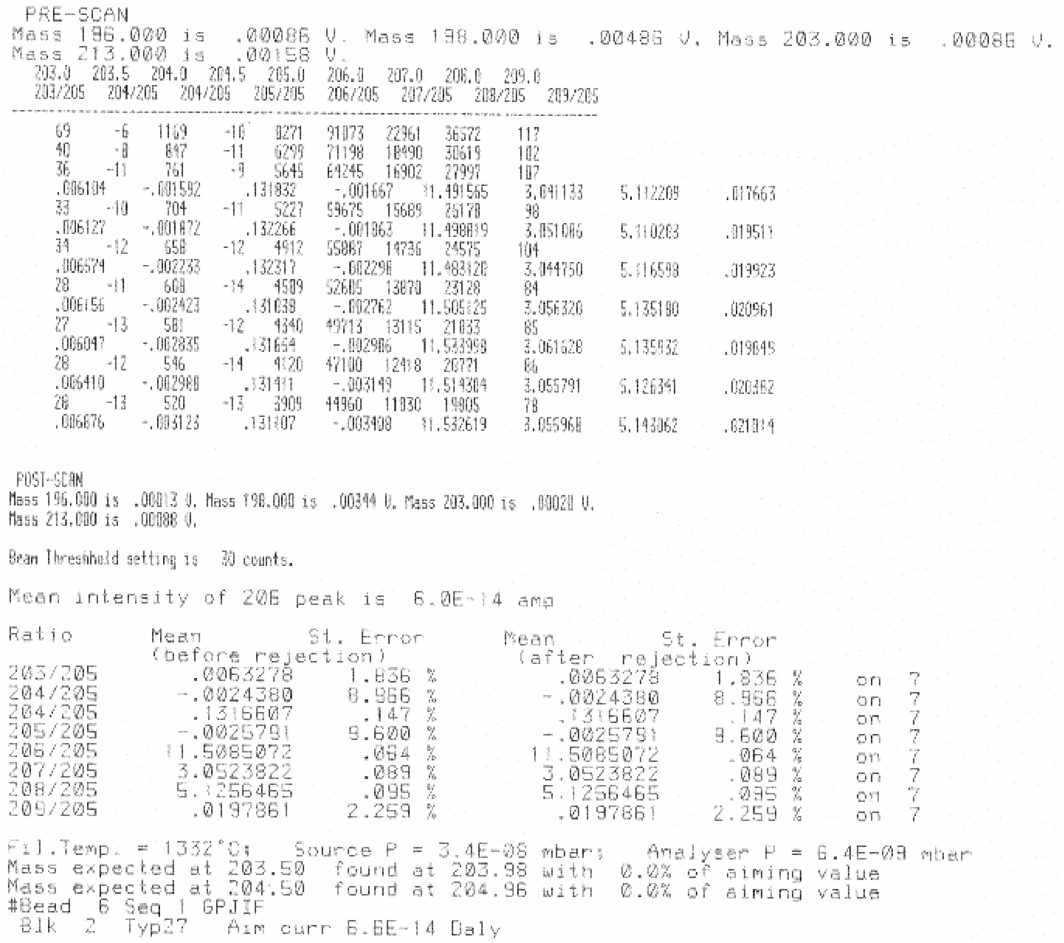
Concentration calculations using IDMS involve the use of a spike that is added to one sample of which the composition has already been measured. As ^{205}Pb is a non-naturally occurring isotope, samples contain a known quantity of ^{205}Pb can be measured for composition and concentration simultaneously. 12 years have been spent refining this method for use with the VG354, specifically for very small samples such as those measuring Pb concentration in ancient ice (Rosman, 2001).

The VG354 mass spectrometer counts ion ratios. The number of atoms/ions for each isotope are quantified and compared using the VG software. This will give an output in the form of ratios generated by the computer. An example of this output can be found in Figure 14.

The errors on the ratios are calculated by the least abundant isotopes' Poisson error (√N/N). Usually the least abundant isotope in a Pb sample is 205. The amount of 205 added to a sample will therefore affect the overall precision of the concentration measurement. Useful isotopic ratios (206/207, 208/207 and 204/206) and their overall error will vary from sample to sample, and are independent of the amount of ^{205}Pb present.

^{205}Pb is produced and purchase in microgram quantities at a cost of ~$5x10^9$ USD/g. This high cost makes it practical only for measuring samples of small Pb quantities. Quantities of ^{205}Pb added to samples is of the order of 4-20 pg in blank and sample sizes ranging from 20 pg-10 ng.

Previous measurements of Pb on leaves have shown concentrations of 0.025 and 0.7 ng/cm^2. The ^{205}Pb method was carried out on a leaf sample of this size and was found to match data returned when a ^{204}Pb spike was employed. The ^{204}Pb method requires sample sizes of 1-100ng to obtain fair precision on quantities and isotopic ratios. Thus the ^{205}Pb method was shown to be an acceptable and precise way to measure concentrations and isotopic ratios.



```
 PRE-SCAN
Mass 196.000 is  .00086 V. Mass 198.000 is  .00486 V. Mass 203.000 is  .00086 V.
Mass 213.000 is  .00158 V.
  203.0   203.5   204.0   204.5   205.0   206.0   207.0   208.0   209.0
  203/205  204/205  204/205  205/205  206/205  207/205  208/205  209/205
----------------------------------------------------------------------------
     69     -6    1169    -10    8271   91073   22961   36572    117
     40     -8     847    -11    6299   71198   18490   30619    102
     36    -11     761     -9    5645   64245   16902   27997    107
     .006104    -.001592     .131832     -.001667    11.491565    3.041133    5.112209    .017663
     33    -10     704    -11    5227   59675   15689   26178     98
     .006127    -.001872     .132266     -.001863    11.498819    3.051086    5.110203    .019511
     34    -12     658    -12    4912   55867   14736   24575    104
     .006574    -.002233     .132317     -.002296    11.483120    3.044750    5.116598    .019923
     28    -11     608    -14    4509   52605   13870   23128     84
     .006156    -.002423     .131038     -.002762    11.505125    3.056320    5.135180    .020961
     27    -13     581    -12    4340   49713   13115   21033     85
     .006047    -.002835     .131654     -.002906    11.533958    3.061628    5.135932    .019045
     28    -12     546    -14    4120   47100   12418   20721     86
     .006410    -.002980     .131411     -.003149    11.514304    3.055791    5.126341    .020362
     28    -13     520    -13    3909   44960   11030   19005     78
     .006676    -.003123     .131107     -.003408    11.532619    3.055968    5.143062    .021014

 POST-SCAN
Mass 196.000 is  .00013 V. Mass 198.000 is  .00344 V. Mass 203.000 is  .00020 V.
Mass 213.000 is  .00088 V.

Beam Threshhold setting is   30 counts.

Mean intensity of 206 peak is  6.0E-14 amp

Ratio       Mean           St. Error       Mean          St. Error
            (before rejection)              (after  rejection)
203/205       .0063278     1.836 %           .0063278     1.836 %     on  7
204/205      -.0024380     8.966 %          -.0024380     8.966 %     on  7
204/205       .1316607      .147 %           .1316607      .147 %     on  7
205/205      -.0025791     9.600 %          -.0025791     9.600 %     on  7
206/205     11.5085072      .064 %         11.5085072      .064 %     on  7
207/205      3.0523822      .089 %          3.0523822      .089 %     on  7
208/205      5.1256465      .095 %          5.1256465      .095 %     on  7
209/205       .0197861     2.259 %           .0197861     2.259 %     on  7

Fil.Temp. = 1332°C;   Source P = 3.4E-08 mbar;   Analyser P = 6.4E-09 mbar
Mass expected at 203.50  found at 203.98 with  0.0% of aiming value
Mass expected at 204.50  found at 204.96 with  0.0% of aiming value
#Bead  6 Seq 1 GPJIF
 Blk  2  Typ27   Aim curr 6.6E-14 Daly
```

Figure 14 Output data generated by the VG354.

5.4.4. Avoiding contamination of the ^{205}Pb spike

The pipettes used are initially cleaned in 1M UP HNO_3 for at least a week. When being used to transfer a sample or spike, a pipette is taken out of HNO_3 and rinsed with MQW. No fluid may be present on the inside of the pipette. This is solved by passing a stream of MQW tangential to the pipette, draining the pipette. (See Figure 15) By inference this creates a low pressure point at the small end of the pipette allowing for the free flow of fluid. This has shown to be the most reliable method for clearing a pipette of fluid. This procedure is also used for cleaning pipettes used to transfer a sample in Si gel to a filament. When transferring spike, 10 ul of HNO_3 is taken into the pipette and ejected three times before spike is taken into the pipette. This has the effect of cleaning the outside of the pipette fully.

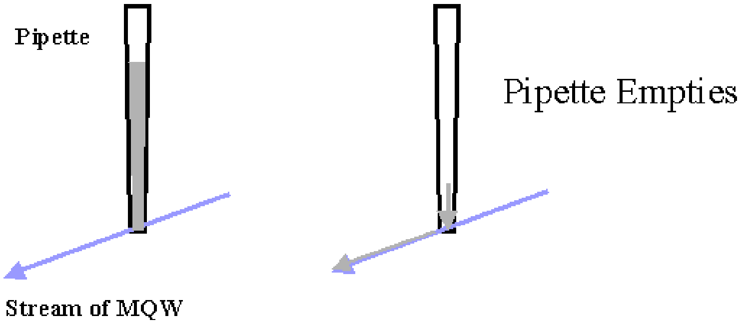


Figure 15 Flushing the inside of the pipette.

5.5 Experimental Development

This section details the evolution of the chemistry procedures; what new methods have been implemented and how they have contributed to the pursuit of better data. The reduction in the magnitude of the procedural blank during the chemistry process is also detailed.

5.5.1 H_2O_2 method

The procedure mentioned in Section 3.1.8 was use to process a number of samples. The procedure required the addition of ~0.1ml H_2O_2 to the samples. The amount of blank being added to the sample was unknown at this time. The H_2O_2 was subsequently tested for it's Pb concentration using different volumes of solution to determine the Pb content of a solution using the gradient formed between samples (figure 16). At the same time this indicates how much residual Pb is present in the containers (teflon beakers) and ultimately the procedure used. A ^{204}Pb spike was used to calculate Pb concentration.

The gradient derived from the measurements indicates the amount of Pb per ml of solution, approximately 3ng/g. Since 0.1g H_2O_2 is added per leaf sample, 300 pg of Pb is added purely from the peroxide. An ideal blank size is <10% of the sample size: samples to be analysed will be between 1 and 2ng, therefore the blank of the volume of H_2O_2 must be reduced, or both. Volume reduction is likely to decrease organic dissolution, in turn affecting the precision/accuracy of the measurement – this is not a viable option. The H_2O_2 blank must be therefore significantly reduced making it viable for lab use.

Unlike most reagents, H_2O_2 is unable be distilled/purified using evaporation techniques. In this study the H_2O_2 was acidified using low molarity HBr and passed through anion exchange resin. This was intended to capture most of the Pb while allowing a relatively large volume of H_2O_2 to be treated. The H_2O_2 cleansing procedure used a prepared column (table 7).

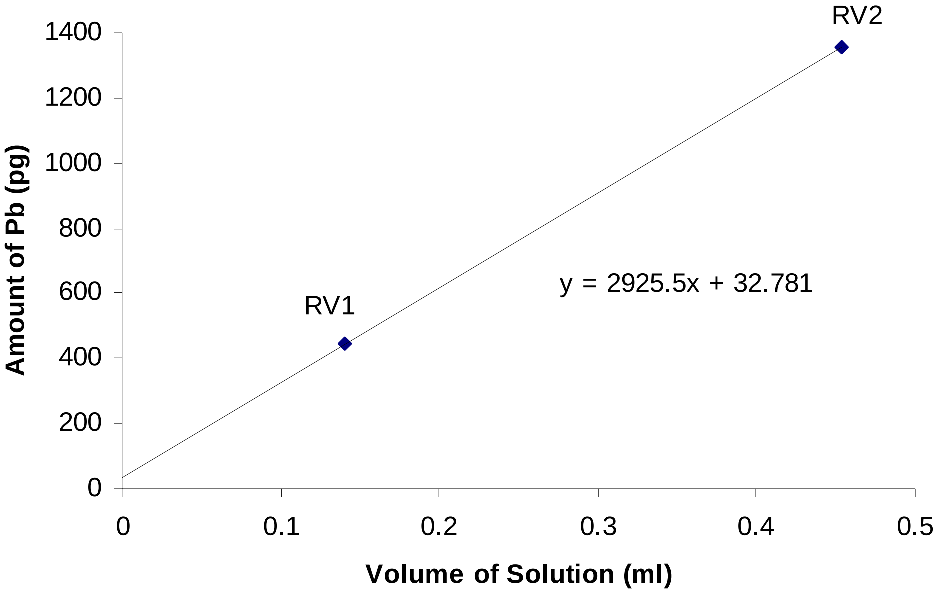


Figure 16 Pb concentration measured in H_2O_2

Resin volume was ~3cm of the column, where 1 column volume (cv)≡resin volume. It was estimated that a full column (~7.2ml)≡4cv. ~100ml H_2O_2 had 0.4g 8M HBr added to it.

Table 7 Preparation method used to clean H_2O_2

Resin transferred to column
60cv MQW used to precondition resin
4cv 11M HCL
Column sides rinsed with MQW
Full col (4cv) MQW
4cv 0.5M HBr
4cv 11M HCL
Column sides rinsed with MQW
4cv MQW
4cv 0.5M HBr
4cv 11M HCL
Column sides rinsed with MQW
4cv MQW
3cv 0.5M HBr
H_2O_2 added

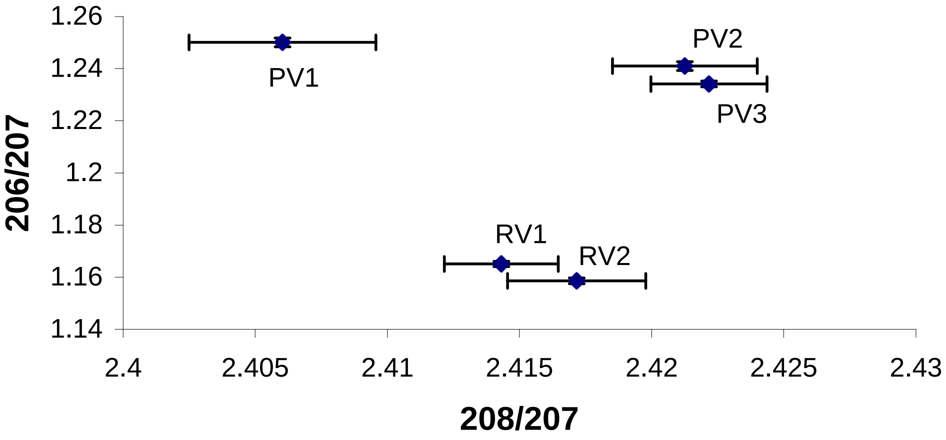


Figure 17 Purified H_2O_2 Pb isotopic composition.

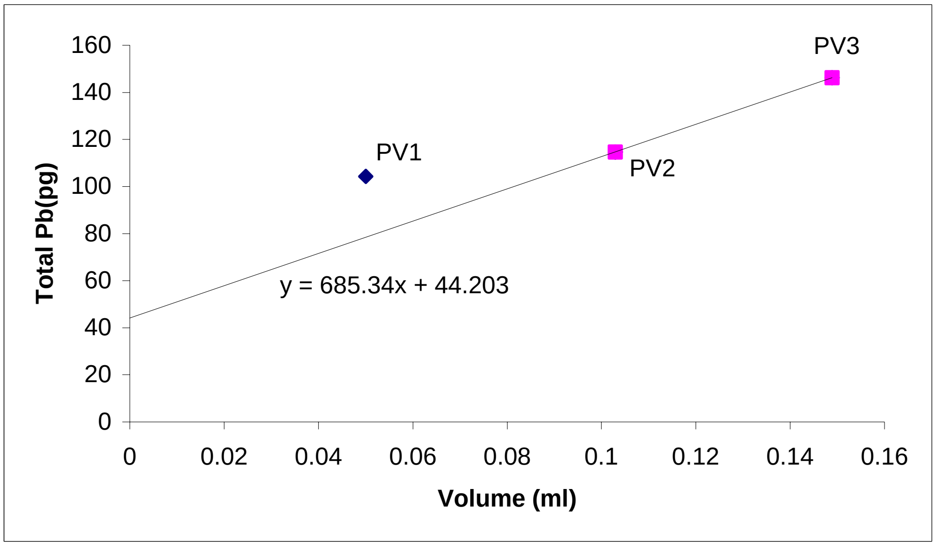


Figure 18 Measurement of Pb amounts in purified H_2O_2

The isotopic composition of the purified H_2O_2 (PV_1, PV_2 and PV_3) shows a different composition measured for PV_1. This implies that some contamination has occurred during the blank processing for the sample. The concentration measured in each sample provides more detail about the samples (Figure 18).

The gradient of the line indicates the concentration of Pb in the purified H_2O_2 as ~700pg/g. This gives an overall blank contribution from 3 drops (each between 0.25-0.3ml) used in the microwave procedure contributing 40-60 pg. This is an small compared to the current procedural blank of ~600pg. If reagent blanks acquired from HCl and HBr were small, the H_2O_2 procedure could be used to analyse the leaves.

The purification efficiency of the cleansing column has shown to be 77%. A second resin separation procedure would be expected to produce a H_2O_2 blank between 5 and 15pg.

5.5.2 Preliminary filter and leaf data

A number of filters and leaves were analysed for preliminary Pb levels and compositions. This included the analysis of procedural blanks for each set of samples (filters and leaves). Available samples included a selection filters and leaves for the period of collection from 22nd May to 27th August 2001, chosen to optimise correlation with Pb amounts and time evolution of the dust content in the air. The results obtained for these are displayed in Figure 19.

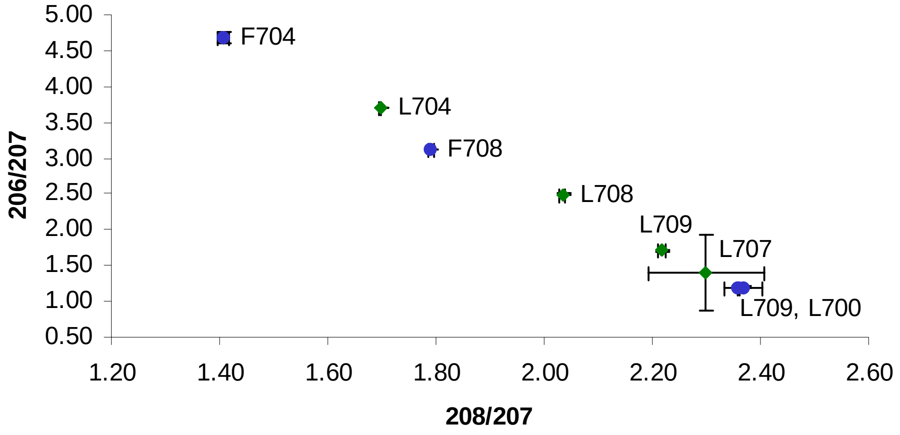


Figure 19 Preliminary fractionation corrected data for leaves and filters

The blanks for both the leaf and filter chemical procedures were significantly higher than expected, at ~600 pg each. The isotopic composition of leaf and filter blanks differ: 206/207 ratios were 1.29 and 1.13 respectively. The heightened ratios for the leaf blank may be attributed to the addition of H_2O_2 to the sample. This is supported by the 206/207 ratio of purified H_2O_2 measurement between 1.24-1.25.

Samples sizes are assumed to be 1-2 ng. Blank size was measured and quantified as ~600pg. this estimates blank contribution somewhere in the range of 30-60%, which is too high for the precision required for these types of measurements. A blank contribution <10% of the total sample quantity is acceptable. Two choices exist that may combat this problem,

(a) Increase sample size so that the added blank is insignificant, or

(b) Decrease the blank size by first identifying and quantifying the blank added to the sample during processing (Section 5.2).

Increasing the sample size would in some cases be acceptable as the amount of Pb on leaves (pg/cm^2) is very high. For measurements of background where the Pb concentration is low however, this would require a large sample area. Leaching more leaf will in turn increase the organic contribution from the sampled leaves. A common procedure applicable to samples of varying sizes needs to be developed: this can only be solved by identifying and reducing the amount of Pb added due to chemistry procedures.

5.5.3 Blank contribution from reagents

This section deal s with the measurement of blank present in reagents used in anion exchange column chemistry. HCl and HBr are the major reagents used for processing filters and leaves. These reagents were analysed for Pb; the results are presented in Figure 20.

The beakers used in blank measurement may sometimes contain residual Pb from previous analyses. Evidence of this can be seen analysing the linear fit to HCl Pb measurement. A possible explanation for a negative value coinciding with no HCl in a beaker is the Pb added during procedures. Contamination in the beakers containing 5 and 7ml of HCl explains the high gradient and negative (V(0ml)=-93pg) point.

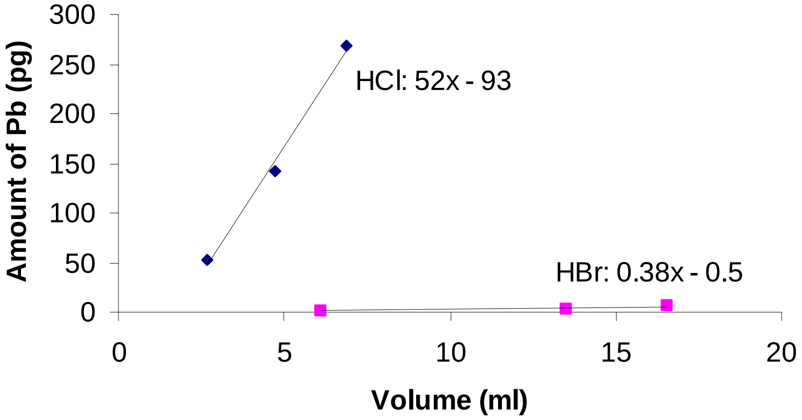


Figure 20 Measurement of Pb in HCl and HBr.

The column chemistry procedure used for filter elution requires ~8ml of HCl, and ~50ml HBr (refer to Table 7). H_2O_2 adds up to 70 pg, giving a total of ~490pg. The measured blanks for leaves and filters is ~600pg, leaving ~110pg unaccounted for. Possible sources of this remainder include the resin and beakers. Beaker blanks will need to be reduced and the resin cleaned before progress is made on future samples. A blank <100pg is the benchmark for samples of concentrations between 1-2 ng.

Reducing the blank will allow for reliable correlations (isotopic composition; Pb concentration) to be made between filters and leaves. It has been shown that the radiogenic component of Pb originating from the Ranger mine can be detected and identified on leaf and filter samples.

5.6 The evolution of the chemistry procedure

5.6.1 HBr column chemistry

The standard chemistry method used for filters (Section 4.4.1). Has been shown to produce imprecise and at times inaccurate results when applied to leaves. (Honeybun, 2001; Honeybun, 2002). This is due to organic interferences present on the sample filament when analysed in the mass spectrometer. It follows that data obtained using this method was unreliable.

5.6.2 HBr-Column chemistry implementing H_2O_2– HNO_3 Organic digestion

The H2O2-HNO3-microwave method has produced results of high precision, improving the measurement of samples via the method mentioned in 4.4.1 by a factor of 10 (Honeybun, 2002). Organic interferences are not present in the final sample meaning they are not present when a leaf sample is analysed mass spectrometrically.

5.6.3 HNO_3 Column Chemistry

Subsequent measurements of the Pb levels in HCl and HBr were taken to identify any contaminated reagents. (Table 8)

Table 8 Levels of Contamination in various reagents

Sample	208/207	95%CI	206/207	95%CI	Pb(pg)	95%CI	Volume (ml)	Concentration (pg/ml)
HCL (10M)	2.27	0.01	1.741	0.002	224.1	7.7	14.98	14.96
HBR (2M)	2.4417	0.0005	1.215	0.002	134.2	0.3	12.309	10.90
MQW	2.38	0.09	1.15	0.04	7.8	-	12.736	0.61

The HCl and HBr showed high Pb concentrations. High 206/207 ratios not supported by a change in 208/207 suggest a non-radiogenic contaminant source. It was concluded that the HCl was contaminated due to the erosion of the equipment used to produce the acid. The 8M HBr from which the 2M HBr batch was created from was known to have a Pb concentration of 20pg/g. The extra Pb measured is likely to be a result of the transfer of HBr solution and MQW to a different PE bottle during the dilution process. A column chemistry procedure required the total Pb added to the sample to be less than 100 pg.

The issue was resolved by suggesting a column chemistry technique that used HNO_3 as the elutant. The amount of Pb added to the sample would therefore be limited to what was in the dilute HBr and resin.

The first testing of the HNO_3 procedure produced unreliable results for one of the test samples, though procedural blanks of 14 and 15pg were achieved. This confirmed that the new method was an excellent choice for measuring Pb in dust on leaves. The unreliability of the measurement arises from elements or compounds present in the sample at filament loading time. This can be avoided by running a second chemistry column to filter out unwanted components. This means a second column and evaporation procedure is performed on the samples. The final procedure used for processing a leaf sample is available in Table 9 and Table 10. This was used for over 33 samples requiring no repeat measurements. Samples sizes ranged from 200pg-100ng, producing procedural blanks of size 20-60pg.

Table 9 Column Chemistry procedure used to separate Pb from dust on leaves

Add 1-1.5cm resin (1cv) to column
Precondition with 3x6cv MQW
2x6cv HBr (0.2M)
6cv MQW
6cv HNO_3 (1M)
6cv MQW
3-4cv HBr (0.2M)
Sample added in HBr
3-4cv HBr (0.2M)
3cv MQW
Elute Pb with HNO_3

Table 10 Total Experimental procedure used to separate Pb from dust on leaves

1	Leaf is removed PE storage bag onto fresh gladwrap using teflon acid cleaned tweezers
2	Appropriately sized leaf section is acquired using acid-cleaned (HNO_3) scalpel
3	Leaf is replaced in PE storage bag.
4	Leaf section in placed in teflon beaker, enough HNO_3 to cover leaf is added
5	Leaf leached in HNO_3 for 1.5-2 minutes
6	Leaf taken out of solution; rinsed with MQW allowing backwash to drain into beaker, and stored
7	Solution evaporated on hotplate
8	Sample redissolved with HBr
9	Sample processed using HNO_3 column chemistry
10	Steps 7-9 repeated
11	H_3PO_4/Si gel added to sample, evaporated on hotplate

5.7 Bead Preparation

Once evaporated for a final time, samples in beakers exist as a dried pool of Si gel +sample, or an Si gel blob (>sand grain). ~4ul Si gel is added to the beaker, redissolving most of the sample along with any residual organics. This is transferred to a triple rhenium filament via a pipette cleaned using the technique described in Section 4.6.3.1.

The samples are heated @ 1.4 A until they appear to be hydrologically reduced. The current is increased, often resulting in the blackening of the Si gel containing dust from a leaf sample. The Si gel further reduces, and the current is stepped at 0.2A. Each step is held for ~1 minute before proceeding. Eventually the sample will begin to fume (white smoke) where the stepping procedure is halted. The current is sharply raised, achieving an orange filament for enough time to burn organics and fuse the sample to the filament. Increasing the current too steeply results in the destruction/oxidation of the sample.

Samples are loaded to a carousel (contains up to 16 samples) and is mounted in the VG354. The samples are degassed over night @3.9As (side filaments) for half an hour each. This rids the sample of volatile elements (such as external organic components) yielding a clean and highly precise measurement.

6 Results

6.1 Leaf-Filter Correlation

Results for leaf analyses, filter leaf correlations etc are found in the following tables

Table 11 Leaf and filter data for simultaneous sample collection

Place	Sample	208/207	95% CI	206/207	95% CI
eriss	Filter 704	1.550	0.007	4.00	0.02
eriss	Filter 710	1.80	0.01	3.13	0.02
Jabiru	Filter 709	2.26	0.04	1.58	0.03
Jabiru	Filter 707	2.39	0.03	1.15	0.01
eriss	Leaf 704	1.68	0.01	3.74	0.03
eriss	Leaf 708	1.90	0.01	2.70	0.02
eriss	Leaf 710	0.98	0.01	6.50	0.08
Jabiru	Leaf 709	2.3	0.5	1.6	0.4
eriss	Leaf 697	1.42	0.02	4.95	0.02

Table 12 Temporal data for leaf and filter intercomparison.

Date (2001)	***eriss***	Jabiru	***eriss***	Jabiru
22.5 – 22.6	Leaf 704	Leaf 709	Filter 704	Filter 709
22.6 – 24.7	Leaf 708	Leaf 707		Filter 707
24.7 – 27.8	Leaf 710		Filter 710	
27.8 – 20.9	Leaf 697			

Table 13 Annual cycle of Pb concentration and isotopic composition at Jabiru East measured between May 2001 and July 2002.

Sample	**date start**	**date end**	**ng/m³**	**95% CI**	**206/207**	**95% CI**	**208/207**	**95% CI**	**206/204**	**95% CI**
Filter 704	22-May-01	22-Jun-01	N/A	N/A	4.000	0.020	1.550	0.007	82.200	N/A
Filter 708	22-Jun-01	24-Jul-01	2.2	0.32	3.290	N/A	1.790	0.002	67.227	0.22
Filter 710	24-Jul-01	27-Aug-01	N/A	N/A	3.130	0.020	1.800	0.010	N/A	N/A
Filter 697	27-Aug-01	20-Sep-01	1.1	0.15	2.229	0.002	2.063	0.002	39.545	0.06
Filter 702	20-Sep-01	19-Nov-01	1.1	0.17	3.142	0.003	1.738	0.002	67.087	0.17
Filter 696	22-Nov-01	13-Dec-01	1.4	0.20	1.687	0.002	2.188	0.002	27.806	0.11
Filter 693	13-Dec-01	17-Jan-02	1.5	0.22	1.174	0.001	2.322	0.002	18.225	0.06
Filter 695	17-Jan-02	22-Feb-02	0.9	0.13	1.114	0.001	2.337	0.002	17.455	0.04
Filter 694	22-Feb-02	29-May-02	0.7	0.09	1.424	0.001	2.261	0.002	23.001	0.02
Filter 698	29-May-02	29-Jul-02	0.8	0.12	1.738	0.002	2.180	0.002	28.993	0.05

6.2 Dispersion Data

Table 14 Isotopic Composition, population and spatial data for leaves collected near Ranger Mine, NT

Sample	53L	UTM	Mine(km)	208/207	95%CI	206/207	95%CI	206/204	95%CI	Pb/cm^2	error
Leaf #1	10446	4326	11.306	2.379	0.010	1.167	0.014	17.862	0.635	4.137	0.005
Leaf #2	6706	-2314	7.094	2.211	0.011	1.672	0.079	27.742	0.987	171.513	0.211
Leaf #3	-6463	726	6.504	1.820	0.002	3.131	0.002	62.653	0.220	667.121	1.185
Leaf #4	-6610	-299	6.617	1.876	0.002	2.958	0.004	57.951	0.153	167.175	0.235
Leaf #5	-6658	-1629	6.854	1.559	0.003	4.156	0.013	95.984	0.538	12.278	0.015
Leaf #6	-6368	-2713	6.922	2.098	0.012	2.273	0.033	40.568	0.681	7.454	0.009
Leaf #7	-7038	-3787	7.992	2.177	0.003	1.857	0.003	31.327	0.128	245.077	0.392
Leaf #8	-8468	-4306	9.500	2.131	0.002	1.884	0.002	31.986	0.088	178.876	0.419
Leaf #9	-9758	-4280	10.655	2.093	0.004	2.185	0.004	38.430	0.232	82.822	0.123
Leaf #10	-10943	-3658	11.538	2.174	0.055	1.774	0.017	30.180	2.966	331.525	0.390
Leaf #11	-4668	1110	4.798	2.288	0.001	1.405	0.001	22.270	0.020	2821.019	5.484
Leaf #12	-4558	1963	4.963	1.550	0.002	4.123	0.008	98.592	0.193	121.605	0.275
Leaf #13	-2663	260	2.676	0.851	0.001	6.740	0.005	304.632	3.133	668.748	2.128
Leaf #14	-4281	-17475	17.992	2.383	0.006	1.139	0.004	17.582	0.112	17.964	0.019
Leaf #15	-15737	-16009	22.449	2.398	0.009	1.171	0.004	18.095	0.154	10.792	0.018
Leaf #16	-2788	3213	4.254	2.377	0.006	1.355	0.011	22.566	0.217	38.600	0.077
Leaf #17	-2943	4368	5.267	2.273	0.005	1.675	0.006	29.578	0.110	13.361	0.022
Leaf #18	-1430	2089	2.532	1.803	0.002	3.274	0.006	66.395	0.955	35.589	0.078
Leaf #19	-1364	1182	1.805	1.934	-	3.144	-	60.680	-	23.064	-
Leaf #20	-9410	12856	15.932	2.342	0.002	1.212	0.001	18.879	0.051	189.207	0.246
Leaf #21	-8478	10948	13.847	2.292	0.004	1.593	0.003	25.989	0.073	18.983	0.026
Leaf #22	-6432	9144	11.180	2.347	0.147	1.773	0.605	29.702	10.714	1.203	0.002
Leaf #23	-2508	1062	2.724	1.503	0.001	4.348	0.003	107.368	0.477	584.612	1.346
Leaf #24	-1965	697	2.085	0.915	0.002	6.655	0.017	295.393	1.460	449.694	0.840
Leaf #25	-438	-715	0.838	0.375	0.002	8.536	0.057	1577.580	705.219	20886.165	548.289

Table 13 (cont.)

Sample	**53L**	**UTM**	**Mine(km)**	**208/207**	**95%CI**	**206/207**	**95%CI**	**206/204**	**95%CI**	**Pb/cm²**	**error**
Leaf #26	-105	-3525	3.527	2.038	0.013	2.242	0.006	39.329	1.548	873.229	4.917
Leaf #27	-10	15	0.018	0.818	0.001	7.398	0.002	457.857	3.527	693.452	2.634
Leaf #28	0	0	0.000	1.411	0.003	5.078	0.008	138.026	0.628	823.762	3.782
Leaf #29	-676	125	0.687	1.375	0.002	4.846	0.015	132.408	0.671	477.056	2.358
Leaf #30	-1482	303	1.513	0.912	0.067	6.718	0.385	291.533	9.440	2114.608	18.863
Leaf #31	-8407	5500	10.046	1.896	0.003	2.684	0.013	50.180	0.433	66.448	0.090
Leaf #32	-2865	2257	3.647	2.071	0.004	2.359	0.007	43.092	1.434	63.137	0.182
Leaf #33	262	-1340	1.365	0.488	0.000	7.736	0.009	589.542	1.901	13039.742	438.119

7 Discussion and Analysis of Results

This section provides detailed analyses of the results as presented in section 6.0.

7.1 Leaf and filter correlation

^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb isotope ratios on filters that collected aerosols at ***eriss*** and at Jabiru Town are compared with leaves that collected air in the respective time period. The leaves were acid washed on the day when the pump for aerosol collection was started, to ensure that the collection period is essentially the same.

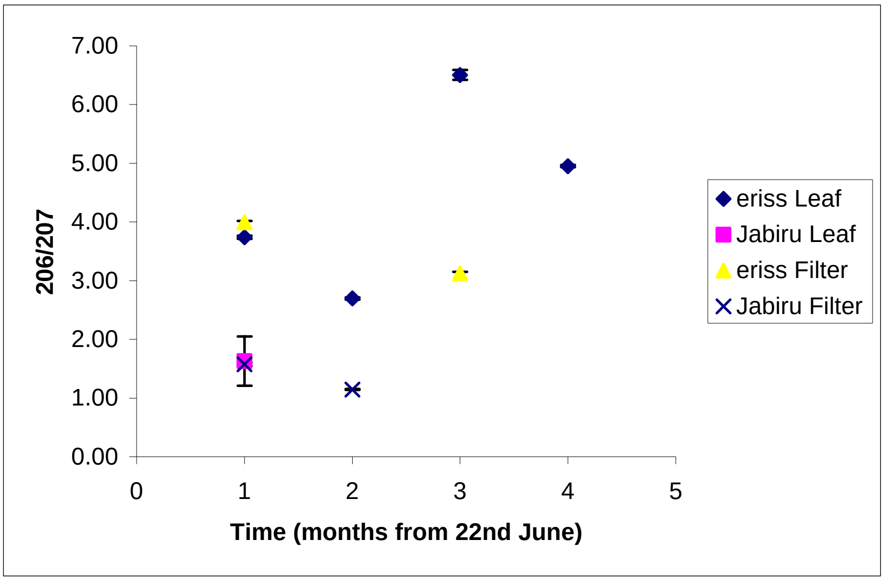


Figure 21 206/207 for each collector media for each month

Figure 21 and 22 show the Pb isotopic data and compares filters and leaves. The measurements exhibit a high accuracy indicating that data are valuable and organic interferences are low. There appears to be a strong correlation for the first set of samples with filters and leaves exhibiting similar ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb isotope ratios in both Jabiru an Jabiru East. Measurements performed in the third month, however, do not exhibit a correlation. The reason for that may be the difference between a passive collector (leaf) and an active collector (filter).

Different particle sizes may be collected on the filter compared to the leaves, with the leaves being more susceptible to collect smaller particles, which may have been transported from a more distant source. In contrast larger, resuspended soil particles may have been collected on the filters and may contribute particles with less radiogenic Pb isotope ratios, as indicated in our data. Our comparison emphasizes that leaves, although possibly not representative as indicators for airborne Pb concentrations, are a good collection medium for smaller dust particles. In fact, leaves may naturally enhance the isotopic fingerprint of dust transported over medium to long range distances as they preferably collect smaller particles.

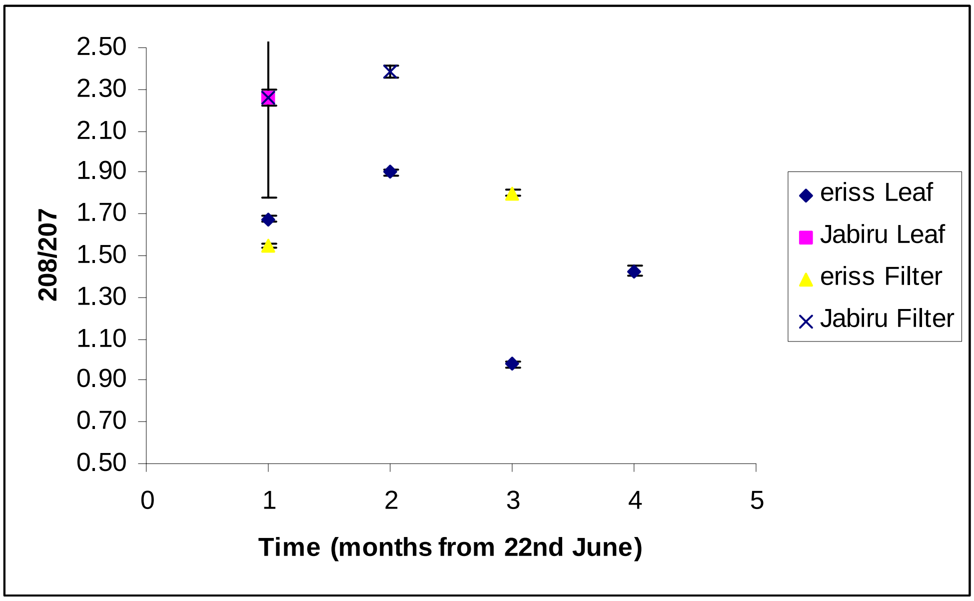


Figure 22 208/207 for each collector media for each month

7.2 Dispersion data

Figure 23 shows a three isotope plot of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb isotope ratios indicating a mix of two sources. One endmember is radiogenic Pb originating from Ranger Uranium mine with ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of 9.690 and 0.0494, respectively. The endmember source is natural crustal Pb, probably mixed with anthropogenic Pb from exhaust emissions, showing ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of 1.139 and 2.383, respectively.

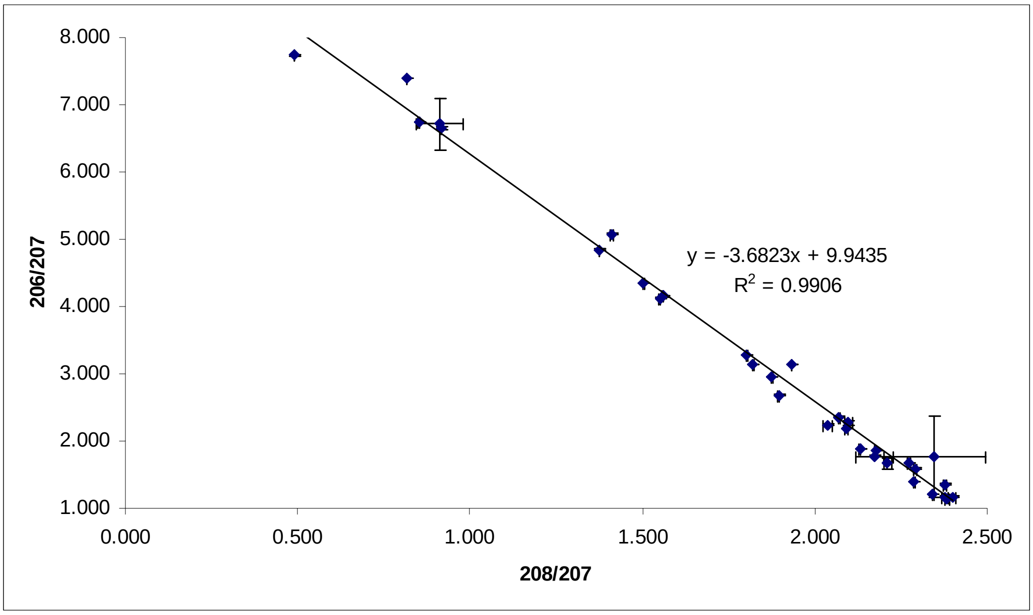


Figure 23 ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb showing correlation of data as a mix between two sources

7.2.1 Isotopic Ratio Mapping

7.2.1.1 Isotope ratio change in NW Direction

The NW transect is in the main wind direction, thus the NW transect is expected to provide the most pronounced impact from radiogenic Pb (Figures 24-28).

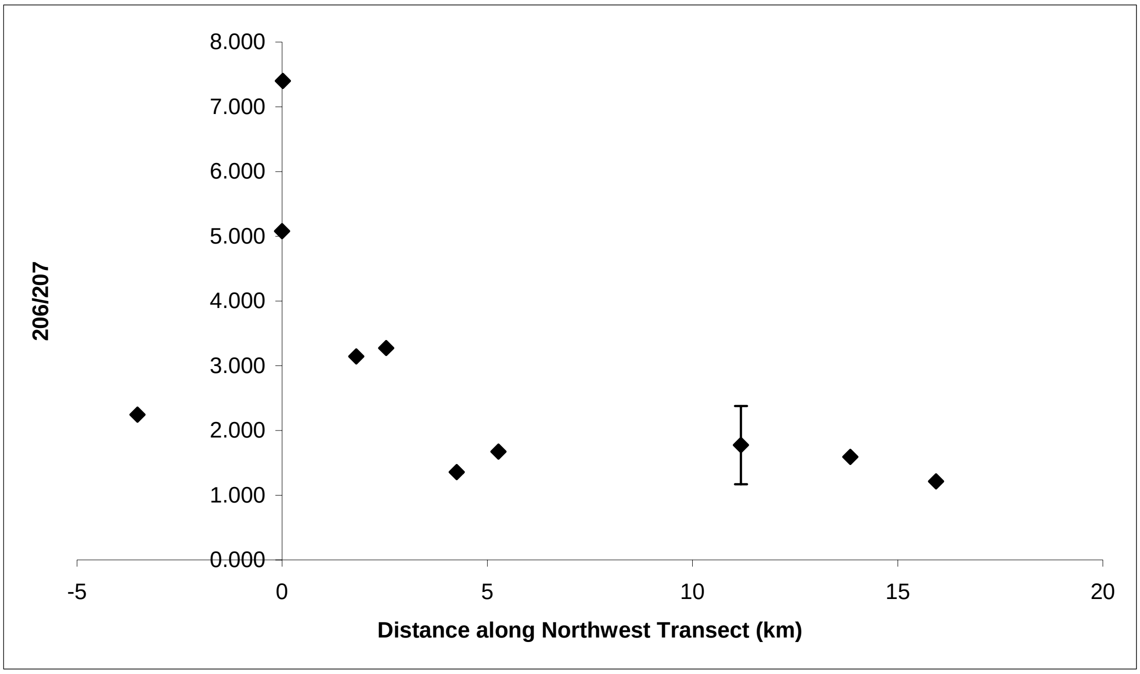


Figure 24 Change in ^{206}Pb/^{207}Pb with distance along NW transect.

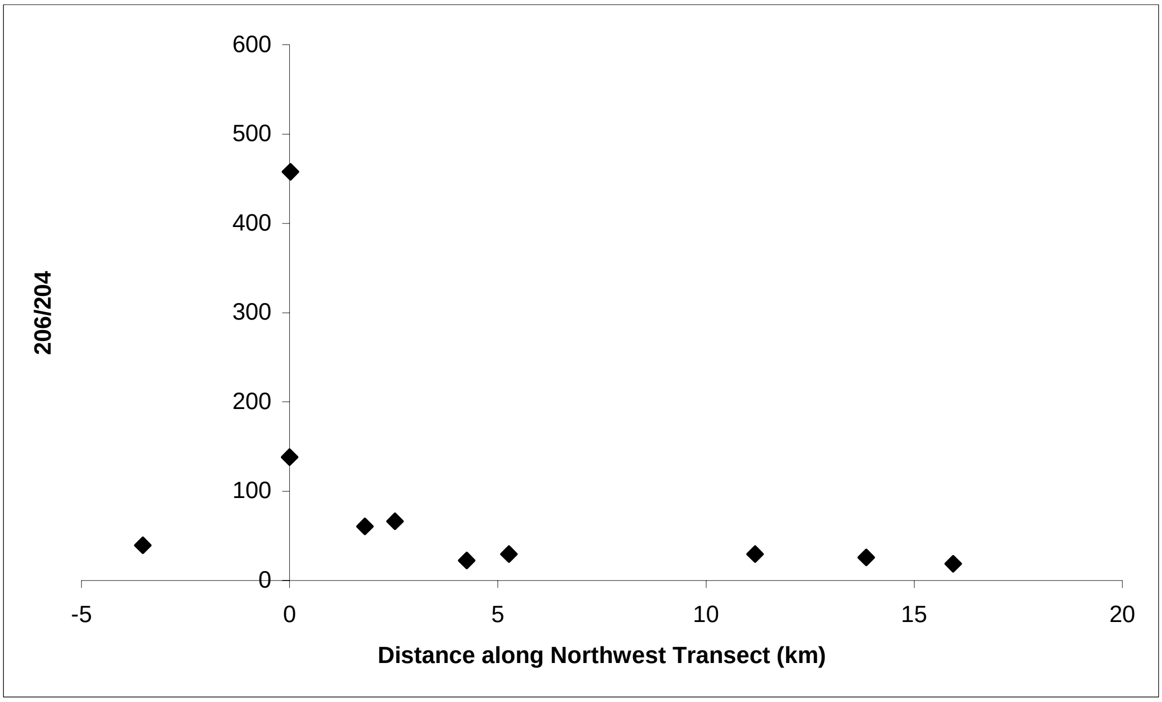


Figure 25 Change in ^{206}Pb/^{204}Pb with distance along NW transect.

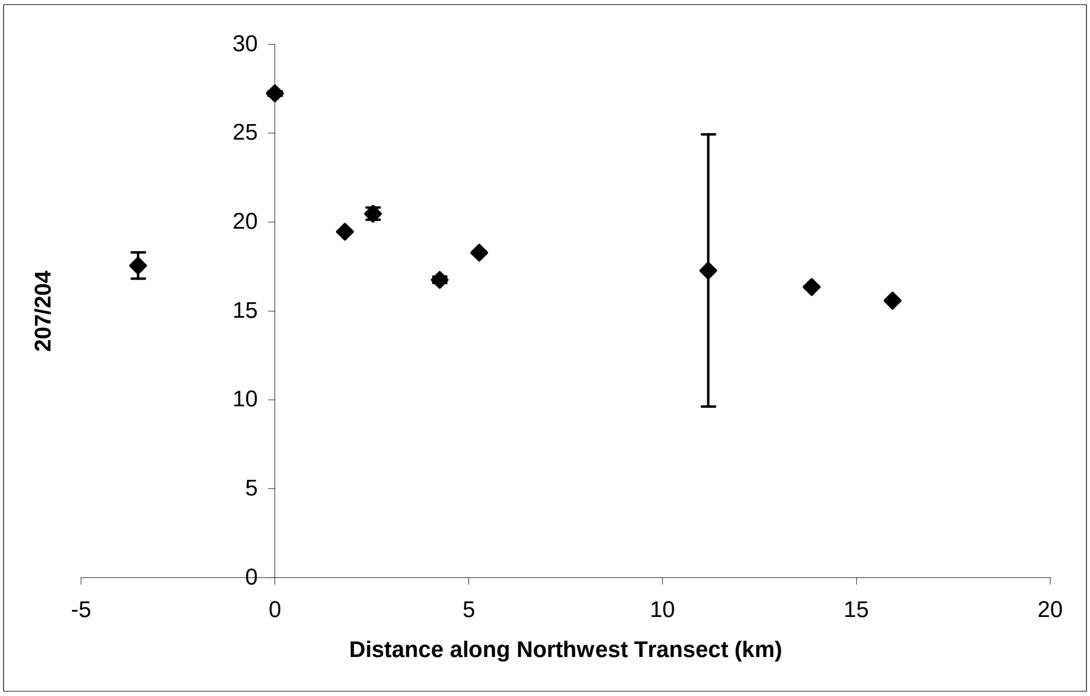


Figure 26 Change in ^{207}Pb/^{204}Pb with distance along NW transect.

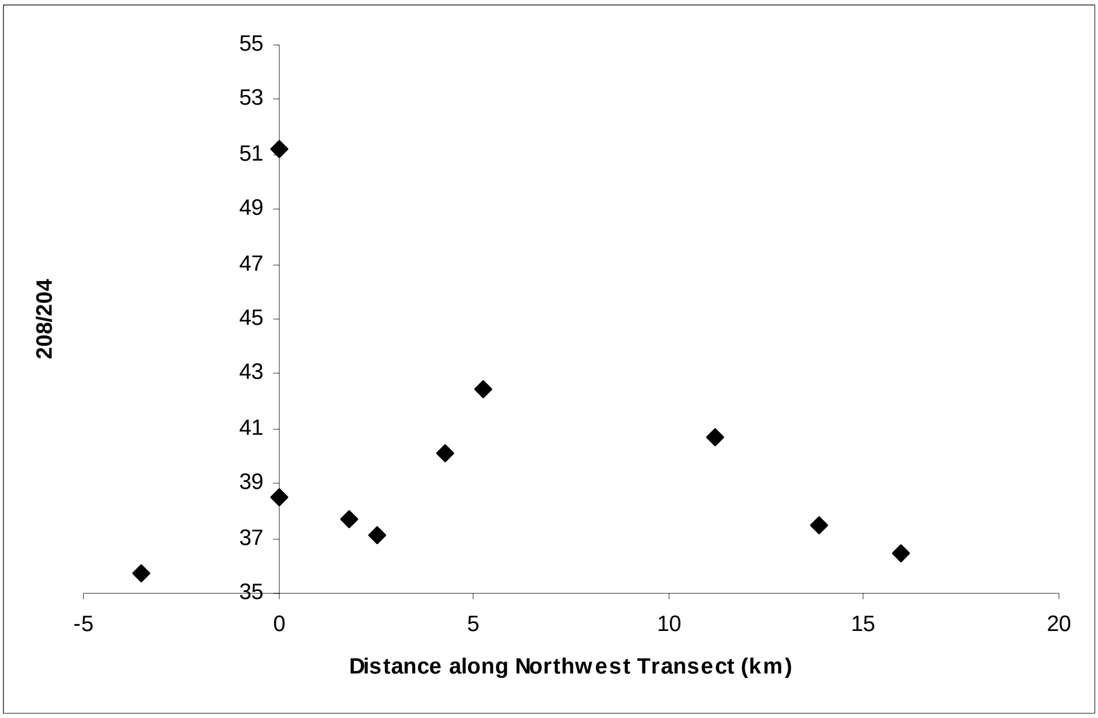


Figure 27 ^{208}Pb/^{204}Pb vs distance along NW transect.

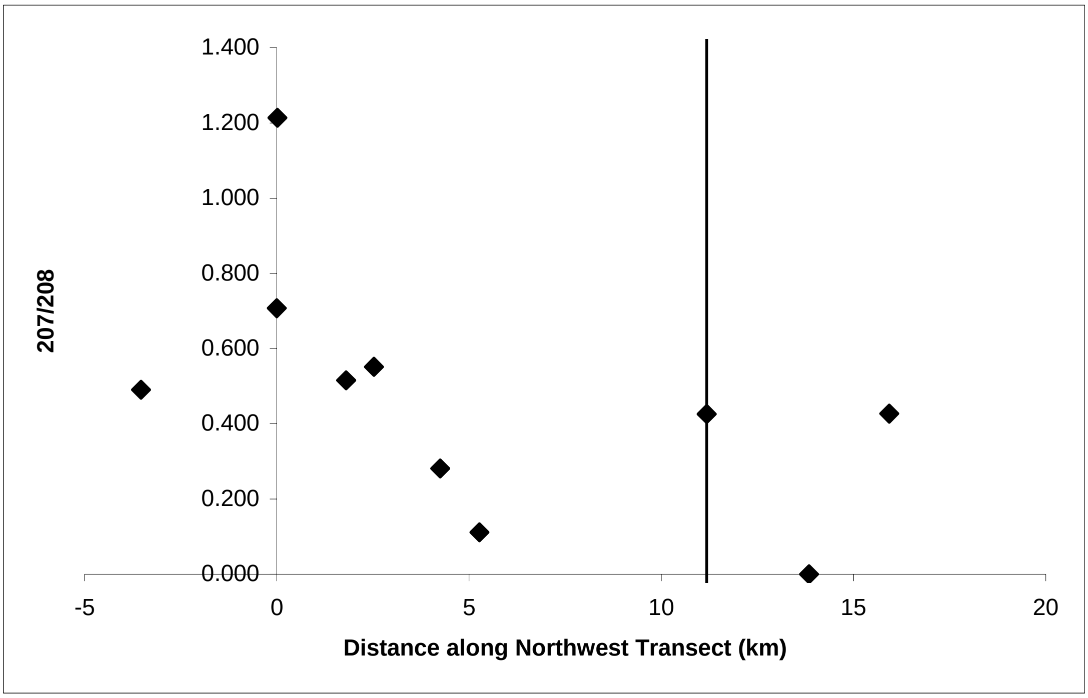


Figure 28 ^{207}Pb/^{208}Pb vs distance along NW transect

The Pb concentration (Pb/cm^2) on the leaves is variable over the NW transect tending towards lower concentrations further from the minesite.

7.2.1.2 Isotope ratio change in WNW Direction

The results obtained show an initial increase in the isotope ratio at 2-3 km. Howver, this is most likely artificial due to a low ratio obtained close to the mine, while heavy earth movement was on the way. Ratios decrease as the distance extends to 10 km (figure 29).

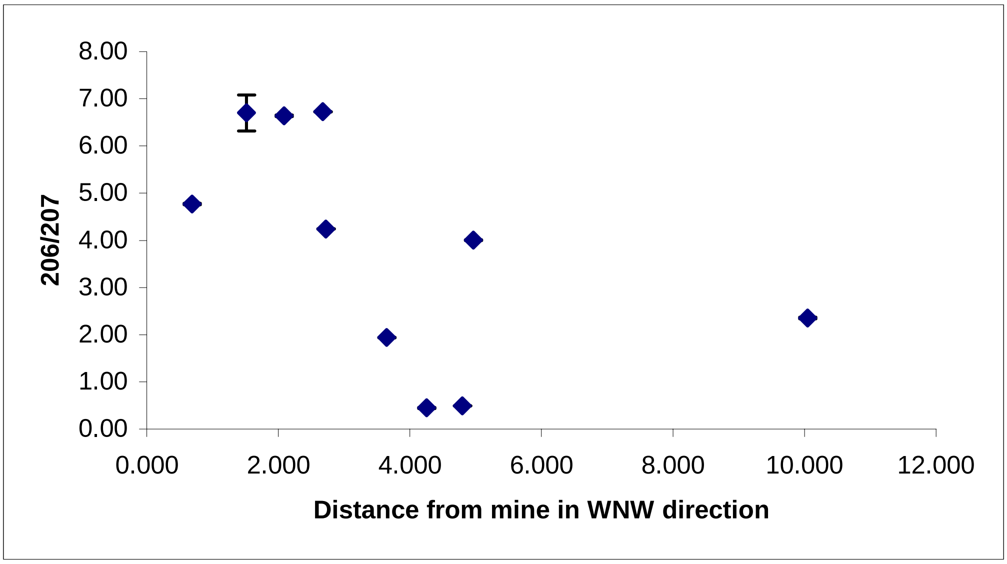


Figure 29 Change in 206/207 with distance in WNW direction

7.2.1.3 Isotope ratio change in West Direction

Figure 30 shows the changes in in 206/207 isotope ratios with distance in west direction.

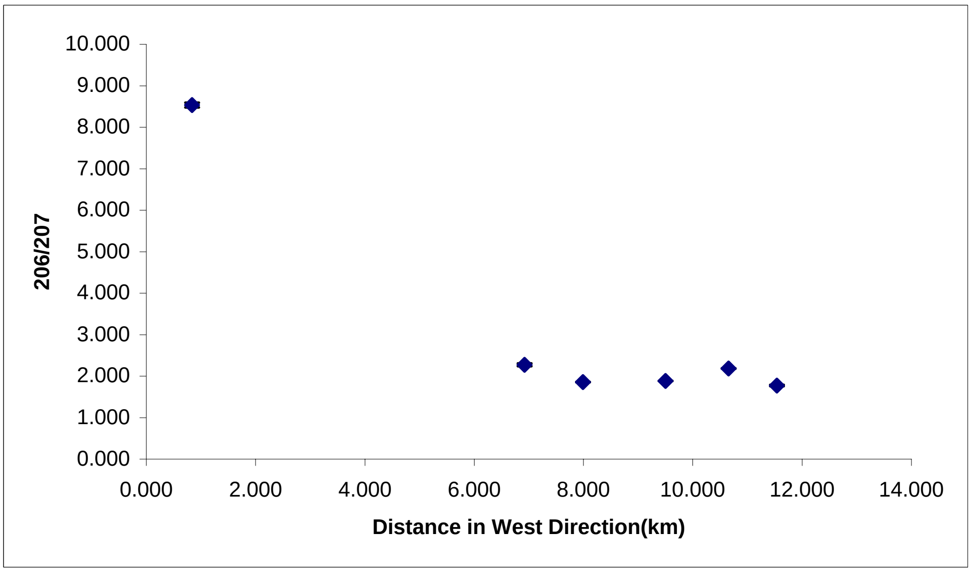


Figure 30 Change in 206/207 with distance in west direction

7.2.1.4 Isotope ratio change with angle.

An equidistant radial sector was analysed for change in isotope ratio with angle. As would be expected, the ^{206}Pb/^{207}Pb isotopic data increases as the angle decrease (moves closer to the major wind direction). This shows the dispersion curve for ^{206}Pb/^{207}Pb for constant distance from the mine site.

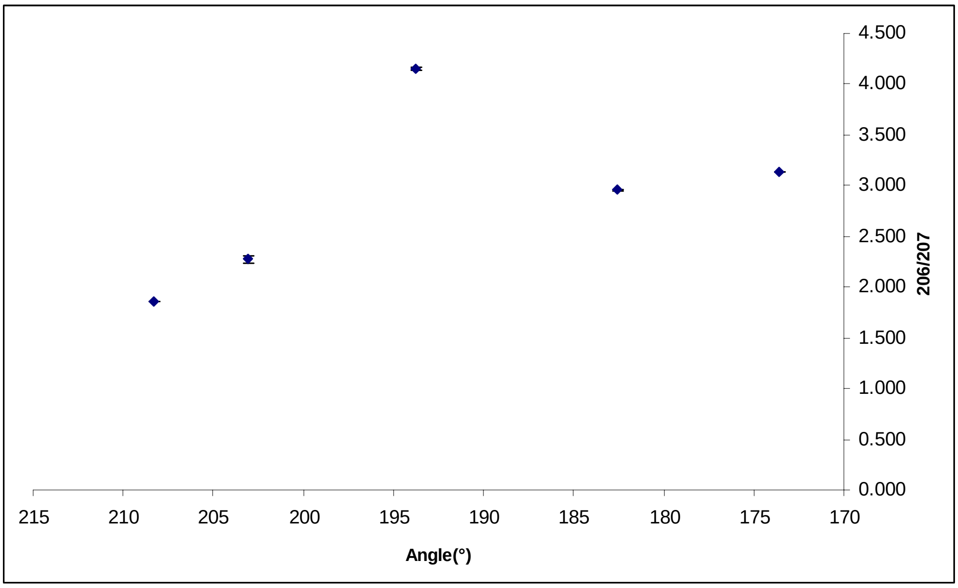


Figure 31 Change in ^{206}Pb/^{207}Pb with angle calculated from relative (53L, UTM) coordinates

7.2.2 Percentage contribution of dust from Ranger uranium mine deposited on leaves

Assuming a two component mix inferred from figure 23 the percentage Pb deposited on leaves originating from Ranger uranium mine can be calculated, using:

$$(1-\frac{(206/207_{RUM}-206/207_{meas})}{(206/207_{RUM}-206/207_{nat})})\cdot 100=\%RUM$$

with:

$206/207_{RUM}$: ^{206}Pb/^{207}Pb isotope ratio of radiogenic dust from Ranger (9.690)

$206/207_{meas}$: ^{206}Pb/^{207}Pb isotope ratio measured

$206/207_{nat}$: ^{206}Pb/^{207}Pb isotope ratio of natural dust (~1.15-1.20).

A contour map has been plotted showing the percentage contribution from Ranger to the Pb deposition in the vicinity of the mine. Assuming that the Ranger fingerprint is enhanced by the leaves' greater collection efficiency for smaller dust particles this represents a maximum for airborne Pb levels. In addition, this is a snapshot for the dry season and it is expected that dust deposition, therefore airborne dust concentration, will be lower during the wet season.

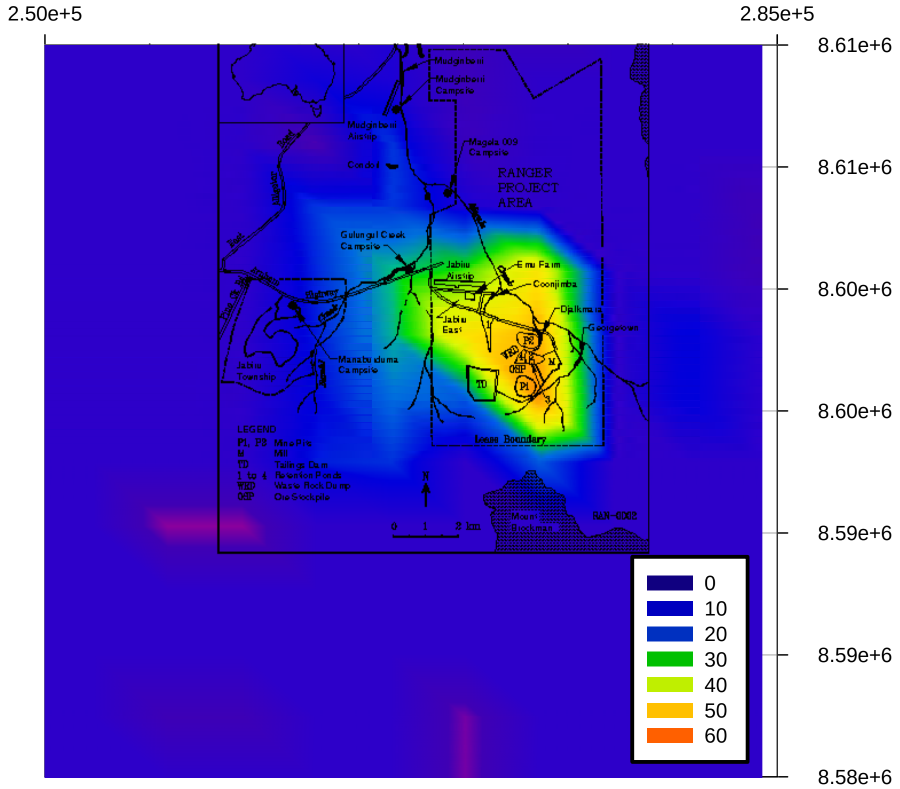


Figure 32: Contour map of the percentage contribution of radiogenic dust deposited on leaves near Ranger uranium mine. Sampling sites were not distributed evenly throughout the area shown, therefore contributions are only indicative and range from 0 per cent (dark blue) to ~ 60 per cent (orange).

7.2.3 Subtracting the Background

The Pb concentration on leaves (pg/cm²) does not correlate strongly with distance from the mine site. This may be due to two factors.

i) the leaves have not been prepared in any way. Young leaves that may have collected dust for a few months are compared to those which may be over a year old.

ii) leaves have been collected in all directions near the Ranger mine.

It has been shown in Section 7.0 that the data is a result of mixing between a common background and a highly radiogenic isotopic signature. Assuming that all ^{204}Pb measured in the sample represents common Pb, common ^{206}Pb, ^{207}Pb and ^{208}Pb isotope abundances can be calculated from ^{204}Pb and subsequently subtracted from the measured ratios to correct for the background.

Figure 33 shows all background corrected ^{206}Pb/^{207}Pb ratios plotted versus the ^{208}Pb/^{207}Pb isotope ratios. Uncertainties can be quite high however, within uncertainties, Pb from the mine with an ^{206}Pb/^{207}Pb isotope ratio of 9.690 as measured in mine borne particulates (Gulson et al., 1996) can be identified. Only samples number 16 and 17, along the NW transect (see figure 34) exhibit ratios different to the ratio expected if particles were Ranger mine borne. The reason for this is unknown but may be dust which may have been dispersed at an earlier time in the mine's history or dust originating from different radiogenic sources.

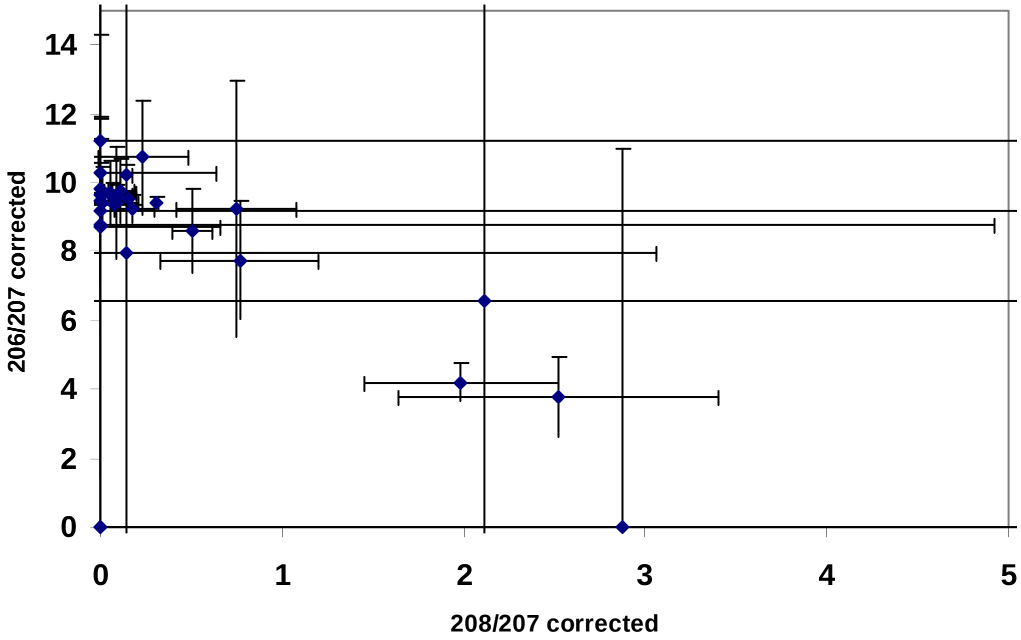


Figure 33 Background corrected ^{206}Pb/^{207}Pb ratios plotted versus the ^{208}Pb/^{207}Pb isotope ratios

During the process anomalous points were identified and deemed unusable by the background subtraction procedure. These were #25, #1, and #15. The ion counts during #25 carousel run in the VG were inconsistent, leading to an imprecise measurement of the 20x/204 ratios. #1 and #15 were isolated background samples: an explanation can be given that the dust collected on these leaves contained no radiogenic component from Ranger.

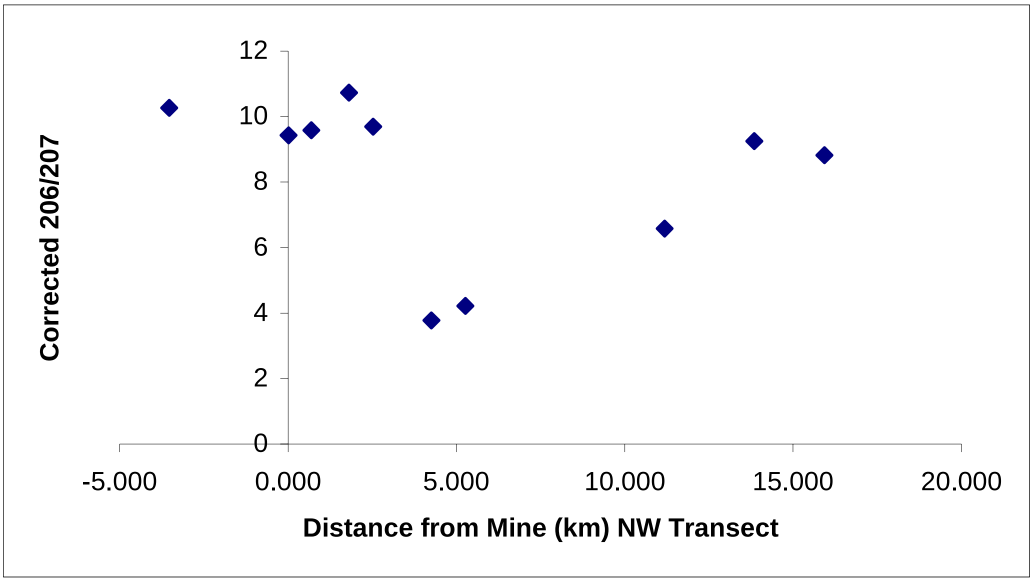


Figure 34 Background subtracted values for 206/207 vs NW distance (no uncertainties given).

7.2.4 Detection limit for radiogenic dust

The data obtained after background subtraction can be used to identify the fallout rate of radiogenic Pb from the Ranger mine. For this exercise, points corresponding in the W, NW and WNW direction were used.

Assuming that the Pb fallout from the mine drops with $1/r^2$, plotting the background corrected Pb isotopic ratio change against r^2 should allow for the calculation of

i) fallout rate

ii) maximum distance radiogenic dust may be detected from the minesite.

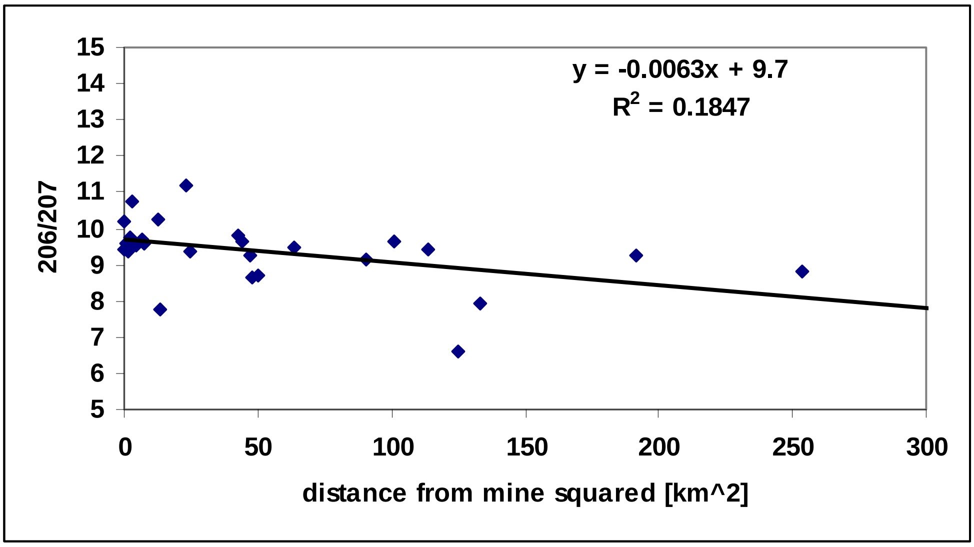


Figure 35 Distance squared vs background subtracted 206/207

The data shown in figure 35 produces the linear relation fallout rate of 0.006, forcing the linear fit through 9.7 which is assumed to be the orebodies ^{206}Pb/^{207}Pb isotopic ratio.

$$\frac{206}{207} = -.006 \times r^2 + 9.7$$

This tells us the fallout rate -0.044 per km, and the maximum fallout distance when 206/207=0.

$$\frac{9.7}{0.006} = r^2$$

This puts the maximum distance that radiogenic Pb from the mine may be detected at approximately 40 km.

7.2.5 Pb deposition on leaves of *Acacia spp.*

Although *Eucalypt* are the dominant tree species in Kakadu National Park, *Acacia* spp. leaves were chosen as passive dust collectors. Reasons for that included:

- *Acacia* leaves are easily accessible as *Acacia* do not grow as tall as *Eucalypt*. In some areas *Eucalypt* leaves would not have been accessible from the ground.
- *Acacia* spp. often are pilot species for rehabilitation. Results from this study may be easier to transfer to sites such as the rehabilitated Nabarlek mine or the tailings area in the South Alligator River Valley. Both these sites are mainly populated by *Acacia* spp.

- A site had to be chosen for the intercomparison of filters and leaves. This site was on the ***eriss*** compound next to the Environmental Radioactivity laboratories. An *Acacia* was located next to the low volume air sampler.

The main assumption is that the collection efficiency of a leaf does not influence the lead isotope ratios measured, as there is no physical fractionation between atomic masses 204 and 208 during transport and deposition of dust. Whereas collection efficiencies, and thus lead loads on the *Acacia* leaves may vary (table 15) lead isotope ratios do not depend on the amount of dust deposited. However, it cannot be excluded that leaf surfaces which favour collection of larger (finer) dust particles may produce varying results due to differences in lead isotopic composition between fine and coarse dust particles.

In chapter 7.1 it has been shown that leaves appear to collect finer particles as compared to the median airborne particle size. Consequently, as it is the fine particles that are transported over long distances, the relative contribution from a distant source to the dust deposition on a leaf may be overestimated. Therefore, the percentage contribution of dust from Ranger (chapter 7.2.2) deposited on the leaves represents an upper limit.

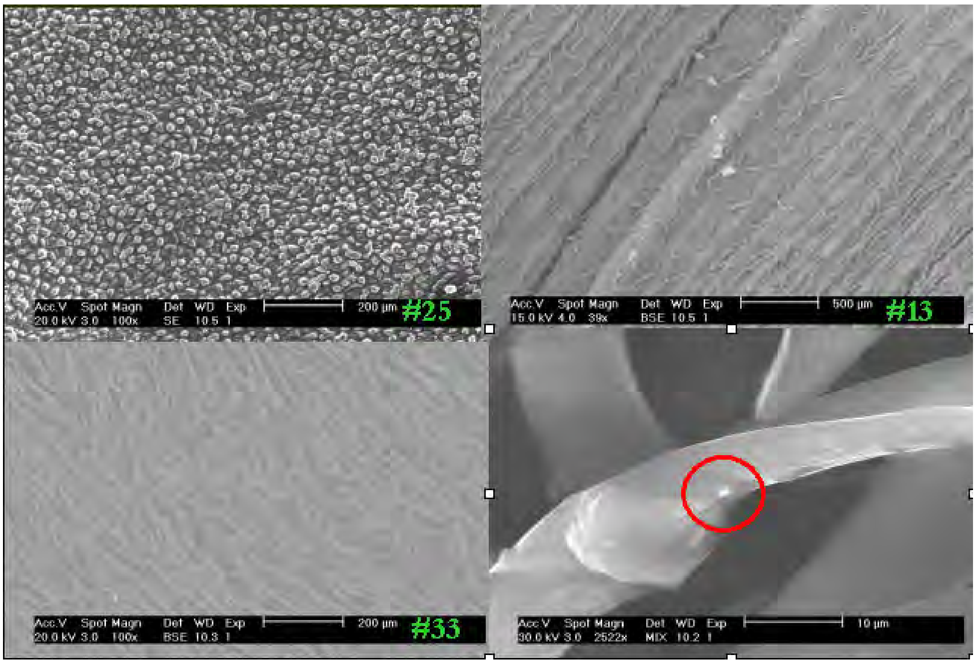


Fig 41 SEM imaging of Leaf #13, #25, #33 (a,b,c) plus a Pb particle attached to leaf #33 (d).

Secondary Electron Microscopy was used to analyse the surface of various *Acacia* spp. leaves (figure 36 a,b,c) and to hunt for and determine the size of dust particles that contain lead. From a visual inspection it is apparent that there are pronounced differences in the surface structure of different leaves. However, in general the size of the particles containing lead was less than 2.5 µm, the lead dust particle shown in figure 36d (bright spot, circled) for instance is estimated to be 1x1x1µm.

Table 15 shows the surface concentration of lead on the three leaves shown in figure 36. The collection efficiency for lead seems to be different, however it cannot be excluded that the increase in the lead inventory on the surface of the leaves is due to the decreasing distance from the Ranger uranium mine.

Table 15 Lead inventory on leaves #13, #25, #33

Sample	**53L**	**UTM**	**Mine Distance (km)**	**Pb/cm²**	**Error**
Leaf #13	-2663	260	2.676	669	2
Leaf #25	-438	-715	0.838	20886	548
Leaf #33	262	-1340	1.365	13040	438

Another factor that may affect the lead load and possibly the lead isotope composition is the phenology of the leaves. Leaves of different ages may have collected dust for different amounts of time and, therefore, the relative contribution of dust from Ranger on the leaf surface may vary. However, if we assume that a new cycle of dust deposition starts with the start of each dry season because:

- Late dry season fires, that present a major threat to *Acacia* woodlands (PWCNT, 2001), effectively burn off old leaves that collected dust during the previous year, and
- Last year's dust is efficiently washed off the leaves during the wet season

then *Acacia* leaves may in fact represent collection media that intergrate over the time period from the beginning of the dry season to the date of leaf collection. However, this has to be investigated in more detail taking into account specifics of leaf morphology and age for example.

7.3 Seasonal airborne Pb concentration and isotope ratios at Jabiru East

Figures 36 and 37 show the Pb concentration and isotopic composition plotted versus the date. As almost 96% of rainfall occurs in between November and April, and almost 60% in the three months of January to March the data show a contrasting difference between the wet and the dry season with higher levels in the dry season as compared to the wet. Airborne Pb concentration seems to decline during the entire period. This may be due to two factors:

- airborne dust concentration shows a strong seasonal cycle with low concentrations during the wet season.

- The total amount of ore mined at Ranger in the dry season of 2002 was only about one quarter of the amount of ore mined during the same period in 2001 (figure 36).

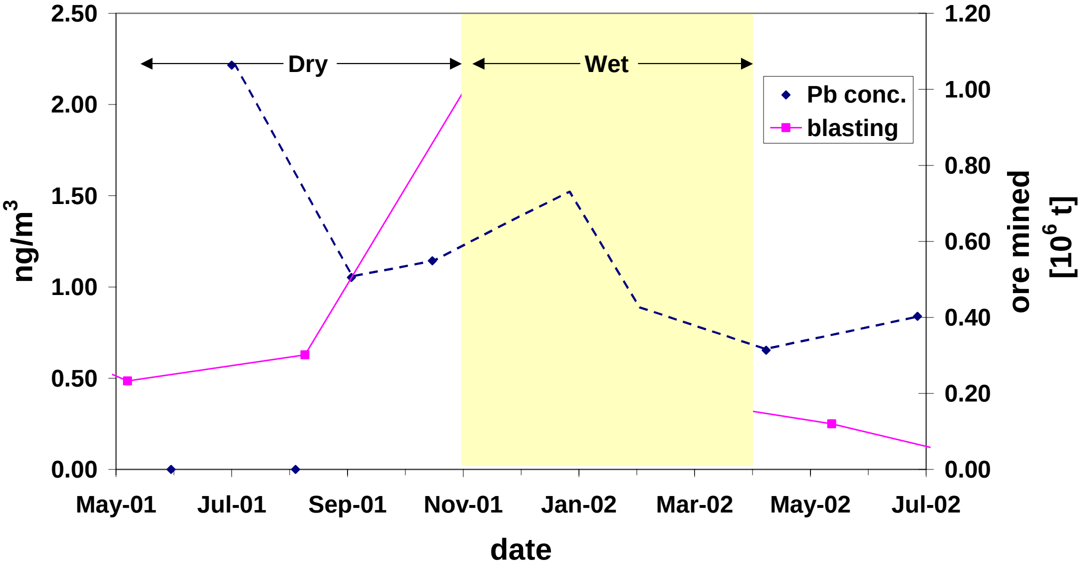


Figure 36: Airborne Pb concentration at Jabiru East plotted versus the date. In addition the amount of ore mined at Ranger (ore blasted) during the sampling period is shown.

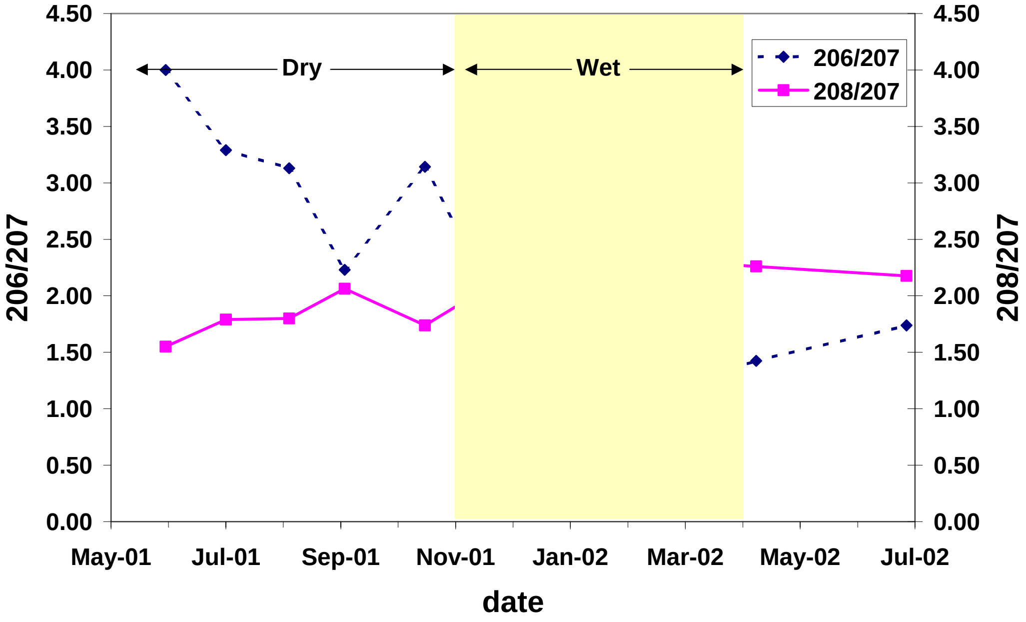


Figure 37: ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios plotted versus the date.

A measure for the the relative amount of Pb from Ranger uranium mine are Pb isotope ratios (figure 37). The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios indicate that during the dry season 2002 the contribution from Ranger uranium mine to airborne Pb at Jabiru was smaller than in the previous year. Again, this is most likely due to the decrease of the total amount of ore mined at Ranger during that period.

The three isotope plot (figure 38) shows the $^{206}Pb/^{207}Pb$ plotted versus the $^{208}Pb/^{207}Pb$. As in the leaf dataset it can be seen that the data are represented by a mixture of two sources.

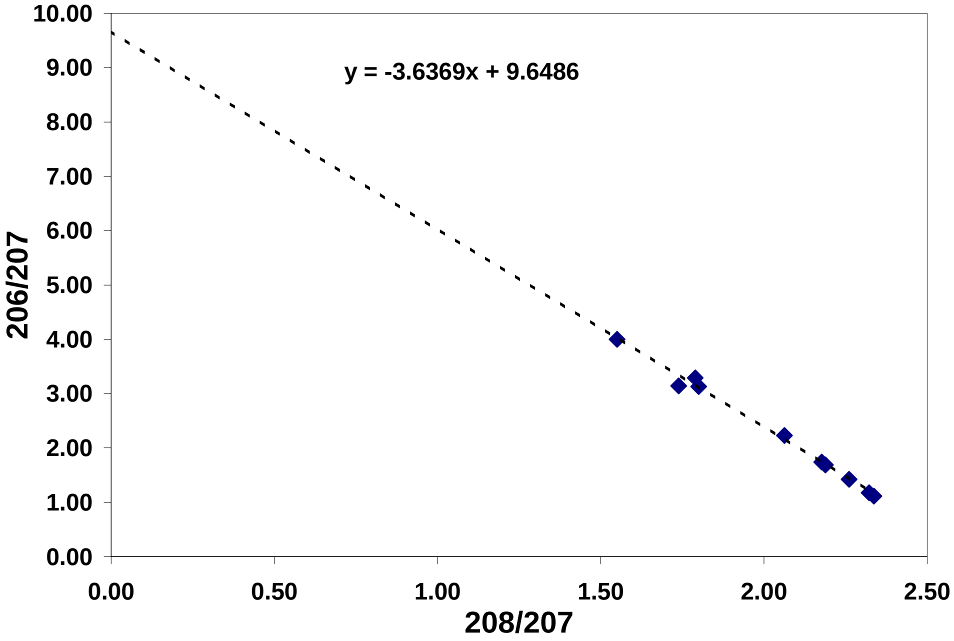


Figure 38: $^{206}Pb/^{207}Pb$ ratios plotted versus $^{208}Pb/^{207}Pb$ on filters from Jabiru East.

The two sources are natural crustal Pb, probably mixed with Pb from diesel and gasoline emissions from vehicle activity and diesel generators at Jabiru East and on the mine site, and radiogenic Pb originating from blasting and mining of uranium ore.

A least square fit to the data reveals the maximum $^{206}Pb/^{207}Pb$ ratio as the intercept with the y-axis. This ratio amounts to 9.65, which, within uncertainties, is the same $^{206}Pb/^{207}Pb$ ratio measured in particulates in the tailingsdam in 1989 (Gulson et al., 1992). This indicates that radiogenic source Pb isotope ratios did not change significantly after ore body #1 was mined out and mining of ore body #3 started in 1996.

Similar to the calculations used in chapter 7.2.2, the percentage contribution of Ranger to airborne Pb levels can be calculated with our data set. The mean annual contribution in 2001/2002 amounted to 13 per cent. This was estimated by calculating the percentage contribution of Pb from the mine collected on the filters and normalizing to the number of days it collected aerosols. During the dry season the average contribution from Ranger was 25 per cent, whereas the contribution during the wet season only amounted to approximately 5 per cent, depending on the start and end of the wet season.

8 Conclusions and Outcomes

Blank identification and elimination

The chemistry procedure used to process Pb in dust on leaves has evolved considerably. The original method used has undergone alterations to transform from an unreliable, imprecise technique, to a repeatable, reliable method with a very low blank.

The evolution may be described as:

Column Procedure	Outcome
Standard HBr method (used for filters)	80-2000pg of contamination (blank) . Organic compounds present.
H_2O_2: HNO_3 microwave digestion + triple column	No organic compounds. 600+pg blank
HNO_3 single column procedure	~15pg blank. Variable amounts of organics (unreliable).
HNO_3 double column procedure	~20-60pg blank. No organics present. Highly reliable method.

The HNO_3 double column procedure is an excellent, low blank procedure that may be used for sample sizes ranging from 200pg-100ng.

Determining the correlation between leaf-filter data

Leaf and filter data for a number of months and locations were compared. It was found that there was little correlation between the two media with respect to the isotopic signatures. The results obtained were interpreted as the difference between active (filter) and passive (leaf) collectors due to different particle sizes collected by each.

Dust dispersion pattern(s)

The dispersion of dust was a major issue dealt with in this report. The dispersion of radiogenic dust compared to background was analysed over W, NW, WNW transects as well as radially. Major dust dispersion occurs in a NW WNW direction, in accordance with the major wind direction. Percentage contribution to overall dust levels in the vicinity of the mine amount to 0 per cent up to 60% on site during the dry season.

Distance-isotope ratio correlation

The $^{206}Pb/^{207}Pb$ ratio was used to characterise dispersion when background was subtracted from the samples. The transects from W, WNW and NW were summed to determine that the furthest distance a fluctuation in the $^{206}Pb/^{207}Pb$ ratio could be detected was approximately 40 km.

Annual cycle

There is a contrasting difference between wet and dry season data. The percentage contribution of mineborne Pb to total airborne Pb at Jabiru East was estimated to approximately 20 per cent during the dry and 5 per cent during the wet season.

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Appendices

A1 Calculating the weight of a sample using ^{205}Pb spike

A ^{205}Pb spike is used to calculate concentration and isotopic composition of the sample in one measurement. The spike has a known isotopic composition, and the amount added to a sample (T) is measured during processing of a sample. Mass spectrometric analysis data output is supplied in terms of atomic ratios. The procedure used calculates N_A and N_S from ratios 204/205, 206/205,207/205 and 208/205.

$$N_O W_O = N_A W_A + N_T W_T$$

W_T is the atomic weight of the spike (also known as tracer)

W_A is the atomic weight of the measured sample

W_O is the atomic weight of the mixture

N_A is the number of atoms in the measured sample

N_S is the number of atoms in the spike

N_O is the number of atoms in the mixture

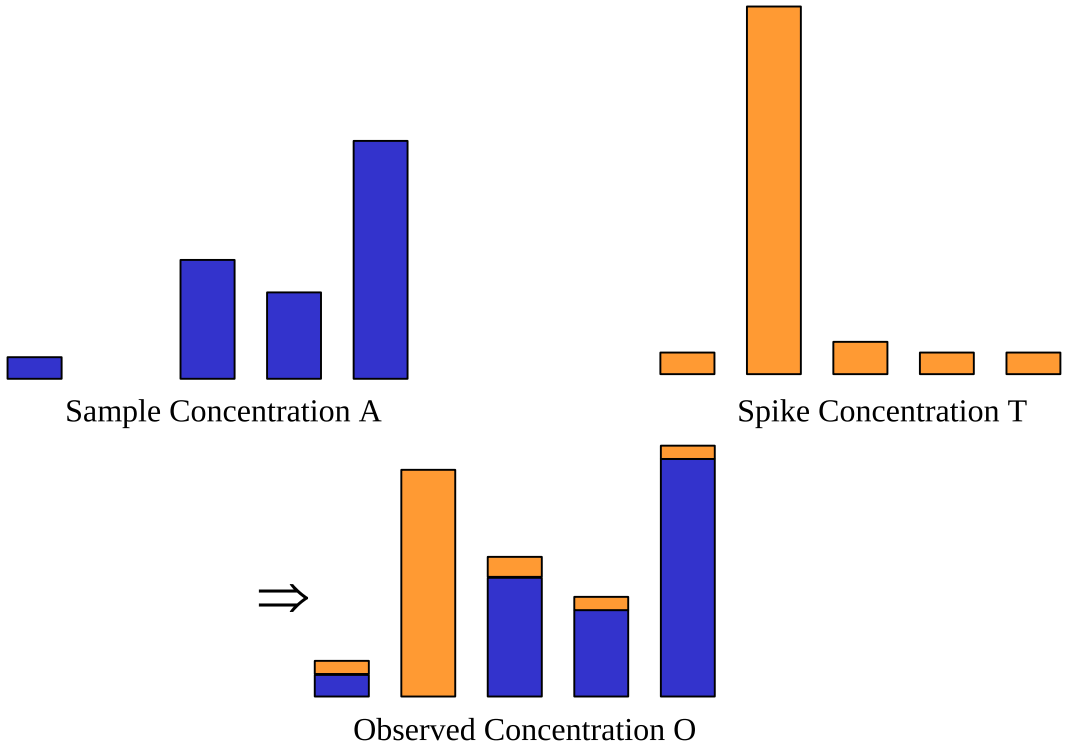

Figure A1: Isotope dilution.

Every measured sample also has the property

$$N_O = N_A + N_T$$

The number of atoms in sample and tracer need only be compared. This can be done by analysing the 20x/205 ratios using the mass spectrometer. The amount of sample (A) relative to the amount spike (T) measured may be determined.

$$A = \frac{N_A W_A}{N_T W_T} T$$

$$A = \left(\frac{N_O W_O}{N_T W_T} - \frac{N_T W_T}{N_T W_T} \right) T = \left(\frac{N_O W_O}{N_T W_T} - 1 \right) T$$

A2 Calculating final values and errors when blank is present

When a carousel is run, a number of samples are analysed as well as a couple of blanks. The blanks indicate the amount of Pb added to the measurement due to chemistry procedures and loading of the sample to the mass spectrometer. A measurment may be characterised by the following equation.

$$R_O O = R_B B + R_S S$$

O, B, S are the observed, blank and sample amounts

R_O, R_B, R_S are the observed, blank and sample isotopic ratios; any ratios common to the blank and sample may be used in the calculation.

An obvious yet vital component of the calcualation :

$$O = B + S$$

The shift in the measured ratio is being quantified

$$R_S = \frac{R_O O - R_B B}{S} = \frac{R_O O - R_B B}{O - B}$$

A factor of known components.

Analytical Error for each point is calculated by

$$\sqrt{\sum_n (\nabla R_S \cdot \Delta n)^2} = \sqrt{\left(\frac{\partial R_S}{\partial O} \cdot \Delta O\right)^2 + \left(\frac{\partial R_S}{\partial R_O} \cdot \Delta R_O\right)^2 + \left(\frac{\partial R_S}{\partial B} \cdot \Delta B\right)^2 + \left(\frac{\partial R_S}{\partial R_B} \cdot \Delta R_B\right)^2}$$

Where ΔO, ΔR_O, ΔB, ΔR_B are uncertainties returned by the data input. Data spread from four blocks are used for this exercise.

The corresponding error components are

$$\frac{\partial R_S}{\partial O} = \frac{R_O}{O - B} - \frac{R_O O - R_B B}{(O - B)^2}$$

$$\frac{\partial R_S}{\partial B} = -\frac{R_B}{O - B} + \frac{R_O O - R_B B}{(O - B)^2}$$

$$\frac{\partial R_S}{\partial R_O} = \frac{O}{O - B}$$

$$\frac{\partial R_S}{\partial R_B} = -\frac{B}{O - B}$$

A3 Calculation of orebody age

The isotopic ratio ^{235}U/^{238}U is assumed to be constant for all orebodies on earth. This is useful in determining the age via Pb isotope ratios. The decay constants of ^{235}U and ^{238}U are known

$$\lambda_{235} = 9.8486 \times 10^{-10}\, yr^{-1}$$
$$\lambda_{238} = 1.55125 \times 10^{-10}\, yr^{-1}$$

The equation for age determination via U and 206/207 ratios is well known in geochemistry

$$\frac{^{207}Pb}{^{206}Pb} = \frac{^{235}U}{^{238}U}\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}$$

(Faure, 2001)

When background was subtracted from the data, a ^{206}Pb/^{207}Pb ratio of 0.1052 was obtained:

$$0.1052 = \frac{1}{137.88}\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}$$

An iterative solution to the above equation may be obtained, whereby the age of the orebody

$$t = 1.718 \pm 0.001 Ga$$

A4 Subtracting the background

There were two ways used to subtract background count.

A4.1 Isotope subtraction by blank equivalence

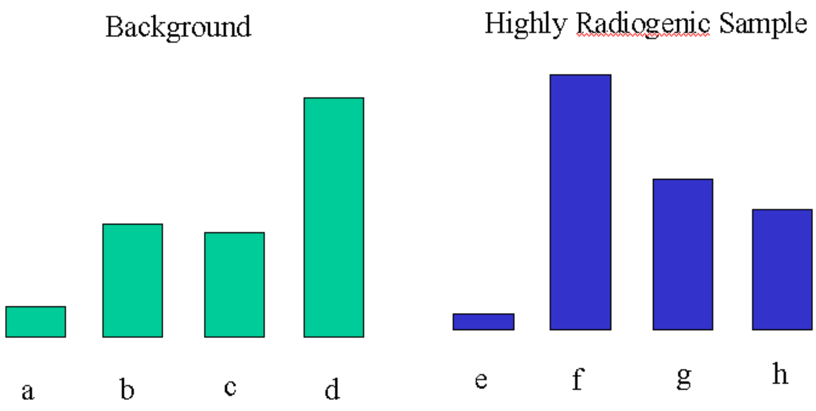

Figure A2 Background and Radiogenic Pb isotope ratios

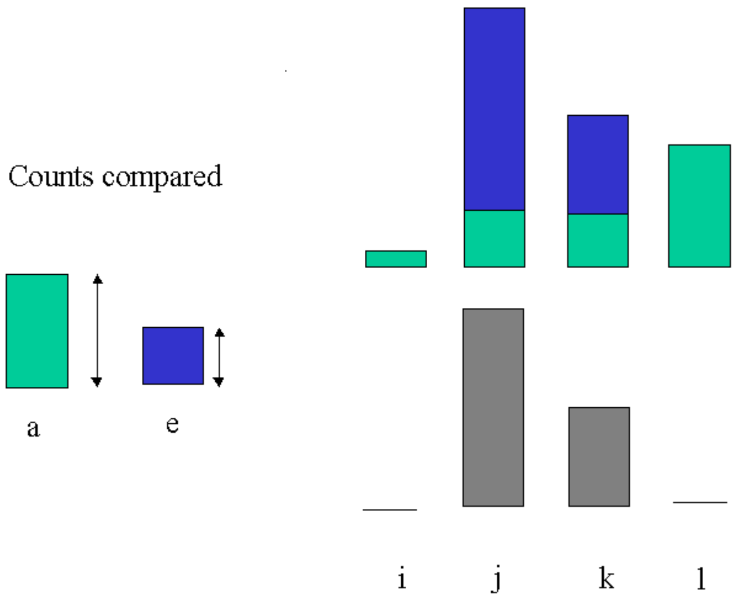

Figure A3 Count comparison and background subtraction

Suppose the background has the counts a,b,c,d for isotopes 204,206,207,208 respectively. The sample has according counts of e,f,g,h. The principle used assumes that all 204 in the radiogenic sample is from a common background. Therefore to find the natural values of the sample, the blank must be subtracted in order to reflect this.

The mathematics required to calculate the final ratios may be expressed as combinations of ratios. This is convenient as the output is expressed as a ratio hence

$$\Sigma = a/b + b/b + c/b + d/b$$

$$a = a/b\,\Sigma^{-1} \quad b = b/b\,\Sigma^{-1} \quad c = c/b\,\Sigma^{-1} \quad d = d/b\,\Sigma^{-1}$$

The calculation is carried out for the sample replacing {a,b,c,d] with {e,f,g,h}. Now that the isotope abundances are in the same form, it is a simple enough process given

$$i = e - Ra = 0$$

Satisfying this equation requires

$$R = \frac{e}{a}$$

the same calculation is carried out on the other isotope abundances

$$j = f - Rb$$

$$k = g - Rc$$

$$l = h - Rd$$

Hence final ratios are obtained simply by

$$j/k \equiv 206/207$$
$$l/k \equiv 208/207$$
$$l/j \equiv 208/206$$

A6.2 Second Isotope Subtraction Method

A similar method may be used which requires simpler calculation (Rosman K, personal communication). Using the above notation:

$$j/i = f/e - b/a$$

$$k/i = g/e - c/a$$

$$l/i = h/e - d/a$$

Hence

$$j/k=\frac{j/i}{k/i}=\frac{f/e-b/a}{g/e-c/a}$$

$$l/k=\frac{l/i}{k/i}=\frac{h/e-d/a}{g/e-c/a}$$

$$l/j=\frac{l/i}{j/i}=\frac{h/e-d/a}{f/e-b/a}$$