Understanding groundwater composition at Kvarntorp, Sweden, from leaching tests and multivariate statistics

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Abstract Due to oil production from alum shale, the Kvarntorp area is heavily polluted. A waste deposit consisting mostly of shale ash and fines is of important concern. Groundwater shows that parameters such as pH, U, V, Ni and Mo are different at different localities around the deposit. Leaching tests indicate that burned and unburned shale residues leave different signatures on leachates. Principal component analysis of groundwater and leaching tests suggest that ground-water is affected by the waste deposit and that it is more influenced by shale ash than by fines.

Key words Alum shale, Kvarntorp, Shale oil, Leaching, Uranium

Introduction

Alum shale is enriched in some trace elements such as U, Ni and Mo, but also organic material. In the Kvarntorp area about 200 km west of Stockholm (see figure 1), alum shale has been used for shale oil production from 1941 to 1966 which has severely polluted the environment. Remains today are water filled open pits and a 100 m high waste deposit. The waste deposit mostly consists of crushed and burned shale – shale ash, 23 Mt, crushed and burned but not totally combusted shale – semi-coke, 2 Mt and also crushed but not further processed shale – fines, 3 Mt (Bäckström 2010). There is also lime waste present in the pile. The different materials react differently to leaching and have thus different impact on the environment. Metals are released both from weathering alum shale and from heaps of burned shale (cf. Falk et al. 2006). The fines still contain pyrite and generate acid rock drainage with low pH and high concentrations of certain elements. However, the presence of lime buffer theses reactions (cf. Puura 1998).

Groundwater wells were installed around the deposit for monitoring purposes. In this project the groundwater was sampled and analyzed to assess its composition. As the waste deposit is heterogeneous, and the exact amount of the different materials is unknown, groundwater analysis in combination with leaching tests can predict possible influences from the solid waste materials on the groundwater composition in the area. For this reason solid samples consisting of fines and shale ash were used in leaching tests.

Methods

Groundwater around the waste deposit was sampled in 2004 and every second month since December 2015. Bailer samplers were used and the wells were emptied the day prior to sampling. Electrical conductivity, pH and alkalinity were measured in the lab within 12 hours after sampling. After filtration (0.20 µm polypropylene) and acidification (1 % nitric acid)

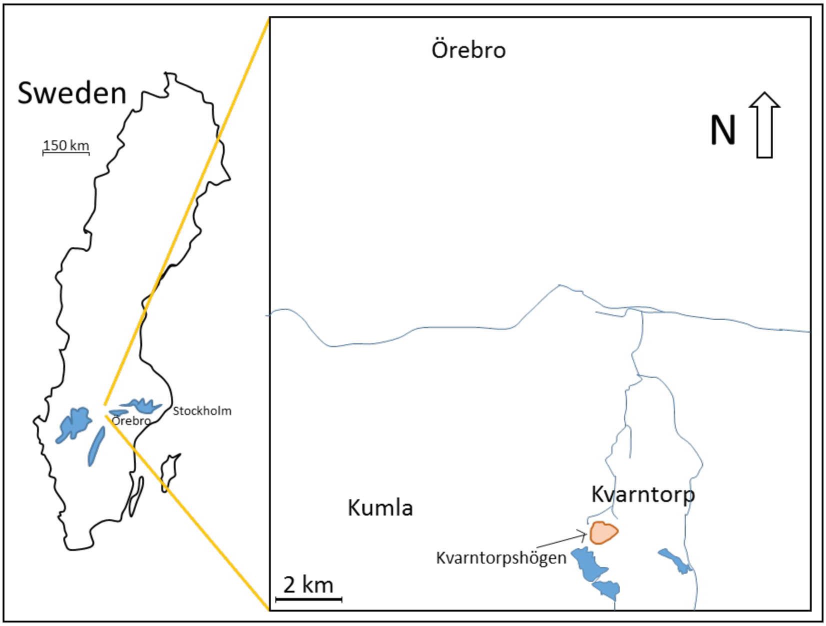

Figure 1 *Map showing the location of the Kvarntorp area and the waste deposit Kvarntorpshögen.*

the element concentrations were analysed with ICP-MS (Agilent 7500cx). Elements prone to suffer from di- and polyatomic interferences (i.e. V, Fe and As) were analysed in collision mode with helium as the inert collision gas. Anions were analysed with capillary electrophoresis using sodium chromate buffer (50 mM) containing TTAB (5 mM) and a 40 cm * 50 µm silica capillary.

Two of the sampling occasions were chosen for PCA analysis – December 2015 and August 2016. The summer 2016 was quite dry, leading to lower groundwater levels for most of the wells in August 2016 compared to December 2015.

Solid samples were collected and used for leaching tests. Three different series were set up in order to elucidate the influence of shale ash and fines on groundwater composition (see figure 2 and 3 for photos of the materials). Six plastic containers were filled with 1 kg solid material each.

Figure 2 *Fines from Kvarntorpshögen.*

Figure 3 *Shale ash from Kvarntorpshögen.*

A sequential system was set up. For system *A* container 1 was filled with shale ash and container 2 with fines. Container 1 in system *B* was filled with fines and container 2 with shale ash. In system *C* both container 1 and 2 were filled with a mixture of shale ash and fines (see figure 4).

In total 20 sampling occasions were effectuated during a span of seven weeks. At every sampling occasion, 600 mL (1 000 mL for the first occasion) deionized water (18.2 MΩ) was first added to container number 1 in each system. The water was then collected and added to container number 2. Sampling procedures are as described in figure 4. Electrical conductivity, pH and alkalinity/acidity were analysed in all leachates.

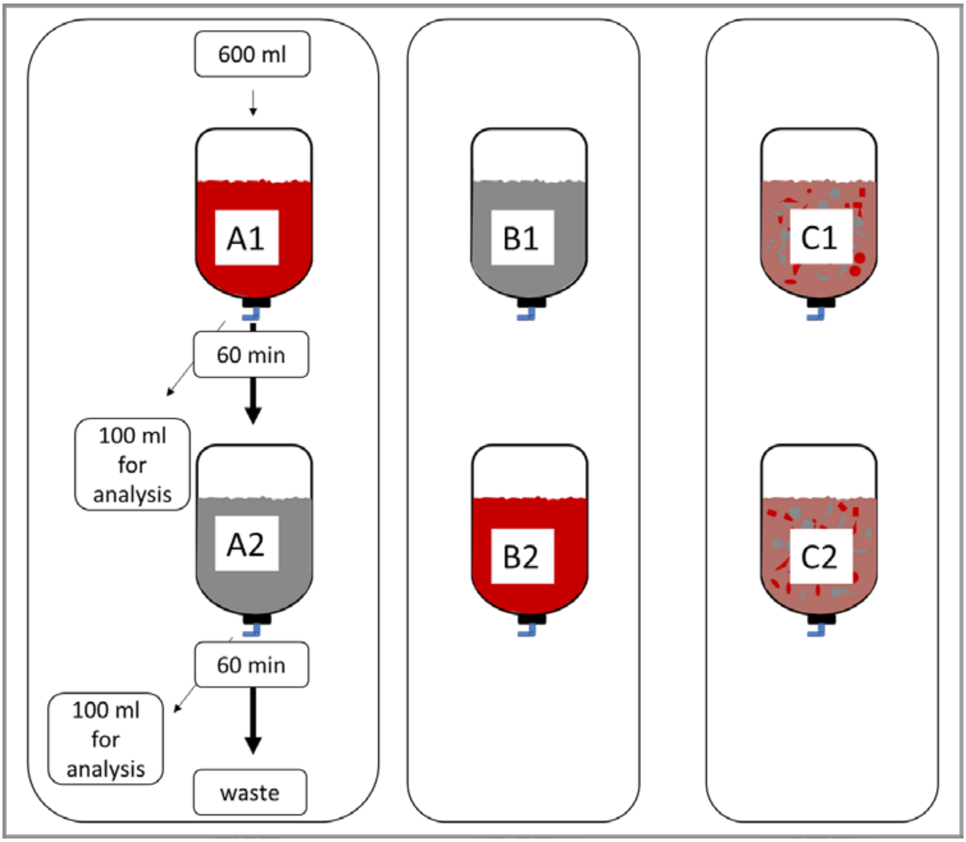

Figure 4 *Leaching systems –A, B and C. The sampling procedures described for system A applies for all three systems. Container A1 contains shale ash, A2 fines, B1 fines, B2 shale ash, C1 and C2 contain a mixture of shale ash and fines.*

Water data was analysed using principal component analysis (PCA) with the chemometric software "*The Unscrambler*". Principal component analysis (PCA) was performed on all groundwater samples from December 2015 and August 2016, and leachate samples from sampling occasion 2 and 19 (37 samples including 25 groundwaters and 12 leachate samples); 25 elements. All parameters were autoscaled and logarithmically transformed.

Results and discussion

Groundwater

Analysis of the groundwater indicate that the wells display very different conditions. An example of the diversity of the composition is shown in table 1 where five wells are displayed regarding pH, U, V, Ni and Mo for water sampled in 2004 and in December 2015. It can be noted that well *G7* has lower concentrations compared to the other wells. *G7* is a deep well (31 m) that reaches all the way down to the sandstone aquifer, unlike the other wells in table 1 (SWECO VIAK 2005).

Burned lime is suspected to be the reason for high pH (10.64) in well *G6*. Well *G1* has the lowest pH (3.97 and 3.2 in 2004) and quite high U concentration (350 ppb). Highest U concentration is found in pH neutral *G8* (1 230 ppb). It can be noted that the highest pH have decreased and the lowest increased from 2004 to 2015.

Table 1 *pH and element concentrations for some of the groundwater sampled in 2004 (according to SWECO VIAK 2005) and in December 2015. Concentrations are in µg/L.*

Well	pH		U		V		Ni		Mo	
	2004	2015	2004	2015	2004	2015	2004	2015	2004	2015
G1	3.2	3.97	129	350	1.5	121	1190	1840	1	14.4
G3	3.6	5.92	16	52	1.8	16.6	235	278	8.2	423
G6	12.2	10.64	0.5	0.9	0.77	0.7	8.1	9.6	142	87.5
G7	10	7.88	0.01	0.01	2.0	0.24	0.5	1.58	2.0	0.90
G8		7.02	1760	1230	12	59.4	7.0	25.9	935	319

Leaching tests

With only shale ash (container *A1*) the leachates had higher pH (4.61-7.29) than leachates from fines (pH 2.24-6.8, container *B1*). With a mixture of both shale ash and fines the pH was found to be in between. Low pH tend to increase as the sampling occasions progress probably due to consumption of easily available acid forming minerals such as pyrite. Also the trace metals indicate a trend, as the concentrations in general are higher in the beginning of the sampling series and then decrease. Surface coating on the material is probably dissolved and washed out in connection to the early sampling occasions. Uranium shows lowest concentration for leachates from shale ash (*A1*) and highest for leachates where both shale ash and fines are involved (see figure 5). Differences in uranium concentrations are probably connected to pH.

Also for nickel, leachates from shale ash display the lowest concentrations (see figure 6). Lower concentrations for molybdenum (see figure 7) in *B1* (fines) than in *A1* (shale ash) is probably due to lower pH in *B1*. This is also a plausible reason for lower Mo concentrations in the leachate in *A2* where the high concentration after passing *A1* is lowered in *A2* due to pH decrease. Also the groundwater indicates pH as the explanation for higher Mo concentrations in *G3* in 2015 (pH 5.92) than in 2004 (pH 3.6).

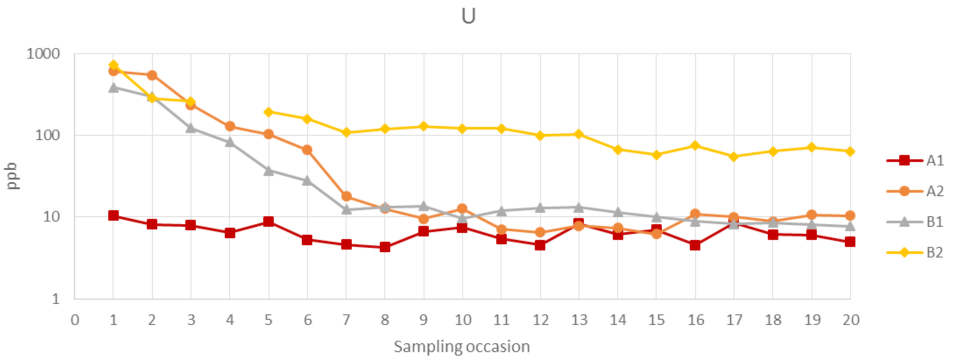

Figure 5 Diagram showing the concentration of uranium in leachates.

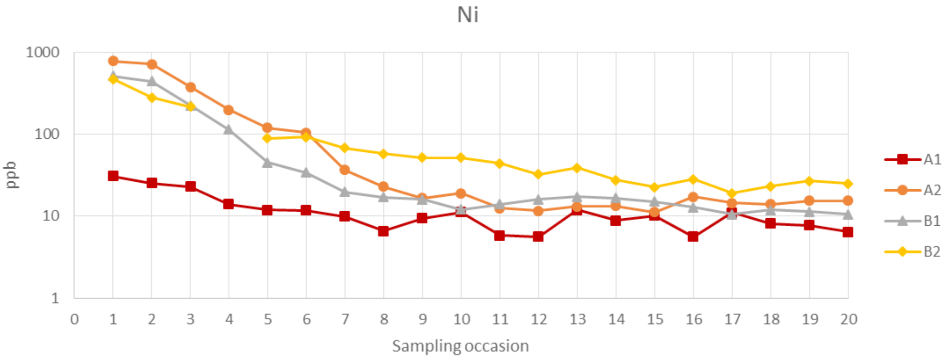

Figure 6 Diagram showing the concentration of nickel in different leachates.

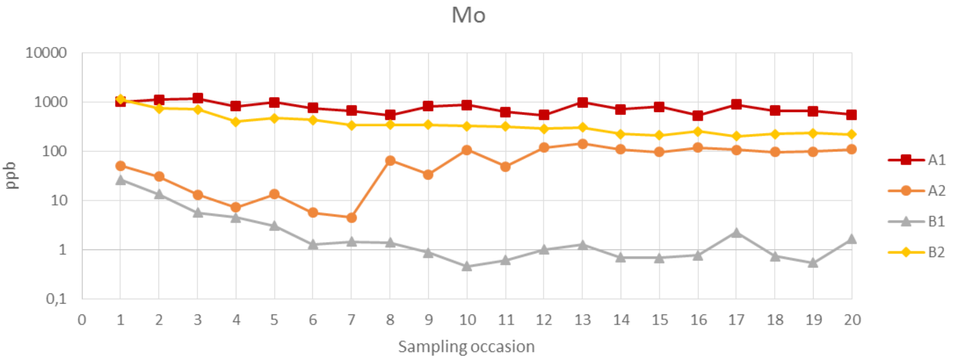

Figure 7 Diagram showing the concentration of molybdenum in different leachates.

Multivariate statistics – PCA

PCA explained 64 % of the variation in the data set using only 2 principal components, indicating similarities between field and laboratory data (see figure 8). Upstream (*G9-G13*) and downstream (*G1-G8*) groundwater are separated in the PCA, indicating a distinct impact on the groundwater around the waste pile. It is noted that the composition in most groundwater is influenced by shale ash to a greater extent than by fines. The deep wells (*G2* and *G7*) are well distinguished from the more superficial wells that have contact with the waste material in the deposit. For the leachates a difference can be noted between the two sampling occasions where sampling number 19 tends to increase along the PC1 axis compared to sampling number 2.

Even though the results from the PCA give indications of similarities between leaching tests and field data, it is important to consider the different conditions in the laboratory and in the natural system. The leaching test was a strictly chemical test and probably abiotic in comparison with the natural system where biotic components have a significant role. The heterogeneity of the waste deposit is reflected by the diversity of the groundwater chemistry. For example a Pearson correlation test for the leachates shows a 0.728 correlation between U and V (significant at the 0.01 level, N = 119), whereas such a test only gives 0.290 (N = 81) for groundwater. For Ni and V the correlation is 0.905 for leachates and 0.546 for groundwater. This strengthens the idea that the complexity of the groundwater is much vaster than a simplified leaching test where it is probable that much of the correlation is connected to the initial outwash of elements from the surface of the solid material.

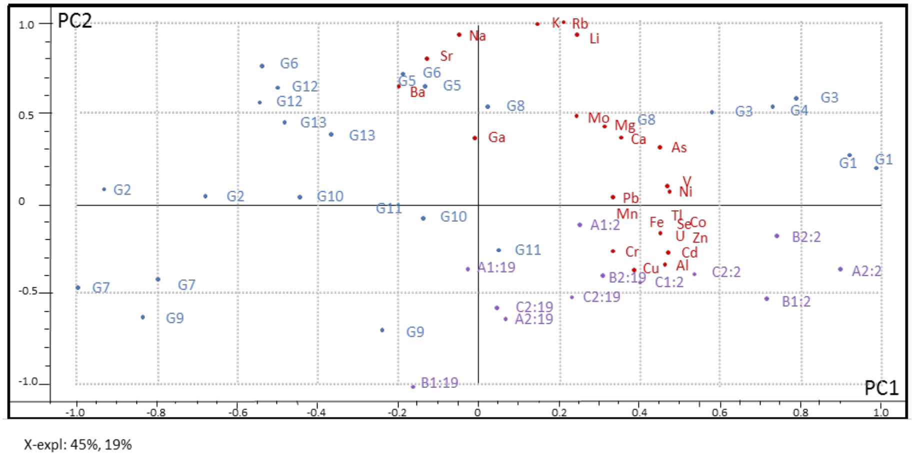

Figure 8 *PCA plot indicating that groundwater is more influenced by shale ash (A1) than by fines (B1).*

Conclusions

High concentrations of trace metals typical for alum shale such as U, V, Ni and Mo were found in groundwater wells around the waste deposit. Leaching tests show that shale ash and fines leave different signatures on the leachates.

This study has shown that the combination of leaching experiments and principal component analysis can be used to understand the evolution of groundwater in a contaminated setting. As the Kvarntorp area is complex and different parameters covariate, further tests are needed to fully understand the processes and water chemistry.

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