7. Column leaching tests

7.1 Introduction

The chemical reactivity of radionuclides is a complex subject that is still not fully understood (Gorman-Lewis *et al*., 2008). For this reason, only the statistical relationships between radionuclides and anions were investigated.

7.2 Objectives and motivation

The aim of this section is to quantify the transportability of radionuclides as would occur over one rainfall season in the study area, and to relate anions as transport mediums to specific radionuclides.

Knowing the mobility and transportability of radionuclides may assist in the implementation of preventative measures prior to the deposition of tailings. It may also assist in efforts to rehabilitate and prevent further transportation of radionuclides away from the TDF.

7.3 Radionuclide migration/leaching

Lottering *et al.* (2008) showed that the dissolution of U and subsequent leaching of U in South African gold mine tailings was maximised through the addition of acid (H_2SO_4) and an oxidant (Fe^{3+}). As U is only soluble in its oxidised state, the experiment used pyrolusite to continuously convert depleted Fe^{2+} back to Fe^{3+} in order to maintain the oxidant concentration. The reaction is as follows:

$$UO_2 + 2Fe^{3+} \leftrightarrow UO_2^{2+} + 2Fe^{2+} \qquad (4)$$

As seen in reactions 1 through 3 (Section 6.2) the pyritic nature of the TDF generates a sulphate environment with a low pH and Fe^{3+} as a by-product of oxidation (reaction 2) thus generating an ideal environment to oxidize and mobilize U as UO_2SO_4 and $UO_2(SO_4)^{2-}$ in the oxidized zone. It can be expected that the oxidized zone (Figure 6.1) will also be depleted with regard to U compared to the saturated zone (Bezuidenhout *et al*., 2005).

Although Th may be mobilized under the extreme conditions (low pH, high salinity, abundant anions, especially SO_4^{2+}) of the oxidized zones in gold TDFs, Th is still fairly resistant to weathering and tends to persist with regard to U (Vandenhove *et al.* 2009., EPA 1999., Aswathanarayana, 1985). Other radionuclides tend to be persistent and resists mobilisation under environmental conditions (Kabata-Pendias, 2011., Madejón, 2012).

7.4 Methodology

In order to measure the mobility of U and Th in gold tailings from New Machavie, four samples were taken from three different TDFs in the New Machavie complex and one sample was taken from tailings deposited in the toe paddock between TDFs 1 and 3. One sample of calcine tailings with a very high U content was used as a control sample. The five different materials were prepared by placing material in leach columns. Five repetitions of leach columns were prepared for each material.

The leaching column design is indicated in Figure 7.1. The leaching columns consisted of a 110 mm diameter PVC pipe with a length of 500 mm and a funnel connection. Within the funnel, geotextile was fitted with a layer of crushed quartz sand (washed with deionised water) to trap any particulate and colloidal material that may have been flushed through the leach column. The leachate was then collected in a sealed collection chamber.

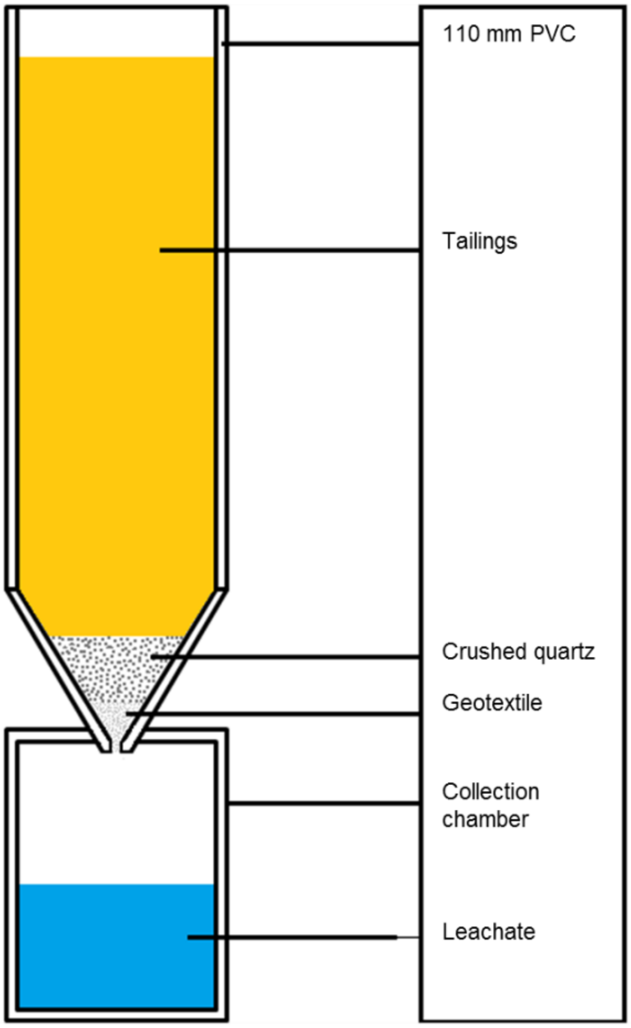


Figure 7.1: Leaching column

A volume of approximately 4700 cm^3 tailings was added into the columns. In order to simulate natural rainfall, the equivalent of one year's rain was added over a period of five weeks. The average rainfall in the Potchefstroom - Stilfontein, area is 631 mm per year. The surface area of the leaching columns was 0.0095033 m^2. Thus a total volume of 6 litres of deionised water was added.

The leachate was collected and analysed for total toxic metal content which included radionuclides as well as anion content. Anions were measured in order to relate the chemical species which were transported to the radionuclides found in the leachate. The tailings were also analysed before and after leaching was done to evaluate the change in radionuclide content over one "rainfall season".

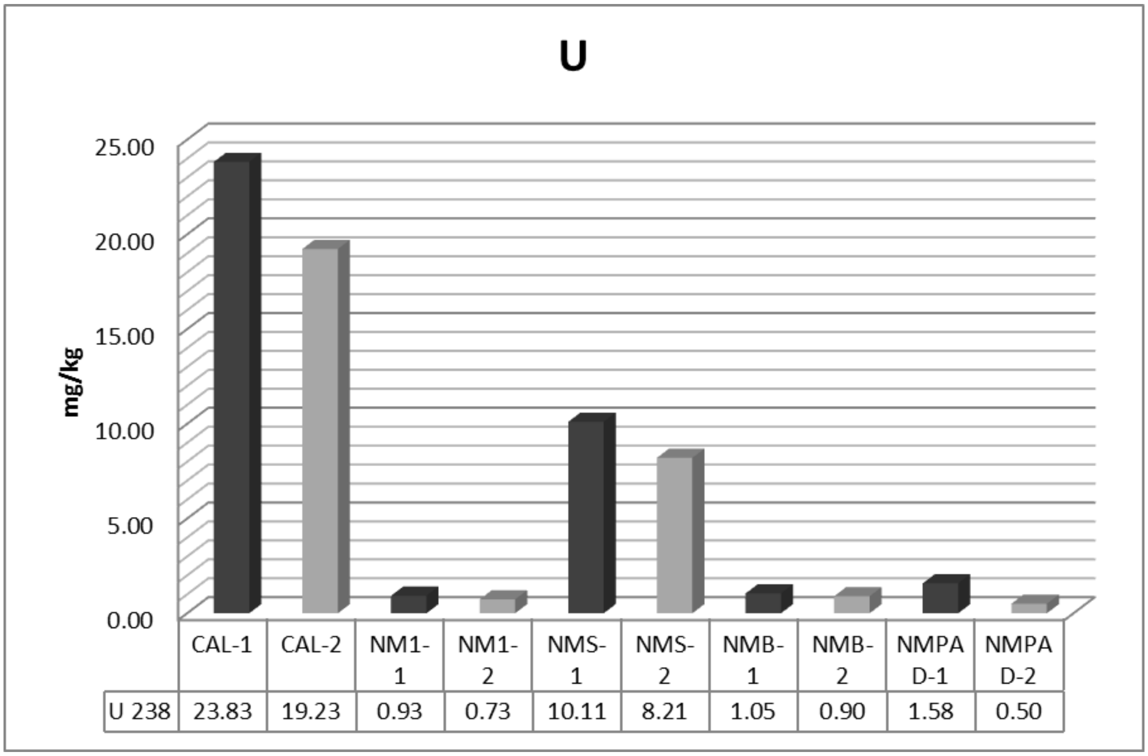
7.5 Results and discussion

7.5.1 Tailings

For each tailings material, a composite sample was taken of the five repetitions before and after leaching. Results are shown in bar graphs with black indicating samples prior to leaching, and grey indicating samples after leaching. Table 7.1 is a description of the samples and their labels. The TDFs mention are indicated in Figure 3.2.

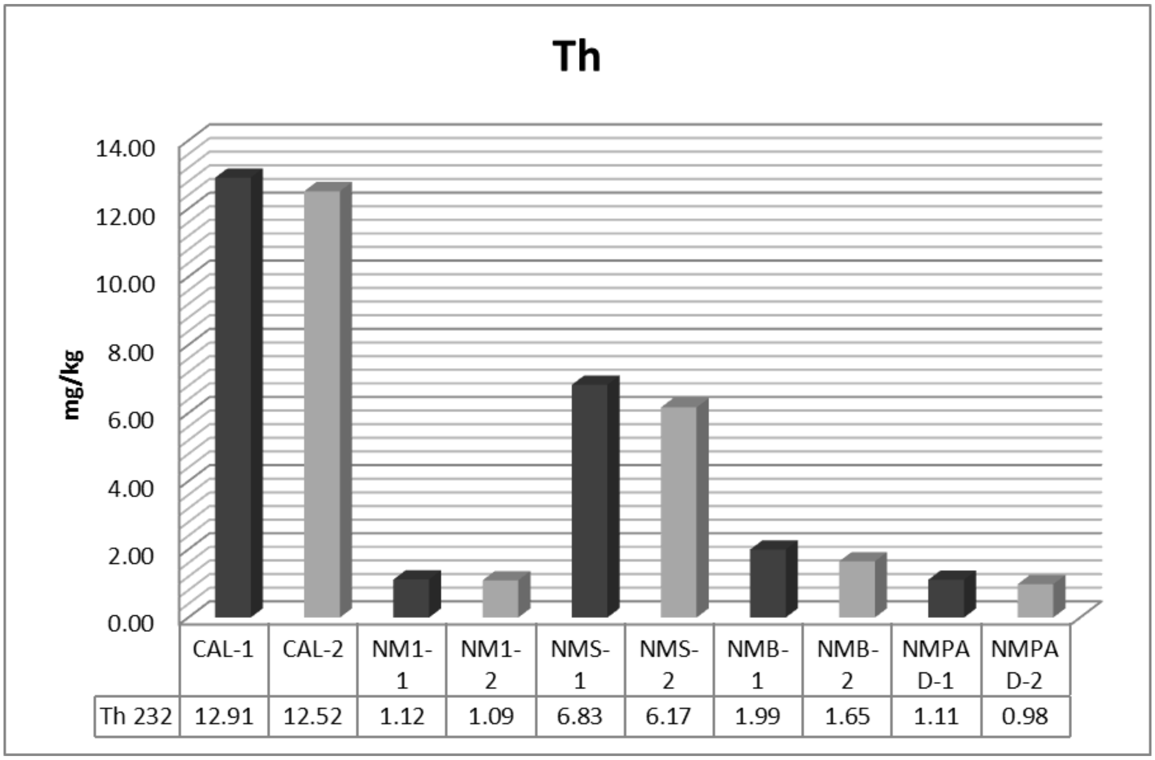
Table 7.1: Sample description

Sample label	Description	Before or after leaching
CAL-1	High U control. Calcine tailings.	Before
CAL-2	High U control. Calcine tailings.	After
NM1-1	New Machavie TDF 1. The TDF that forms part of the rest of this study.	Before
NM1-2	New Machavie TDF 1.	After
NMS-1	New Machavie TDF 2. Highest U TDF at New Machavie complex.	Before
NMS-2	New Machavie TDF 2.	After
NMB-1	New Machavie TDF 3. High inorganic carbon content.	Before
NMB-2	New Machavie TDF 3.	After
NMPAD-1	New Machavie toe paddock samples. Topographically downstream from TDF 1.	Before
NMPAD-2	New Machavie toe paddock samples.	After



	CAL-1	CAL-2	NM1-1	NM1-2	NMS-1	NMS-2	NMB-1	NMB-2	NMPAD-1	NMPAD-2
U 238	23.83	19.23	0.93	0.73	10.11	8.21	1.05	0.90	1.58	0.50

Figure 7.2: Decrease in U content after leaching



	CAL-1	CAL-2	NM1-1	NM1-2	NMS-1	NMS-2	NMB-1	NMB-2	NMPAD-1	NMPAD-2
Th 232	12.91	12.52	1.12	1.09	6.83	6.17	1.99	1.65	1.11	0.98

Figure 7.3: Decrease in Th content after leaching

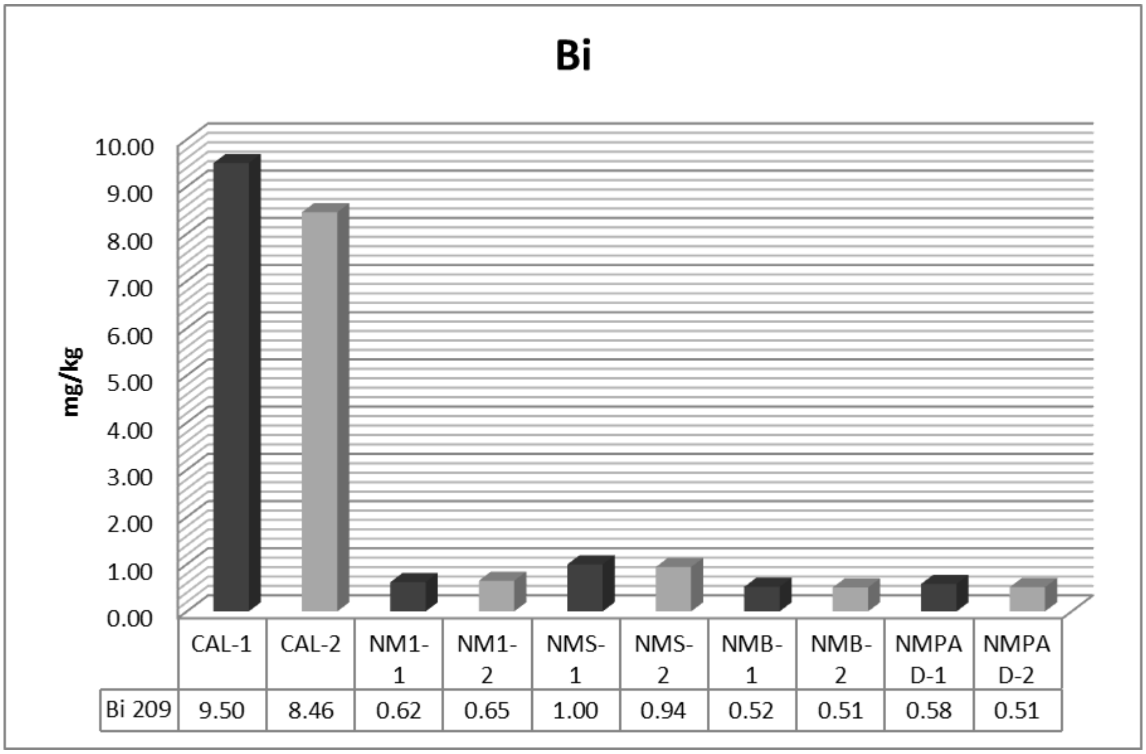


Figure 7.4: Decrease in Bi content after leaching

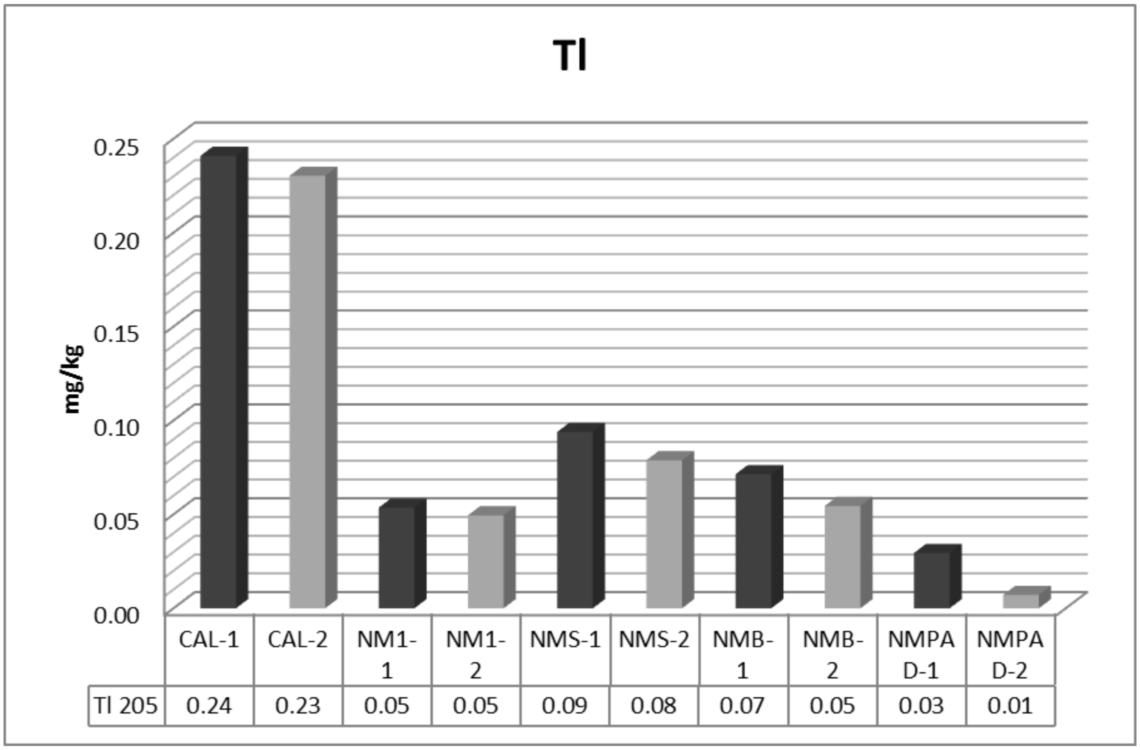


Figure 7.5: Decrease in Tl content after leaching

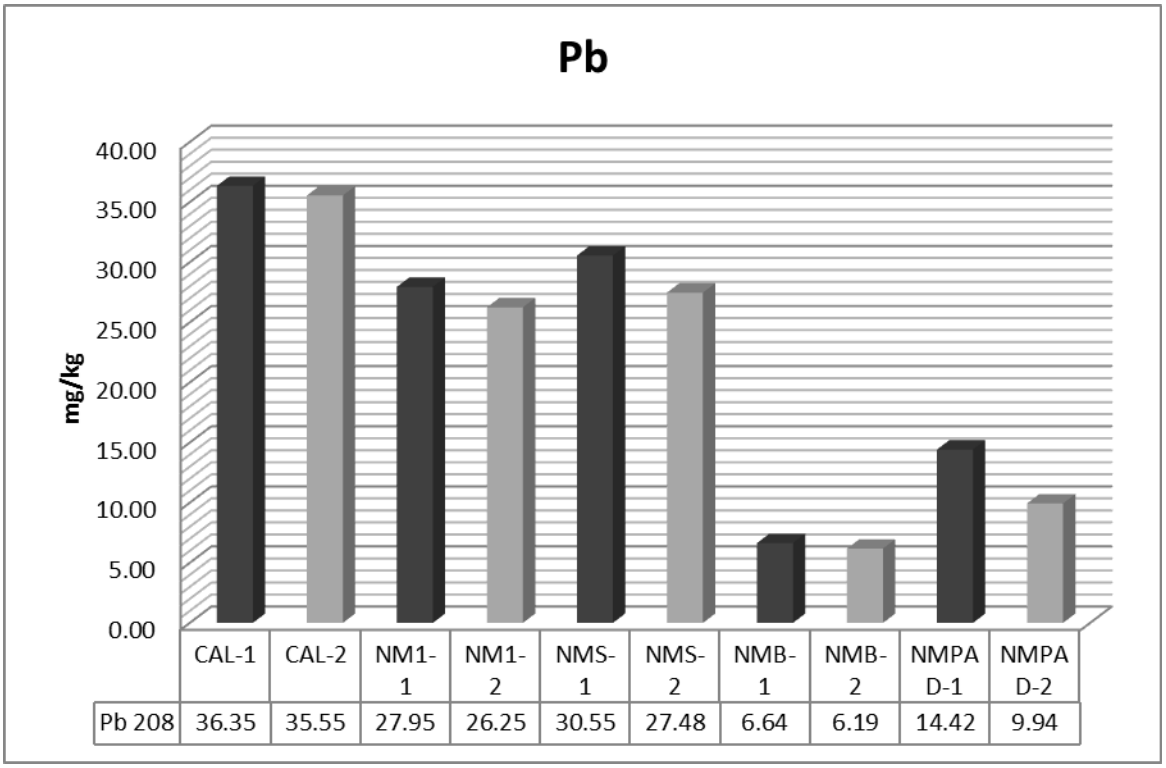


Figure 7.6: Decrease in Pb content after leaching

Samples NM1 and NMB have fairly low U contents as these sites were all taken from highly oxidized locations. Of the sample sites, NMS had the highest U content despite being oxidized (excluding control sample CAL). Sample NMPAD owes its U content to leaching originating from TDF 1 as this site is located in a flow path in the toe paddock of TDF 1. All sites showed a relative decrease in U after the equivalent of a year’s rainfall. NM1 showed a decrease of 20.7% of the total U content. Sample NMS had an 18.8% decrease, NMB had 13.8% and NMPAD had a 68.2% decrease. The control sample showed a decrease of 19.2%. NMPAD had the most mobile chemical species of U as this site is located in the flow path where transported and oxidised U would be found, thus it showed the highest mobility of U.

The general trend seems to be a decrease between 20% and 13% for oxidised tailings. Theoretically, NMB had a higher inorganic carbon content which retained more U than the other sites due to the immobilisation of U on carbon complexes.

Thorium also showed a relative decrease after leaching, with Th decreases of 2% for NM1, 7.2% for NMB, 9.7% for NMS and 12% for NMPAD. Again, NMPAD showed the greatest mobility, as was seen with U. The Control sample had a decrease of 3%.The mobility of Th is significantly lower than U in all samples. Bismuth and Tl tended not to change significantly in any of the samples. Some measurements (NM1-Bi) showed an increase after leaching which can be attributed to measurement error.

Lead also showed fairly little change after leaching except for NMPAD which showed a 31% decrease.

7.5.2 Leachate

All samples are anionically sulphate-dominated as these are all samples originating from gold tailings where pyrite oxidation and the resulting sulphate generation dominate the geochemical processes. For this study the sulphate, nitrate and chloride concentrations were measured. Phosphates, carbonates and bicarbonates were below detectable limits. Anion concentrations were compared to radionuclide concentrations in order to evaluate the effect of anions on the specific radionuclide. The control values were not added to the graphs as the higher values reduce resolution of the graphs and decrease visual interpretability.

- **Uranium**

In all of the leachate samples except for NMPAD, U indicated a strong relationship with the sulphate anion. Correlation coefficients and coefficients of determination for each of the samples were as follows:

Table 7.1: U and anion correlation as well as determination coefficients

		U vs. SO4	**U vs. NO3**	**U vs. Cl**
NM1	**r**	0.961036	0.595372	0.648593
	R^2	0.9236	0.3545	0.4207
NMS	**r**	0.949036	0.408276	0.968903
	R^2	0.9007	0.1667	0.9388
NMB	**r**	0.912874	0.905465	0.578602
	R^2	0.8333	0.8199	0.3348
NMPAD	**r**	-0.12395	-0.56364	-0.71673
	R^2	0.0154	0.3177	0.5137

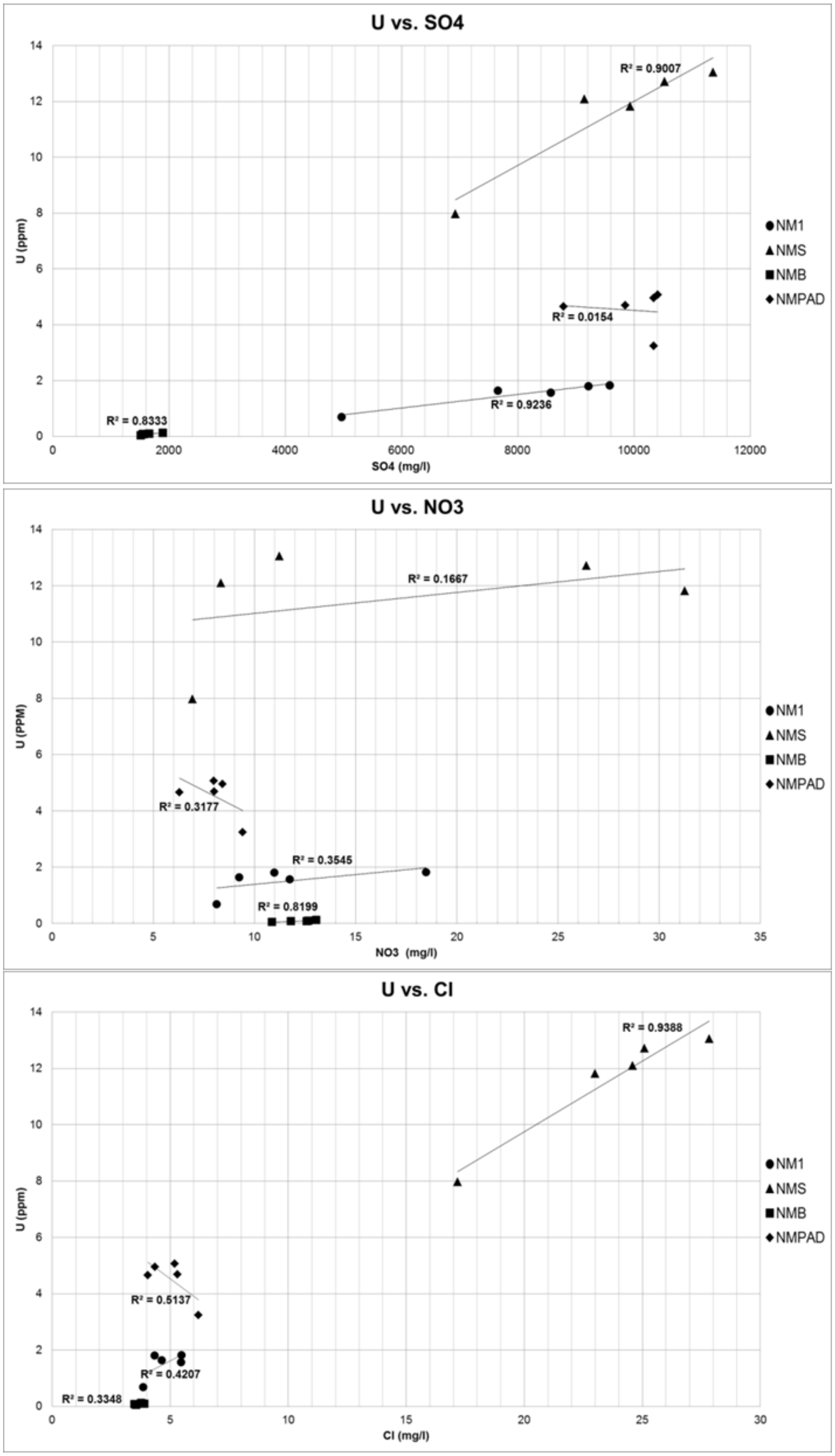


Figure 7.7: U vs. anion scatterplots

All samples except for NMPAD indicated that the sulphate ion is responsible for the transportation of U; sample NMB to a lesser degree since the variation in this sample is higher meaning that even though transportation is sulphate-dominant, another anion (nitrate) also played a large role in transportation. Sample NMPAD indicated no significant relation to any anions except chloride where a relatively strong negative correlation was observed. This indicates that at site NMPAD the chloride anion decreases the mobility of U. Uranium at NMPAD must therefore be dominated by the uranyl ion (UO_2^{2+}) complexed with oxides or hydroxides, whilst the other sites are dominated by Uranyl sulphate species of UO_2SO_4 and $UO_2(SO_4)^{2-}$. Uranyl nitrates ($UO_2(NO_3)_2$) may form in the presence of nitric acid in an oxidizing environment; however, further research is needed to specify a nitrate source. (Chernyaev *et al.* 1963)

- **Thorium**

Table 7.2: Th and anion correlation as well as determination coefficients

		Th vs. SO4	Th vs. NO3	Th vs. Cl
NM1	r	0.974627	0.558457	0.653885
	R²	0.9499	0.3119	0.4276
NMS	r	0.766135	-0.21511	0.858716
	R²	0.587	0.463	0.7374
NMB	r	0.820317	0.475649	0.866185
	R²	0.6729	0.2262	0.7503
NMPAD	r	0.059212	-0.38899	-0.57783
	R²	0.0035	0.1513	0.3339

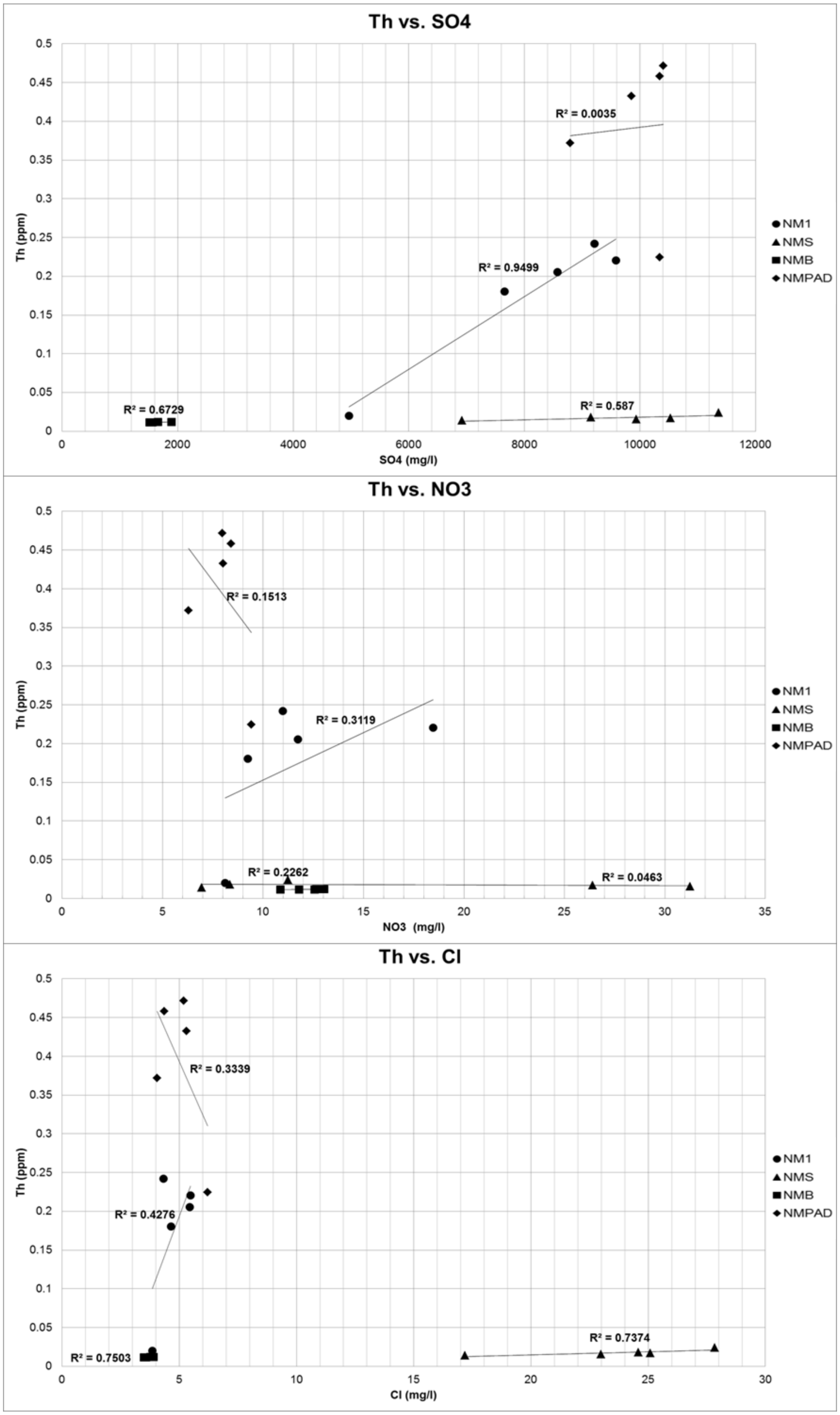


Figure 7.8: Th and anion scatterplots

Thorium indicated relatively strong linear relationships with sulphate anions in samples NM1, NMS and NMB. However, the variability in samples NMS and NMB is too high to relate Th concentration to the sulphate anion. Both of these samples correlate better with the chloride anion where the variability is lower. This indicates that Th in samples NMS and NMB may complex more readily with chloride, and to a lesser degree with sulphate. In all samples, the nitrate anion has weak relationship with Th.

Thorium has a significantly lower mobility than U since the highest concentration of Th measured in the leachate samples was lower than 0.5 ppm compared to 13 ppm U. As indicated in the tailings samples (Figure 7.3), the percentage decrease of Th is significantly lower than U.

- **Lead**

Lead remained immobile during leaching. Very little Pb was detected in the leachate samples (less than 0.03 ppm), indicating that the stability of Pb under oxidising conditions is very high even at low pH and high sulphate concentrations. Lead showed very weak correlations with all anions. Thus sulphate, nitrate and chloride had little to no effect on the mobilisation of Pb during this experiment.

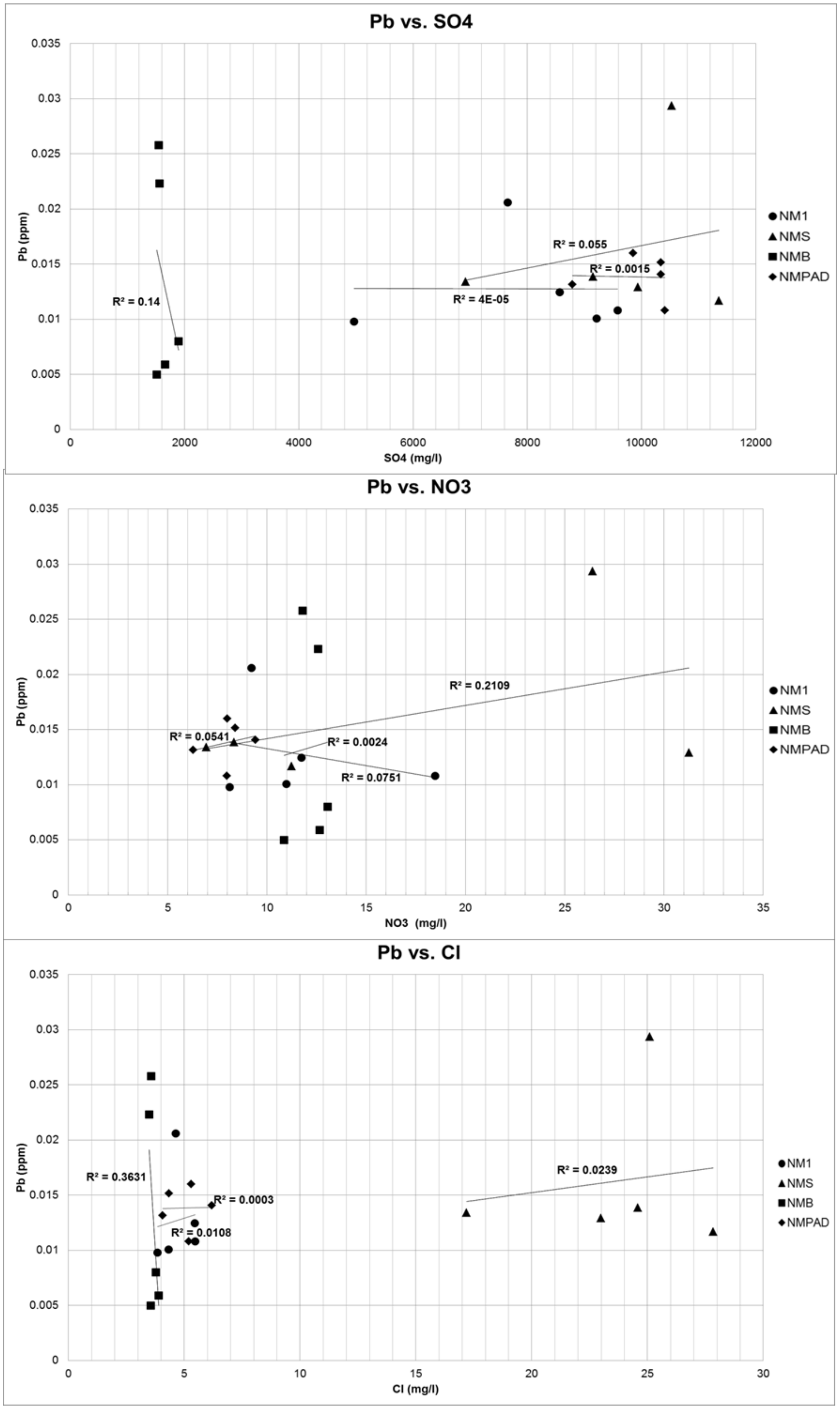


Figure 7.9: Pb and anion scatterplots

- **Bismuth**

Bismuth like Pb also remained relatively stable during leaching. Samples NMS and NMB indicated a strong relationship between Bi and sulphate with a low variability, meaning that sulphate complexation transported Bi in these samples. Sample NMS also showed a strong relationship with chloride. NMPAD revealed negative correlations (although weak) in all three anions.

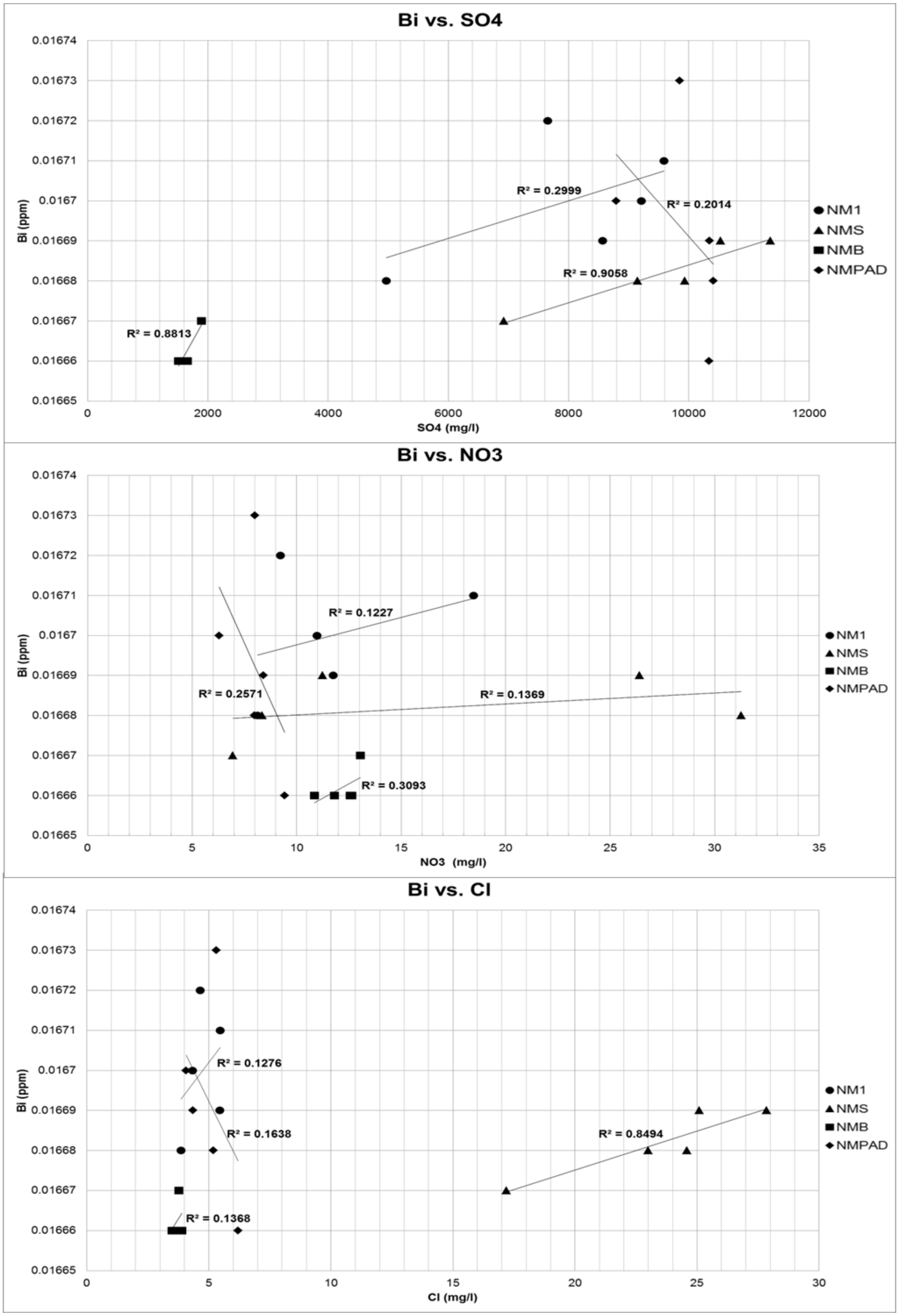


Figure 7.10: Bi and anion scatterplots

- **Thallium**

Thallium also remained stable during leaching. Sample NM1 showed strong correlations in both sulphate and nitrate graphs, although the variability was higher with nitrite. This means that sulphate and nitrate complexation had an influence. Sample NMB also showed some correlation although weak. NMPAD again indicated negative correlation between Tl and anions, and in the case of chloride a very strong negative correlation is observed with a relatively low degree of variability, indicating that lower Tl concentrations can be expected with higher chloride content.

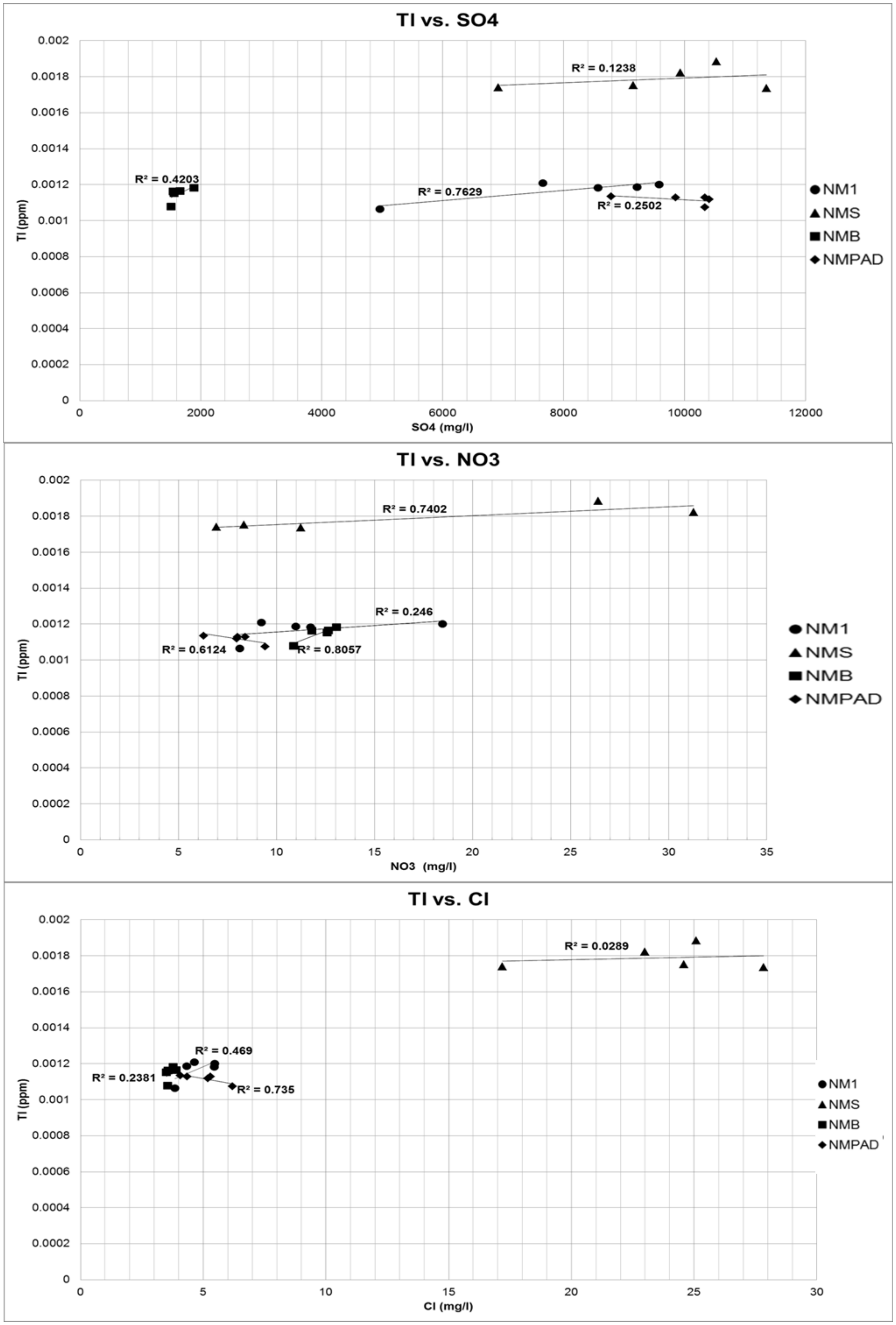


Figure 7.11: Tl and anion scatter plots

7.5.3 Conclusion

All tailings materials indicated a decrease in radionuclides after leaching with deionised water, equivalent to the volume of rainfall that can be expected for the study area during one rainfall season. The tailings material with the highest radionuclide mobility was NMPAD, which can be ascribed to the location and chemical species expected in the toe paddock.

Of all the radionuclides measured, U was the most mobile, producing concentrations as high as 13 ppm in the leachate samples. Uranium also indicated an affinity for sulphate complexation.

In most cases, sample NMPAD decreased in radionuclide content with an increase in anion content, indicating that the anions measured actually decreased the mobility of the radionuclides. In this sample, one would expect a more mobile complexation anion to be responsible for the mobility of radionuclides in this toe paddock material. The uranyl ion (UO_2^{2+}) complexation with oxides and hydroxides as an example, was not measured but it does dominate U mobility under oxidizing conditions with a pH greater than 5 (Hamilton-Jones *et al*. 1979., Gorman-Lewis *et al*., 2008). Gorman-Lewis *et al*. (2008) also indicated that the solubility and complexation of uranyl is an extremely complex process that is still not fully understood, and major deficiencies exist in thermodynamic data sets regarding these mineral phases. This is even more evident for the other radionuclides mentioned in this chapter.

Further research is needed in order to model the environmentally relevant phases of the radionuclides mentioned, as well as more detailed modelling of uranyl phases that occur in this study area and in the general gold tailings environment.

Further research may include the transportability and anionic affinity of toxic metals generally not limited to radionuclides. This is because toxic metals can potentially pose a greater environmental risk than radionuclides.