Concomitant removal of iron and NAPLs within a mine water treatment system

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Abstract

Water entering the mine water treatment scheme (MWTS) at the Blaenavon site in South Wales is co-contaminated with non-aqueous phase liquids (NAPL) arising from historic pitch and coal tar wastes. This paper presents the results of investigations into the transport of the NAPLs through the treatment scheme and the extent to which they are co-removed with ochre formed within the MWTS. The scheme comprises one settling lagoon in series with two reed beds. Water and solid samples were collected along the length of treatment scheme and were prepared by solvent extraction for quantitative and qualitative analyses by Gas Chromatography Mass Spectrometry (GC-MS). Significant quantities of polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) were found in Lagoon 1 with concentrations of the most prevalent PAH being phenanthrene (1460 mg/kg dry solid) and the most prevalent petroleum hydrocarbon being octadecane (1486 mg/kg dry solid). Qualitative analyses using the National Institute of Standards and Technology (NIST) Mass Spectra database identified 92 additional compounds within the MTWS. The general trend was for concentrations of detected compounds and the number of detected compounds to decrease across the MWTS with total PAH concentration decreasing from 5534 to 72 mg/kg dry (ochre) solid by the end of Lagoon 1. There were no detectable levels of PAH or TPH in water downstream of the treatment scheme. Several possible mechanisms are discussed for the removal of the PAH and TPH from the mine water along with the potential for this type of scheme to treat other sources of organic contaminants.

Keywords: ochre, NAPL, passive co-removal

Introduction

Blaenavon was designated a World Heritage Site by UNESCO in 2000 as "an exceptional illustration in material form of the social and economic structure of 19th-century industry". The village and surrounding area was a major producer of coal and steel until the early 20th-century with Big Pit, the last substantial working colliery closing in 1980. This industrial heritage has left a legacy of pollution arising from coal mine drainage as well as leachates from land contaminated by pitch and coal tar.

This paper presents the results of work carried on behalf of the Coal Authority at the Blaenavon minewater treatment scheme (MWTS). The work was undertaken in order to determine the extent of 'tar' contamination, the concentrations of key contaminants, their distribution along a linear transect of the MWTS and to make a preliminary assessment of their likely fate.

Water entering the MWTS was Fe bearing with total dissolved Fe concentration of 7 mg/L (approximately 90% as Fe(II)) at the inflow and <1 mg/L at the outflow. Water enters lagoon L1 (Figure 1) under gravity via a distribution channel as it drains out of the mine workings above. There is no aeration cascade and the volume of water flowing throughout the year ensures that the lagoon and reed beds are always flooded (i.e. the sludge never dries out). The flow rate is ca. 100 L/s. The pH of the water entering the lagoon is 6.5 with dissolved oxygen near saturation and alkalinity 125 mg/L.

Methods

Samples of water and solids were taken from various points along the MWTS as illustrated in Figure 1. The samples were scooped into sample pots which were then sealed prior to transportation back to the laboratory. Solvent extraction was carried out on the water samples by agitating 300mL of sample with 20ml of Dichloromethane (DCM). After 24 hours agitation, each water/DCM mixture was poured into a separatory funnel and allowed to settle for approximately 20 minutes. The DCM was then decanted off and evaporated under nitrogen to a final volume of 10 mL prior to GC-MS analysis.

Sludge samples were weighed and placed in an oven at 36°C for 24 hours to dry. Once dried, the samples were weighed again (allowing determination of moisture content). Dried samples were homogenised by hand and approximately 1 gram (accurately known) of each of the solid samples were then passed though a Dionex Advanced Solvent Extraction (ASE) 100 system which uses hot DCM to extract organic compounds. Once the ASE extractions were completed, the resultant solvent samples were evaporated down under nitrogen to a volume of 10mL prior to GC-MS analysis.

Each sample was analysed three times using different column conditions appropriate to the group of target compounds to be analysed. The standards used for each of the three GC-MS 'runs' were as follows: a certified PAH standard (RESTEK SV Calibration Mix 5), a certified phenolic compound standard (RESTEK 8040 Phenols Mix 1 & 2) and a certified Total Petroleum Hydrocarbons (TPH) standard (RESTEK Florida TRPH). Where peaks and mass spectra matched the certified standards, fully quantitative analysis was possible. In cases where peaks did not match the standards the mass spectrum was analysed against the National Institute of Standards and Technology (NIST) Mass Spectra database using the NIST Search (Version 2.0) software. All samples were further analysed for total carbon. Approximately 0.35 g sub amples were accurately weighed out and subjected to high temperature combustion in the Leco carbon analyser.
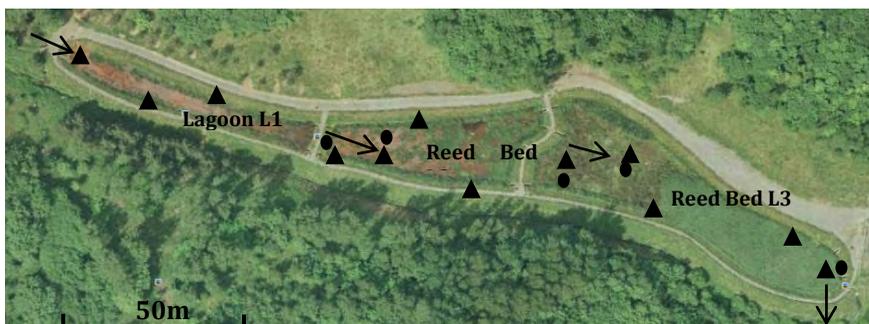
Figure 1 *Aerial view of Blaenavon MWTS. Arrows indicate direction of flow of water, solid sample collection points marked by triangles, water sample collection points marked by circles. Sample points were numbered consecutively with 1 nearest to the inflow.*

Results and Discussion

Contaminant transport

Neither PAHs (polycyclic aromatic hydrocarbons) nor TPHs (total petroleum hydrocarbons) were detectible in any of the water samples taken. By contrast, a wide variety of hydrocarbons were found in the solid samples in Lagoon L1, though these concentrations quickly decreased with distance from the inflow. Tables 1 and 2 give an indication as to the range and concentrations of compounds detected. For the sake of brevity only selected data are shown. It can be seen that the concentrations of both PAHs and TPHs decreased significantly across the length of Lagoon L1 with octadecane and several PAHs decreasing by approximately 2 orders of magnitude.

A possible explanation for the concentration of contaminants near to the inlet of lagoon L1 is that many of the compounds may be present as dense non-aqueous phase liquids and will 'settle out' at the low points in the hydraulic system (due to density). This effect is likely to be exacerbated by the decrease in mine water velocity (and possibly temperature) as it enters the lagoon. Furthermore, the oxidation, precipitation and settling of iron in the MWTS is likely to remove organic contaminants from solution in a 'sweep floc' action (a mechanism which has recently been simulated in the author's laboratories).

In addition to density driven removal mechanisms PAHs and other organic contaminants are known to adsorb onto soils and sediments, something which is often closely correlated with the organic matter content of the material (Dzombak and Luthy, 1982). The highest concentrations of organic contaminants was seen at sampling location L1[-1], which has high total carbon concentrations of over 10% by mass, implying high levels of organic matter in addition to the tar residues. The PAHs are therefore likely to remain strongly associated with this phase, rather than being transported in the aqueous phase.

Table 1 *Comparison of PAH concentrations found in solid samples across Lagoon L1.*

PAH Compounds	L1-1*	L1-2*	L1-3*
Naphthalene	953.5	10.72	0.866
Acenaphthylene	355.9	31.10	n.d.
Fluorene	871.8	146.6	0.720
Phenanthrene	1460	354.6	7.738
Anthracene	403.6	n.d.	3.366
Fluoranthene	518.1	122.1	23.40
Pyrene	280.6	66.21	14.06
Benz(a)anthracene	156.8	37.02	8.833
Chrysene	146.3	29.95	7.425
Benzo(g,h,i)perylene	27.35	5.280	n.d.
TOTAL	**5534**	**859.0**	**72.00**

*All values presented as mg hydrocarbon/kg dried solid

Any organic contaminants which remain in the water column are likely to be rapidly removed through photolysis or biodegradation, as they are relatively short-lived in aqueous solution (Miller and Olejnik, 2001). This explanation for degradation correlates with a lack of observed contamination in aqueous samples. Whilst this is a positive outcome in terms of water treatment it does mean that it was not possible to construct a mass balance for the PAH and TPH going though the MWTS e.g. to calculate a rate of accumulation of contaminants from the sum of the influent and effluent mass flows.

Table 2 *Comparison of TPH concentrations found in solid samples across Lagoon L1.*

TPH Compound	L1-1*	L1-2*	L1-3*
Dodecane	23.76	n.d.	n.d.
Tetradecane	13.19	1.757	n.d.
Octadecane	1486	345.0	7.989
Docosane	5.278	n.d.	n.d.
Tetracosane	20.15	n.d.	n.d.
Hexacosane	3.541	n.d.	n.d.
TOTAL	**1552**	**346.8**	**7.989**

*All values presented as mg hydrocarbon/kg dried solid

Contaminant degradation

PAHs are susceptible to a number of degradation pathways. Photolysis is a possibility, particularly when attached to sediment particles, and may have be degradation via this mechanism on the surface if the settled ochre sludge in the lagoon. However, as the majority of the contamination is likely buried within the sediment, it is expected that this is not a significant degradation pathway at the current time. Volatilisation is also a possibility with the lowest molecular weight (MW) PAHs such as naphthalene, as well as lower molecular weight petroleum hydrocarbons such as dodecane, although this may be limited by depth of contamination within the sediment. Qualitatively, it has been observed that disturbance of the sediments releases a plume of organic contaminants which can

be seen as an oily film on the water associated with a strong smell. This rapidly dissipates however, until the sediments are further disturbed.

Natural microbiological degradation of PAHs has been shown to occur in numerous environments, particularly aqueous solutions but also soils. This may occur aerobically (Cerniglia, 1993) or anaerobically (Meckenstock et al., 2004), although the latter has a significantly longer duration. Half-lives are typically of the order of weeks or months (aerobically) or up to several years (anaerobically). All species may be degraded although it is the species with low molecular weight (typically 2-3 ring PAHs) that are lost most rapidly, leaving the higher molecular weight, less soluble, more toxic and therefore less bioavailable 4-, 5- and 6- ring PAHs (Hinga, 2003).

Tables 1 and 2 reveal the presence of significant quantities of relatively easily biodegraded PAHs and petroleum hydrocarbon species, suggesting that there has either been recent contamination or, that biodegradation may be occurring slowly in the sediment. Ferric iron/sulphate/nitrate may be used as an electron acceptor during catabolism of PAH species under anaerobic conditions, so anaerobic biological degradation might be expected to be occurring in these iron-rich conditions. However, based on current information it is impossible to deduce how fast this might be occurring.

Further remediation options

There appear to be no examples of hydrocarbon remediation in iron-rich sediment similar to that present on the site in question. It is therefore difficult to predict how the sediment bound contaminants might react to different treatment options. The targets of remediation are known however and will primarily be petroleum hydrocarbons and PAHs. Since petroleum hydrocarbons are readily biodegradable in most situations future remediation strategies will focus on PAH degradation, which will be the limiting reaction in such treatment scheme.

Based on the limitations of the data obtained thus far, it is difficult to deduce how fast biological natural attenuation is occurring and so further monitoring is required in order to determine natural PAH attenuation rates *in situ.* However, given the absence of hydrocarbons in the water exiting the MWTS there may be no requirement for additional remediation at the current time and even very slow natural attenuation may be acceptable. Further site investigation will be required to identify whether this is the case.

Ex-situ remediation may be the most appropriate solution if significant quantities of hydrocarbon remain in the future when desludging is required. In this case techniques where mixing occurs, such as windrows or slurry-phase bioreactors, which allow microorganisms access to the contamination in this fine-grained sediment are likely to be a viable option. It is expected that a large proportion of the PAHs and the petroleum hydrocarbons would be biodegradable under optimum conditions using such technologies.

Conclusions

The Blaenavon MWTS provides an unusual combination of both organic and inorganic contaminants in a passive treatment scheme. The lagoon and wetland have, to date, be successful in removing   iron PAH and TPH contaminants. Concentration of the organic contaminants within the ochre sludge suggests that sorption is favoured over aqueous phase transport. It is likely that biodegradation is occurring with respect to PAH and in particular TPH within the iron sludge, though further investigation is required in order to determine rates of reaction with respect to individual organic species.

Acknowledgements

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